Pranav D. Pathak ·
Sachin A. Mandavgane *Editors*

Biorefinery: A Sustainable Approach for the Production of Biomaterials, Biochemicals and Biofuels

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Preface

Nowadays, there are growing concerns about the consumption of resources and the impact caused by the conversion of these resources into good and services. At present, biomass seems to be a suitable alternative material for the production of many value-added products. However, its sustainability has been not examined. In this regard, the biorefinery concept offers an opportunity to develop a bio-based economy, given the series of value-added products that can be obtained from this facility.

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce biomaterials (activated carbon, animal feed, etc.); fuels/power (e.g. biodiesel, bioethanol, biogas, methane, gasification, direct burning) and chemicals (antioxidants, enzymes, dyes, etc.). Thus, industrial biorefinery is a new and promising route for conversion of waste biomass to the value-added products. By producing various array of products, a biorefinery takes advantage of the several components in biomass along with their intermediates and optimize the use of resources and minimize wastes, thus maximizing benefits and profitability.

To achieve global sustainability goals, agriculture must improve supply chains and valorize agricultural waste. Waste streams from the agro-industry are rich in carotenoids, flavonoids, phenolic acids, glucosinolates, and cell wall components such as cellulose, hemicellulose, lignin, and pectin, so they have a huge potential for being turned into value-added products and for boosting the country's economy. In recent years, many studies and researches have been conducted to explore the sustainable valorization of agricultural waste as biomaterials, biofuels, and other biochemicals. The goal of the book is to put all of the new developments and accomplishments in the field of biorefinery in one place so that the full potential of different types of agricultural biomass can be used. When possible, the pros and cons of different technologies are also talked about, taking into account local energy needs, government policies, environmental effects, and education in biorefinery.

It is an ideal reference book for researchers and industry professionals working in the areas environment, biotechnology, chemicals, materials, fuel, power, energy, agriculture, agriculture waste management, life cycle assessment, etc. Also, research scholars, researchers doing interdisciplinary research, industrialists and scientists in learning techniques and technologies related to biorefinery. Any enthusiastic readers interested in doing smart technology innovations are the focused audience. This book also features case studies that demonstrate the importance of integrating processes and technologies when imagining biorefineries.

The book consists of about 15 chapters invited from various authors from the globe. It includes the chapters written by renowned experts from industries, research, and academia. The chapters are mainly focused on the current research, technologies, and current literature of valuable interest.

The book is divided into three parts. Part I is dedicated to the valorization of agricultural waste for numerous high-value biochemicals. Part II mainly focuses on biomaterial production and their potential applications. In the third part, we examine the environmental impact assessment and the life cycle analysis (LCA) of various biomass processing options in order to provide a techno-economic evaluation of agricultural biomass using a biorefinery approach. That adds depth to the topics and helps readers grasp them.

We'd like to say a big thank you to all the experts and leaders from universities and research institutions who helped make this book better and more up to date. Without you and your team's hard work, this book would not have been written. We are also grateful to Springer Nature for making this book well enough. We'd also like to thank the Springer Nature editorial team, especially Dr. Bhavik Sawhney, the Editor, and Machi Sugimoto, the Editorial Assistant, for their quick help and advice during the project.

We sincerely hope that this book will live up to the high standards set by its audience, and we would be very appreciative of any feedback or ideas you might have to help us make the book even better.

Thank you,

Pune, India Pranav D. Pathak
Nagpur, India Sachin A. Mandavgane

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Sachin A. Mandavgane is a Professor and head of Chemical Engineering Department at the Visvesvaraya National Institute of Technology, Nagpur. His research specialization is biomass and waste utilization, biorefinery, sustainable engineering, and scientific validation of traditional sciences. He is the author of around 130 publications with 3200 citations and h-index 30. He has produced 9 PhDs and has 10 patents in his name. He has developed a process of making lightweight and thermal insulating construction material using paper mill waste. He designed and commissioned a potato peel biorefinery plant, which is the first of its kind globally. His process of on-farm paddy straw digestion to manure has been successfully commercialized. He offers consultancy to industries to perform Life Cycle Assessment. His teaching interests include use of social media for teaching and UG research. He received FICCI’s Higher Education award for his innovative pedagogy in 2014. He offers a course ‘Innovative Design’ to nurture open and inclusive innovation. He is among the first few in India to develop a credit course on ‘Sustainable Engineering´ and ‘Biorefinery Engineering’.

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Part I

Biochemicals

Mixed Culture Polyhydroxyalkanoate Production as a Wood Processing Biorefinery Option

1

Suren L. J. Wijeyekoon and Ian D. Suckling

Abbreviations

AD	Anaerobic digestion
ADF	Aerobic dynamic feeding
ATP	Adenosine triphosphate
COD	Chemical oxygen demand
DO	Dissolved oxygen
DS	Dissolved solids
EPS	Extracellular polymeric substance
GAO	Glycogen accumulating organisms
HV	Hydroxyvalerate
LDPE	Low-density polyethylene
Mcl	Medium-chain-length
MMC	Mixed microbial consortia
Odt	Oven-dry tonnes
PAO	Polyphosphate accumulating organisms
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PP	Polypropylene
PS	Polystyrene
RNA	Ribonucleic acid
SBR	Sequencing batch reactor

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Scl	Short-chain-length
SCW	Supercritical water
ThOD	Theoretical oxygen demand
TMP	Thermo-mechanical pulp
TSS	Total suspended solids
VFA	Volatile fatty acids
WF	Wood fibre
WFRTC	Wood fibre-reinforced thermoplastic composites
WO	Wet oxidation
WPC	Wood plastic composites

1.1 Introduction

Sustainably grown forest biomass is one of the largest available feedstocks for bio-based manufacturing. Currently, forest biomass is used for construction, furniture, energy (primary) production, pulp and paper manufacture and chemical (secondary) production. Future secondary uses will be for biofuel, biochemical and bioplastic production. Forest biomass can be hydrolysed to sugars for use as a carbon source for biochemical transformations (Suckling et al. 2017). Alternatively, residual carbon from existing biomass processing could be harnessed as a biorefinery opportunity. A biorefinery integrates biomass conversion processes and equipment to produce biofuels, power, heat and bio-based chemicals from biomass. For example, losses of organic carbon from pulp mills in the form of wood residues, liquid process effluent and volatile organic carbon emissions can be recovered and transformed into value-added compounds and materials. Such biorefinery opportunities improve the profitability and environmental performance of existing biomass-based industries, such as pulp mills.

One such opportunity for valorising residual carbon is through production of biopolymers such as polyhydroxyalkanoates (PHAs). Microbiologically produced PHAs are a family of polyesters that have similar properties to petroleum-based thermoplastics such as polypropylene (PP) and low-density polyethylene (LDPE) but are fully biodegradable (Morgan-Sagastume et al. 2010). PHAs are considered as one class of biopolymers of the future and are expected to gradually replace conventional plastics. They are distinct from other bio-based biopolymers such as polylactic acid and polybutylene succinate due to their polymerisation by microorganisms, biodegradability and biocompatibility. This biotechnology opportunity lends itself to diverse products such as films, filaments and injection-moulded products (Mehrpouya et al. 2021) that could potentially enhance pulp mill revenue.

Different PHA structures with different properties are produced by bacteria, and they are characterised as short-chain-length (scl, 3–5 carbon atoms) and medium-chain-length (mcl, 6–14 carbon atoms) PHA, depending on the number of carbon atoms in their monomeric unit. Polyhydroxybutyrate (PHB) is the most widely known scl-PHA, but is difficult to process due to its crystalline structure resulting in stiff and brittle properties when it is processed into bioplastic (McAdam et al. 2020). The copolymer PHBV (3-hydroxybutyrate-co-3-hydroxyvalerate), which is synthesised by bacteria in the presence of odd number of carbon containing volatile fatty acids (VFA), exhibits better polymer processing properties like toughness and flexibility (Jung et al. 2019). These properties improve with increasing 3-hydroxyvalerate (HV) content. Scl-PHAs are mostly used for disposable product manufacture such as packaging, whereas mcl-PHAs are used for the production of surgical sutures, implants and drug delivery systems (Chen 2009).

Pure microbial culture fermentations use sugar as a feedstock for PHA production. The cost of these purified microbial polyesters is currently three to four times higher than that of conventional PP and LDPE plastics (Kourmentza et al. 2017). Most of these costs are for purification (40%), carbon source (40%) and sterilisation (10%) of plant and equipment (Bengtsson et al. 2008a). A waste organic carbon source-based mixed microbial consortia (MMC) production process has the potential to significantly reduce these costs. Major cost reductions can be achieved in feedstock cost (low-value waste feedstocks), fermentation costs (no sterilisation), fermentation equipment costs (less expensive reactor construction material, lower degree of process control required) and the culture procurement cost (use of open mixed cultures present in wastewater). A further advantage of using MMC is that the cultures can use a wide variety of complex feedstocks as opposed to the need for expensive pure sugars for pure culture production. There is also the option of producing composite materials with PHA-containing biomass (Thompson et al. 2010). The option eliminates purification costs, thus making this type of PHA production very cost competitive.

Challenges for commercial PHA production from MMC are:

- Lower yields from mixed culture processes compared with pure culture systems, requiring larger plant and equipment with high capital investment.
- Need for process development to further increase yields from complex feedstocks.
- Integration to existing primary production processes to make PHA production viable using waste residues.
- Development of efficient and cost-effective polymer-biomass separation technology.
- Developing a market for a waste-based PHA product (very important).

Despite significant advances in mixed culture PHA production, wide commercialisation and industrialisation is still struggling due to high production costs. The technical feasibility of PHA production from pulp mill wastewaters has only been demonstrated at lab and pilot scale (Anjali et al. 2014; Bengtsson et al. 2008a, b; Bhuwal et al. 2013; Jiang et al. 2012; Loge 2005; Yan et al. 2006). Authors' recent work using biosolids as a feedstock demonstrated the potential of a MMC accumulating PHA up to 40% of dry cell weight (Wijeyekoon et al. 2018). Other studies have demonstrated the feasibility of achieving up to 77% and 89%

PHA in MMC using substrates paper mill wastewater and acetate, respectively (Jiang et al. 2012; Johnson et al. 2009).

One of the main barriers to commercial-scale PHA production from waste resources is the availability of sufficient quantities of feedstock for an industrial-scale PHA production plant. Only a few manufacturing sectors have access to feedstock of sufficient quantity; the wood processing sector is one of them.

The main objective of this article is to review some forest biomass conversion technologies, discuss some strategies of mixed culture PHA production, estimate the PHA production potential from a wood processing site waste streams and describe a conceptual design for a PHA production facility incorporating wastewater treatment from a pulp mill. Product concepts, market pathways and potential applications are also addressed. The article does not go into depth in addressing process development, process integration and market potential.

1.2 Feedstocks

The pulp and paper sector generate significant quantities of waste residues from their manufacturing operations. These wastes are treated and disposed (wastewater), burnt as fuel (wood residues), vermicomposted (sludge) and landfilled incurring waste management costs. Primary wood processing operations such as saw milling produce sawdust and bark which currently have low-cost disposal/use options. Table 1.1 shows the organic waste streams and their estimated quantities generated

Table 1.1 Organic waste arising from an integrated wood processing site in New Zealand

Waste type	Source	Quantity (T/year)	Strength	Composition	Availability
Wastewater	Pulping process	3500×10^3	2 g/L of COD[a]	1 g/L wood sugars, 0.5 g/L extractives, 0.5 g/L lignin fragments	16 h/day
Primary sludge	Clarifier	20,000	25% solids	Mainly wood fibre	Consistent production
Secondary sludge	Pond	Not estimated	15–30% solids if dredged and air dried	50–70% organic	Not available
Sawdust	Primary wood processing	100,000	40–50% solids	30% lignin, 69% wood sugars, 1% extractives (resin and fatty acids)	Consistent production
Wood residues	Wood processing	100,000	40–60% solids		Consistent production

[a] *COD* chemical oxygen demand

from an integrated wood processing site in New Zealand encompassing primary and secondary wood processing (from an unpublished study carried out by the authors).

Pulp mill wastewater treatment performances and cost efficiencies have seen a significant improvement over the years, yet challenges still exist and environmental consent issues do arise from time to time (Hubbe et al. 2016). Treatment plant capacity and sludge disposal are critical issues for mills to deal with (Scott and Smith 1995). Landfill capacity expansion is an ongoing challenge involving significant costs and environmental concerns. Opportunities to divert solid waste streams from landfills and extract value from the considerable organic waste stock are prudent ways of minimising risks associated with waste disposal (McGrouther et al. 2013). One way forward is to look at options higher up in the waste management hierarchy, moving away from treatment/disposal to resource extraction.

1.3 Feedstock Conversion Processes

Not all forms of feedstock can be readily used for PHA production. For example, solid materials need conversion to soluble form. Soluble sugars (monomeric or oligomeric) or VFAs are the preferred forms of feed for PHA production. While soluble sugars are used mostly in pure culture PHA production, VFAs are the feed of choice for MMC due to the risk of glycogen (another form of microbial storage compound) and extracellular polymeric substance (EPS) formation with sugars. Most of the mixed culture PHA production studies have used VFA-containing feeds as the preferential feed form to minimise glycogen production (Dias et al. 2006). Fermented sugars are widely used as VFA-containing substrates for MMC PHA production (Albuquerque et al. 2010b). Only few studies have used unfermented sugar substrates for MMC PHA production (Venkateswar Reddy and Venkata Mohan 2012a).

Woody biomass conversion processes for wood sugar production have been demonstrated at reasonable scale (Sect. 1.3.1). Production of VFAs from woody residues, though technically feasible, is still at laboratory scale, with little information available at present to make any yield or cost estimates. Bowers et al. (2014) have demonstrated the use of softwood hydrolysate for PHA production.

The authors have previously investigated glucose as a feed for mixed culture PHA production (unpublished data). Though feasible, PHA yields were found to be lower than that for an acetate feed. However, literature shows that similar PHA yields can be achieved from sugars and VFAs, although feed costs ($/kg PHA) are marginally different (Salehizadeh and van Loosdrecht 2004).

Woody residues can be converted to monomeric sugars via acid digestion and enzymatic hydrolysis processes (Albuquerque et al. 2007). Wet oxidation is also a potential technology for conversion of woody biomass to VFAs. The authors in their previous studies have developed platform technologies in this area, achieving conversion of certain solid streams to either sugars or organic acids (Andrews et al. 2014, 2015; Baroutian et al. 2013, 2015, 2016). A generic description of the conversion technologies to produce sugars and VFAs with referenced details of such processes together with yield and cost information (where available) is detailed in Sect. 1.3.1.

The authors developed a mass balance-based model to estimate PHA production from wood processing residues. The model was used to estimate flows and unit sizing of a concept design PHA production plant. For the model, the woody feedstock conversion to wood sugars and VFAs is assumed to occur according to processes described in literature. Both sugars and VFAs were considered as substrates and the model did not differentiate the PHA yield based on the feed type. Thus, both types of feed were considered as carbon sources in the conceptual design. Given that there are feedstock conversion processes available which yield both wood sugars and VFAs from woody biomass, the concept design allowed for both forms of substrates to be examined and compared on an equal COD (chemical oxygen demand) loading.

1.3.1 Processes to Produce Sugars

Before feedstocks such as sawdust can be converted to PHAs, they must first be converted into a form digestible by bacteria. One of the most promising approaches involves hydrolysis of the cellulose and hemicelluloses in the wood into simple water-soluble sugars like glucose (Fig. 1.1). Routes for converting lignocellulosic substrates, including wood, agricultural residues such as corn stover or sugarcane bagasse and dedicated energy crops such as miscanthus or energy cane, into sugars have attracted a lot of scientific and commercial attention in the last 10 years, as the resulting sugars can be fermented to ethanol for use as a biofuel (Duque et al. 2021). These same conversion routes can be applied to PHA production.

Cellulose is hydrolysed to glucose, while the hemicelluloses are converted to a mixture of five- and six-carbon sugars. The composition of the latter depends on the hemicelluloses in the initial feedstock; for softwoods it is mainly a mixture of mannose, xylose, glucose and galactose (Bhaumik and Dhepe 2015; Wijeyekoon

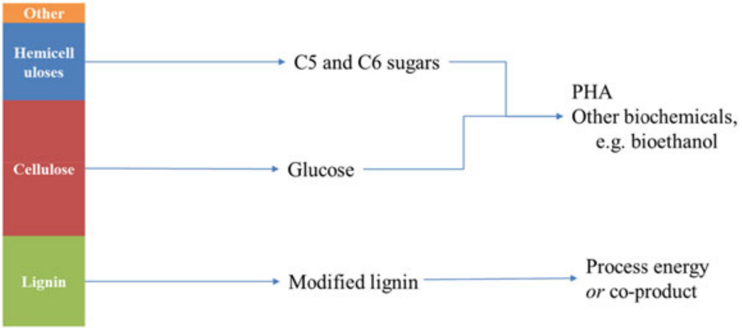

Fig. 1.1 Production of monomeric sugars and lignin by hydrolysis of lignocellulosic biomass

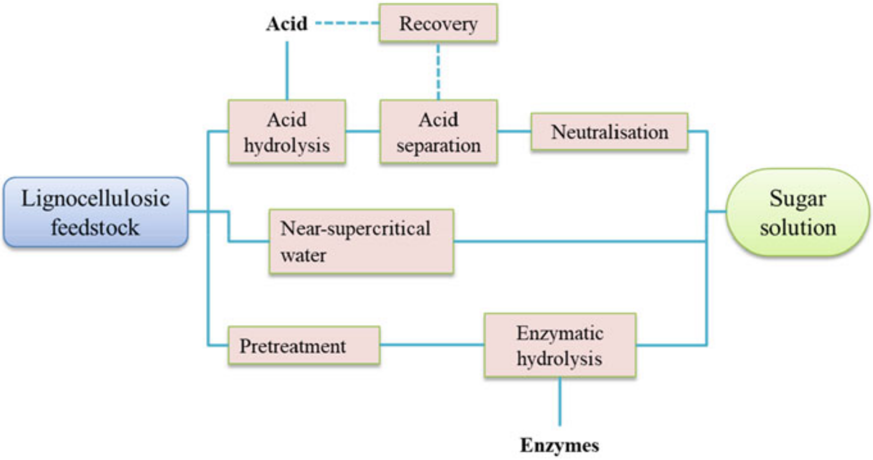

Fig. 1.2 Pathways for hydrolysis of cellulose and hemicelluloses

and Vaidya 2021). The lignin in the biomass generally serves as a source of process energy but can be recovered from some processes for sale as a coproduct.

Hydrolysis of carbohydrates to the monomeric sugars is commonly performed using acids, enzymes or near-supercritical water (SCW) (Fig. 1.2) (Wijeyekoon and Vaidya 2021).

1.3.1.1 Dilute Acid Hydrolysis

Processes for acid hydrolysing lignocellulosics using dilute mineral acids (e.g. H_2SO_4) have been known for a long time, with more than 20 lignocellulosic ethanol plants operating commercially up to or during World War II (Rinaldi and Schuth 2009; Taherzadeh and Karimi 2007). Most were subsequently closed for economic reasons, but a few still remain operational, virtually all in Russia. Dilute acid hydrolysis typically involves treating biomass with dilute acid (e.g. 0.5–3% H_2SO_4) at high temperatures (at least 130 °C) and pressures. The hydrolysate is then neutralised and filtered to separate the sugar solution from the insoluble lignin (plus gypsum, if lime is used for neutralisation). Sugar yields depend on the substrate, but in the case of softwoods rarely exceed 45% by weight of the starting wood (60–70% of theoretical) (Rabinovich 2010).

In spite of their commercial maturity and applicability to a wide range of lignocellulosics, including wood, dilute acid processes have received little recent attention as a route to cellulosic sugar. This mainly reflects the low sugar yield and the difficulty of utilising the residual “hydrolysis lignin”.

1.3.1.2 Concentrated Acid Hydrolysis

Hydrolysis of lignocellulosics by concentrated sulphuric and hydrochloric acids has also been studied for many years (Rinaldi and Schuth 2009; Taherzadeh and Karimi 2007). Processes using concentrated (e.g. 30–70%) acids are generally found to give higher sugar yields, typically greater than 90% of theoretical, and to require milder conditions (e.g. 40 °C, for 2–6 h) than dilute acid processes. However, acid consumption is higher, the acid must be recovered for both economic and environmental reasons, inhibitors are generated and economically separating the sugars while recovering the acid can be problematic. Concentrated acid hydrolysis has been re-investigated in recent years by a number of companies (Kong-Win Chang et al. 2018).

1.3.1.3 Enzymatic Hydrolysis

Enzymatic processes to convert the cellulose in lignocellulosic substrates into monomeric sugars have attracted a lot of recent scientific and commercial attention, with a number of commercial plants being built by several companies including GranBio (Brazil), Raizen, Beta Renewables (Italy), Poet-DSM (US), Dow DuPont (USA) and Clariant (Germany). Such processes are considerably more complex and costly than using enzymes to hydrolyse starch in corn, as was used for first-generation ethanol production.

Some form of chemical or physical pretreatment of the biomass is invariably required prior to enzyme hydrolysis of lignocellulosics (Fig. 1.3). This disrupts and/or removes the lignin and hemicelluloses to make the cellulose accessible to the cellulase enzymes (Haghighi Mood et al. 2013; Silveira et al. 2015). The requirement for a pretreatment stage, along with the cost of the enzymes, adds considerably to the cost of enzymatic processes.

One of the simplest, most effective and widely used pretreatments involves heating the lignocellulosic biomass in water or directly with steam typically at 160–230 °C, often in the presence of dilute acid as catalysts. There are many variants on this basic approach, with most hydrothermal pretreatments involving heating at temperatures of between 160 and 230 °C (Chandra et al. 2007; Galbe and Zacchi 2007; Haghighi Mood et al. 2013; Mosier et al. 2005).

For the enzyme hydrolysis stage, cellulase enzymes are added to a slurry of the pretreated biomass in water and mixed, typically for 24–72 h at 30–55 °C, to produce a solution of the sugars plus a lignin-rich insoluble residue. Commercial cellulase

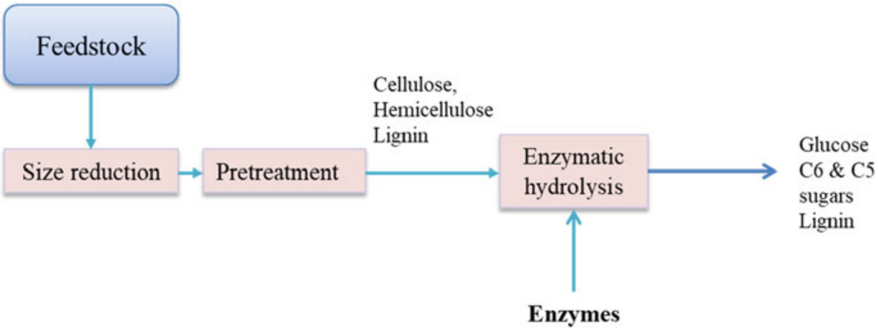

Fig. 1.3 Production of sugars by enzymatic hydrolysis

enzymes are proprietary cocktails containing all the enzymes needed to break cellulose and hemicelluloses down to monomeric sugars. High yields (>80%) of sugars can be obtained, depending on the nature of the pretreated biomass, enzyme cocktail and hydrolysis conditions. If ethanol is the final target, the enzyme hydrolysis is sometimes followed by a fermentation stage. For example, when using corn stover as a feedstock, a yield of 590 kg sugars/tonne dry feedstock (90% of theoretical sugars plus starch) can be achieved (Humbird et al. 2011).

Enzymatic processes are typically more feedstock-sensitive than acid hydrolysis processes, with successful enzymatic hydrolysis requiring the feedstock, pretreatment and enzyme cocktail to be matched and the biomass to be more homogeneous. Softwoods, such as radiata pine, are considered to be amongst the most difficult feedstocks for enzymatic processes, typically requiring a more severe pretreatment and a higher enzyme dose (Huang and Ragauskas 2013). In addition, the current commercial enzyme cocktails lack the necessary enzymes needed to fully degrade galactoglucomannans, the dominant form of hemicellulose in softwoods; this is important for good sugar yields (Cameron et al. 2015).

Pretreatment processes which can remove all or part of the lignin from the wood or other lignocellulosic materials can also be very effective at producing a digestible cellulose (Kandhola et al. 2017). Such processes are already used commercially at a large scale for the production of wood pulp. While such approaches produce a digestible substrate, chemical costs are higher, so they generally only become financially viable if the lignin can be recovered and sold as a coproduct along with the sugars. Various sulphite-based and organosolv pulping processes, which allow a useful lignin to be isolated, have been re-examined as pretreatments prior to enzymatic hydrolysis. For example, Borregaard has evaluated a sulphite-based process at a demonstration scale for the coproduction of cellulosic ethanol and lignosulphonates (Gargulak and Lersch 2012), and Lignol operated a pilot-scale organosolv process to produce ethanol and lignin (Arato et al. 2005). A challenge with this approach is establishing lignin markets of sufficient scale to match that needed for a commercial biofuel plant.

1.3.1.4 Hydrolysis in Near-Supercritical Water (SCW)

A less-developed process involves hydrolysis in SCW. When water is heated above its critical temperature and pressure ($T > 374$ °C and $P > 22.1$ MPa), it acts as an acidic organic solvent capable of dissolving most organic compounds. Woody biomass can be degraded into monomeric sugars and some phenolic compounds by a short treatment in SCW (Kim et al. 2010; Saka and Ueno 1999). While temperatures and pressures required are high, the reaction times are very short and no added chemicals are required.

The most active company in this area is Renmatix. In their process, the biomass (corn stover, cane bagasse, energy grasses and woody plants) is first hydrolysed under mild conditions to degrade and solubilise the hemicelluloses, and then a second stage in SCW is used to hydrolyse the cellulose (Renmatix 2019). Most of the lignin remains insoluble, along with some of the carbohydrates. The company has a demonstration plant (3 odt biomass/day) and claims high yields of clean sugars and low production costs, but to date little publically available information on either the yield of sugars or the costs of production has been reported.

1.3.2 Processes to Produce Volatile Fatty Acids

The following sections describe processes that can convert biomass into VFAs containing liquors for use as feed for PHA production.

1.3.2.1 Anaerobic Digestion

Anaerobic digestion (AD) is a well-established process for the biological conversion of organic matter to organic acids and finally to methane and carbon dioxide (biogas). Many commercial-scale AD plants degrade organic matter, including lignocellulosic material, to biogas for energy production or as a waste treatment. However, lignin is recalcitrant to biodegradation and wood extractives are toxic to the anaerobic organisms (Sekido et al. 1990). Therefore, AD is a technology that could be used to process liquid waste streams such as pulp mill effluent without additional pretreatment.

Acidogenesis (Fig. 1.4) in AD would allow the conversion of complex organic material to a form (VFA) that is more suitable for PHA production. Partial digestion without the need for gas production would reduce the capital cost requirement of the AD process. Acidogenic fermentation of organic waste residues is the most predominant technology investigated as a pretreatment option for PHA feedstocks. Olive oil mill effluents (Dionisi et al. 2005), sugar molasses (Albuquerque et al. 2010b), municipal sludge (Bengtsson et al. 2017), pulp mill effluents (Anjali et al. 2014; Bengtsson et al. 2008a, b; Bhuwal et al. 2013; Jiang et al. 2012; Loge 2005; Yan et al. 2006) and food waste (Venkateswar Reddy and Venkata Mohan 2012b) have been fermented to produce a VFA-rich stream for MMC PHA production at lab and pilot scale.

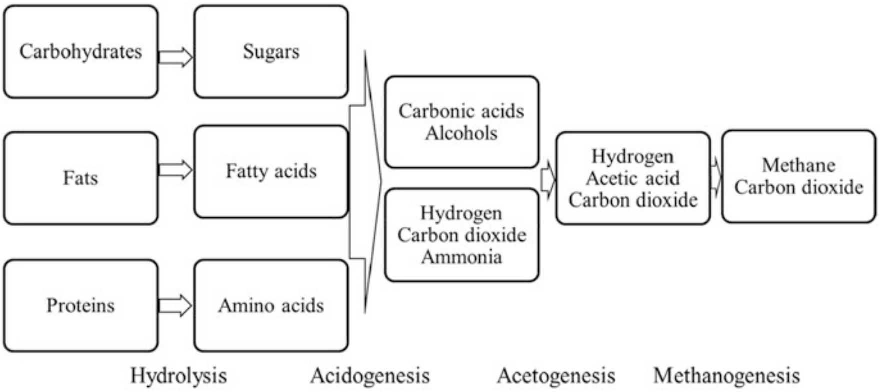

Fig. 1.4 The key process stages of anaerobic digestion

However, undigested organic matter may add to the downstream processing cost and have unknown effects on the PHA production process and on the product composition.

1.3.2.2 Wet Oxidation

Wet oxidation (WO) involves liquid-phase deconstruction of organic and inorganic components at elevated temperatures and pressures. The technology enables the conversion of woody residues to VFA-containing liquors. The reported breakdown of lignin and resin acids in wood makes the WO products more amenable for biological processing (Baroutian et al. 2013). Typical conditions for wet oxidation are 150–320 °C under 20–150 bar of pressure for 15–120 min. This technology is established at full scale on a variety of wastes, both industrial and domestic. Potential to use WO for woody feedstocks has been reported at lab scale (Alexander 2014) and in filed patent (Merrill and Petersen 2014). A total carboxylic acid yield of 25 wt% has been reported for WO of sawdust (Alexander 2014). Scion possesses significant knowledge on WO and has developed the proprietary TERAX® WO-based sludge treatment process which is in the pre-commercialisation stage at present (TERAX® 2013).

Due to very limited publically available information on commercial-scale WO plants treating woody residues, no reliable cost estimates can be put forward for producing VFAs from wood feedstocks. It is anticipated that this technology could rapidly evolve given the deconstruction potential of readily available lignocellulosic feedstocks for biofuel and biomaterial production. There are published works that have demonstrated PHA production from wet-oxidised sewage sludge including authors' recent work (Morgan-Sagastume et al. 2010; Wijeyekoon et al. 2018).

The different pre-processing technology options yield different products containing a spectrum of oxidised compounds at specific concentrations. These may pose challenges to the PHA production process.

1.3.3 Theoretical Sugar Yields

When assessing the different solid residues as feedstocks for PHA production via sugars, it is useful to first compare the theoretical (i.e. maximum possible) yield of sugars which can be obtained from the different substrates. These can be calculated from the amount of cellulose and hemicelluloses in the different substrates. The values in Table 1.2 suggest that clean wood and sawdust are going to produce the highest theoretical yields, while bark is not a very useful residue for sugar production [Kibblewhite et al. 2010; Uprichard 1991]. The lower concentration of carbohydrates in the forest residues (Table 1.2) can be attributed to the presence of bark and pine needles and to the lower carbohydrate content of branches.

Actual sugar yields will generally be lower than the theoretical yields and depend on the efficiency with which the cellulose and hemicelluloses are converted to the monomeric sugars in each of the substrates. The authors caution that, particularly for the wood processing and forest residues, the compositions, and therefore the

Table 1.2 Estimated chemical compositions and theoretical sugar yields for different substrates (g/100 g oven-dried substrate)

	Composition					Theoretical sugar yield
	Ash	Extractives	Lignin	Cellulose	Hemicelluloses	
Wood[a]	0.3	0.5	28	42.2	24.0	72
Bark	2	65	15	12	6	20
Sawdust	0.5	0.5	28	42.2	24.0	72
Forest residues	2	5.5	28	59.7		66
Primary sludge	43	0.1	8	47.0		52

[a] Radiata pine, a soft wood

Notes:

1. The composition of wood and clean bark was taken from Kibblewhite et al (2010) and Uprichard (1991), respectively
2. The composition of forest residues can vary widely depending on where and how they are collected. The authors assume here a mixture of 84% stems (containing 9% bark), 14% branches and 3% needles
3. The authors assume an ash content of 43% in primary sludge and that all other solids are a 50: 50 mix of TMP fibre (with the same composition as the wood) and bleached softwood Kraft pulp
4. As these materials contain components other than those reported here, totals may not add up to 100%
5. When carbohydrates such as cellulose are hydrolysed to their monomeric sugars, mass yields are >100% as water is added on hydrolysis of the glycosidic linkages

theoretical sugar yields, will depend on where and how the residues are collected. For example, the yield of sugars from the forest residues will vary depending on the proportion of stem wood, bark, branches, needles and dirt in the samples (Uprichard 1991).

It is important to note that sugars derived from hydrolysis of wood or wood residues are not directly comparable to a traditional commodity sugar derived from corn or sugar cane, as the wood sugars contain a mixture of C6 and C5 sugars as a relatively dilute solution which also contains other contaminants such as furfurals, residual lignins, etc.

Actual conversion yields for the different wood residues need to be obtained before further decisions on the suitability of the derived sugars for PHA production can be determined. Forest residues are generally more contaminated (and less consistent in composition and size) than the clean wood frequently used for process development work. At best, components such as ash or bark present in the feedstocks will act as inert dilutants reducing sugar yields. They may also cause additional processing problems such as the formation of inorganic deposits during processing, equipment wear or bark extractives affecting enzymatic hydrolysis. Furthermore, as indicated above, such wood sugars may contain contaminants such as furans, lignin fragments and acids, so the susceptibility of the organisms used in PHA production to these contaminants will need to be checked in case detoxification is required.

1.4 Mixed Microbial Consortia PHA Production Process

The mixed microbial consortia PHA production process is typically a two-stage operation. The objective of the first stage is to grow PHA-producing bacteria and is known as the consortia enrichment stage. Once the mixed consortia are enriched with PHA-producing bacteria, the biomass is transferred to the second stage where the objective is to allow the enriched consortia to accumulate PHA. The second stage is known as the PHA accumulation stage.

The process can be schematically depicted as in Fig. 1.5. The solid feedstocks can be transformed by processes described in Sects. 1.3.1 and 1.3.2 to sugar- and VFA-containing feed streams. This feed stream is preferentially used as the carbon source for PHA accumulation stage, although it can be used for stage 1 as well. The wastewater from a pulp mill is preferentially used as the carbon source for stage 1, thereby treating this stream as well as obtaining a lower cost feedstock for bacterial biomass growth.

1.4.1 Consortia Enrichment

A wide variety of bacteria are able to accumulate PHAs as an intracellular carbon storage mechanism. This stored carbon, in the form of polyester/fatty acid, is used during famine periods by bacteria that are exposed to feed/famine feeding regimes. The ability to store carbon as PHAs is a key survival mechanism of these bacteria.

Current commercial-scale PHA production uses natural isolates or engineered microbial strains along with pure feedstocks such as glucose (Koller et al. 2017; Możejko-Ciesielska and Kiewisz 2016). Mixed microbial consortia PHA production involves the use of open cultures (non-sterile conditions) enriched with PHA-accumulating organisms. Enrichment is achieved by applying selective ecological pressure for the preferential growth of PHA accumulators. The principle is to engineer the conditions, rather than the organisms (Kourmentza et al. 2017).

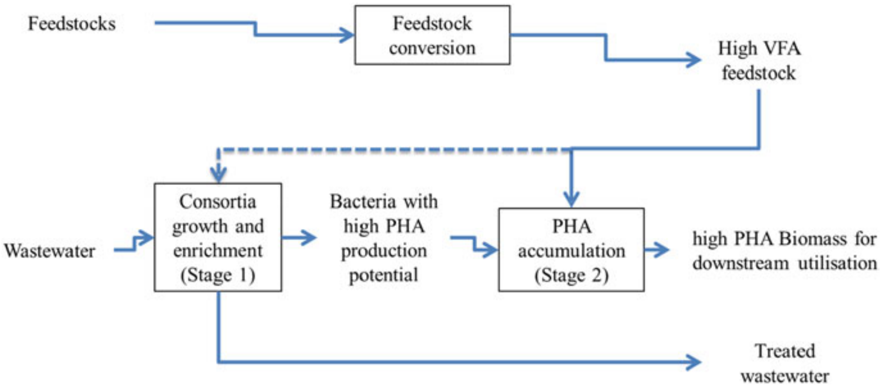

Fig. 1.5 Schematic diagram for the two-stage MMC PHA production process

There are a number of ways by which culture enrichment could be achieved. The most common techniques are the anaerobic-aerobic selection and the feast-famine approach. PHA production was first observed in a biological phosphorus removal wastewater treatment process in which alternate anaerobic-aerobic conditions are employed. Thus, early enrichment strategies used anaerobic-aerobic alternate conditions where the glycogen accumulating organisms (GAO) and polyphosphate-accumulating organisms (PAO) stored PHA under the anaerobic phase. The stored PHA is metabolised under the aerobic phase resulting in a higher adenosine triphosphate (ATP) yield compared to the anaerobic substrate (Kourmentza et al. 2017). However, the PHA production was found to be low (≈20% w/w) as these bacteria depend on the accumulation of glycogen or polyphosphate from the stored PHA. At least one study has shown that higher PHA accumulations (≈60% w/w) could be obtained under anaerobic-aerobic enrichment conditions where PHA is accumulated in the aerobic phase without depending on the glycogen or polyphosphate reserves (Albuquerque et al. 2007). There are currently no commercial-scale PHA production processes that employ this enrichment strategy. There is also less research efforts being applied to improve the performance of this process. However, the strategy does offer some benefits such as energy saving from the anaerobic periods of operation.

The second strategy to culture enrichment, aerobic dynamic feeding (ADF) or feast-famine approach, has been the more successful one in terms of PHA accumulations with up to 90% of dry cell weight, being demonstrated in lab-scale studies (Jiang et al. 2011; Johnson et al. 2009). The limiting condition imposed under feast-famine conditions is the carbon availability where the bacterial consortia is subjected to alternate phases of excess carbon (feast) and carbon starvation (famine) under aerobic conditions. Under these conditions, bacteria that are able to produce and store PHA have a competitive advantage over non-PHA-producing organisms in the MMC as they are able to use the PHA as a carbon and energy reserve during carbon deficiency (Albuquerque et al. 2007; Reis et al. 2003). The cyclic exposure to alternate feast and famine phases provides an advantage to the PHA-producing organisms, resulting in their enrichment in the MMC. It is hypothesised that a long starvation period applied limits the required ribonucleic acid (RNA) and enzymes for cell growth of non-PHA producers during the feast phase. However, during the feast phase, PHA producers can polymerise PHA with the aid of the PHA synthase enzyme (Kourmentza et al. 2017). This allows the channelling of available carbon to PHA accumulation giving rise to higher yields.

Most of the recent research has been on improving the ADF operational parameters to improve PHA yields. A significant number of research publications and reviews are available on this subject (Albuquerque et al. 2010b; Anjali et al. 2014; Bengtsson et al. 2008a, b, 2017; Dias et al. 2006; Jiang et al. 2012; Johnson et al. 2009; Kourmentza et al. 2017; Loge 2005; Salehizadeh and van Loosdrecht 2004; Venkateswar Reddy and Venkata Mohan 2012a, b; Wijeyekoon et al. 2018). Operational parameters such as C/N ratio of the substrate, feast-famine ratio, carbon loading rate, dissolved oxygen (DO) concentration, pH, temperature, hydraulic and solid retention times, etc. have been investigated, and a good understanding on their influence on PHA accumulation has been reached. Most importantly, continuous PHA production has been shown to be possible in continuous stirred tank reactors (Albuquerque et al. 2010a). This is an improvement from using sequencing batch reactors (SBR).

1.4.2 PHA Accumulation

The PHA accumulation stage follows the enrichment stage in the two-stage PHA production process. The enriched PHA-producing culture is allowed to accumulate PHA to its fullest potential by supplying an appropriate substrate. PHA accumulation is generally promoted under conditions that have a limited supply of an essential nutrient for growth in an environment that has excess carbon, such as VFAs containing stream produced from woody biomass. This accumulated PHA-containing biomass is later harvested for extracting the PHA.

Culture enrichment is crucial for obtaining high PHA-containing biomass. Poor enrichment leads to the growth of non-PHA-producing organisms which not only dilute the PHA-containing biomass but also consume the substrate for their growth, reducing PHA yield. The issues with waste-derived substrates are the availability of organic compounds other than the sugars and VFAs that promote the growth of non-PHA-containing organisms, and the dilute nature of the substrate that increases the working volume. One strategy to minimise the growth of both PHA-producing and non-PHA-producing microorganisms during the accumulation phase is to supply substrates without nitrogen or phosphorus which are essential for bacterial growth. Forest biomass-derived substrates are nitrogen limited and therefore ideal for this purpose. On the other hand, high substrate concentrations can cause inhibition and limit PHA accumulation.

Amongst other operational parameters, the substrate feeding strategy is known to affect the PHA productivity. Fed-batch feeding is known to produce high PHA productivity, but this drops as the PHA is being accumulated. A sustained productivity is shown when continuous feeding is employed (Wijeyekoon et al. 2018). Reported PHA yields and productivities for continuous feeding are 0.8 Cmol PHA/Cmol S and 1.2 g PHA/L h for fermented molasses (Albuquerque et al. 2011). An appropriate substrate loading rate needs to be developed based on the substrate used. Widely varying loading rates are reported in literature with 3.5–5.5 Cmol VFA/Cmol X/day for low biomass loading rates (Kourmentza et al. 2017). Controlling the substrate addition based on pH or DO concentration is proven to be effective in terms of substrate conservation and inhibition prevention.

1.4.3 PHA Recovery

PHA recovery is the processes by which the intracellularly produced PHAs are retrieved for beneficial use. This entails a number of downstream operations depending on the required form of PHA and its beneficial use. These operations could significantly increase the cost of MMC PHA production and therefore should be carefully selected. Although a number of techniques have been reported for the recovery of PHA, a biorefinery opportunity precludes the use of some techniques considering the environmental sustainability of the overall process. Therefore, new strategies and techniques are required to improve the economic and environmental sustainability of the recovery process.

The PHA recovery can be principally divided into the following phases:

1. Biomass harvesting
2. PHA extraction
3. PHA purification

Biomass containing intracellularly accumulated PHA needs to be harvested prior to extracting the PHA. Settled biomass from the accumulation phase is concentrated by filtration or centrifugation. This wet biomass, consisting of both PHA-containing and other cells, can be further processed to extract the PHA. The extraction process could be any one of or a combination of drying, grinding and chemical or biochemical extraction (Kourmentza et al. 2017). It should be noted that drying of MMC biomass is very challenging, requiring large amounts of heat energy. Thus, wet processing methods are preferred.

PHA extraction by chemical and biochemical means is done to disrupt the cell biomass and solubilise the PHA. Generally, alcohol precipitation is used to solubilise and concentrate PHA that has been extracted by various solvents. On the other hand, if cell disruption by physical or biological means precede PHA extraction, then PHA granules can be separated by filtration or centrifugation. Final purification of the PHA is either by drying or washing with water, detergents or alcohol.

1.5 PHA Production Potential

In estimating the PHA production potential from the feedstocks listed in Table 1.1, the feedstock organic fraction was expressed as COD using the yields and conversion factors listed in Table 1.3. A conversion of 75% of the theoretical sugar yields was assumed with 10% sugar/VFA concentration after feedstock transformation.

For the ThOD estimation, the sugars and VFAs were assumed to be in the form of $C_6H_{12}O_6$ and CH_3COOH, respectively. The volumetric and organic loads of the transformed feedstocks based on the conversion factors are as given in Table 1.4.

The yields and conversion factors from Table 1.3 were used to estimate theoretical PHA production potential from the processed feedstocks. Two cases were considered for the estimation of soluble substrate yield: (1) a best-case conversion of the theoretical maximum of each waste stream to sugars and volatile fatty acids and (2) a worst-case conversion of 50% of the theoretical maximum (Table 1.5). The two-stage process polymer yield of 0.14 kg PHA/kg COD was then used, based on the work of Pozo et al. (2011) and Bengtsson et al. (2008a), who used Kraft mill wastewater as the carbon source.

Table 1.3 Conversion factors and yields

Factor/yield	Value
COD/DOC[a]	2.5
Biomass production (kg TSS[b]/kg COD)	0.5
PHA yield on substrate (kg PHA/kg COD)—for PHA accumulation stage	0.30
PHA yield on substrate (kg PHA/kg COD)—for the two-stage process	0.14
Theoretical oxygen demand (ThOD) for sugar/VFA (kg O_2/kg substrate)	1.07
Theoretical yield of sugar from primary sludge (kg sugar/kg DS[c])	0.52
Theoretical yield of sugar from sawdust (kg sugar/kg DS)	0.72
Theoretical yield of sugar from wood residue (kg sugar/kg DS)	0.66
Yield of VFA from sawdust (kg VFA/kg DS)	0.25

[a] *DOC* dissolved organic carbon
[b] *TSS* total suspended solids
[c] *DS* dissolved solids

Table 1.4 Modelled volumetric and organic flows of transformed feedstocks

Feedstock	Volumetric flow (m^3/year) × 10^3	Organic load (COD T/year)	COD concentration (g/L)
Wastewater	3500	7000	2
Primary sludge	19.6	1960	100
Sawdust	243.7	24,370	100
Wood residue	224.1	22,410	100

Table 1.5 PHA production potential from feedstocks

Feedstock	Wastewater	Primary sludge	Sawdust	Wood residue
Total dry solid loading (T/day)	8[a]	14	129	129
Soluble organic substrate (COD T/day)	15	4–8	46–93	43–85
PHA production potential (T/day)	1.0–2.1	0.5–1.0	6.5–13.0	6.0–12.0

[a] As total carbon in solid and dissolved form

The PHA production potential from all of the waste residues considered was estimated to be between 14.0 and 28.1 T/day. At the lower range, the production constitutes approximately 11% of the world's known PHA production capacity (Kourmentza et al. 2017). For the proposed conceptual design, the entire stock of wastewater carbon was considered for biomass production with the required carbon for PHA production coming in from the other transformed residue streams. Thus, the PHA production in the design is limited by the quantity of biomass production from wastewater.

1.5.1 Conceptual Design

A concept design for a PHA production plant is schematically depicted in Fig. 1.6. The scheme shows essential unit operations for PHA polymer production and extraction (lysis plant). The unit operations for feedstock conversion are not illustrated and are shown as a single unit operation. Depending on the required PHA product form, the lysis plant unit processes could vary.

The concept is based on a two-stage PHA production process containing biomass production and PHA accumulation stages. The wastewater COD and the extracted wood sugars or VFAs constitute the organic substrate for these two stages. The lower-cost fermented wastewater is primarily used in the first stage with provision for supplementing with woody residue-/sludge-derived sugars and VFAs if required. The wastewater is initially screened and clarified to remove floating and suspended solids. The clarified wastewater is then fermented to convert most of the organic matter to VFA. The acidogenic fermentation requires 2 days of retention time. Pulp mill wastewater at a temperature of nearly 40 °C is ideally suited for mesophilic fermentation.

The continuous flow of fermented wastewater is held in a holding tank until the feeding cycle of the biomass reactor begins. Prior to feeding to the biomass reactor, the fermented wastewater is cooled to 30 °C by the cooler discharges from downstream processes.

The cooled fermented wastewater and optionally the wood sugar-/VFA-containing liquor is fed to the biomass reactor where nutrient and pH adjustments are made. The COD is used for biomass growth in the SBR where a feast-famine

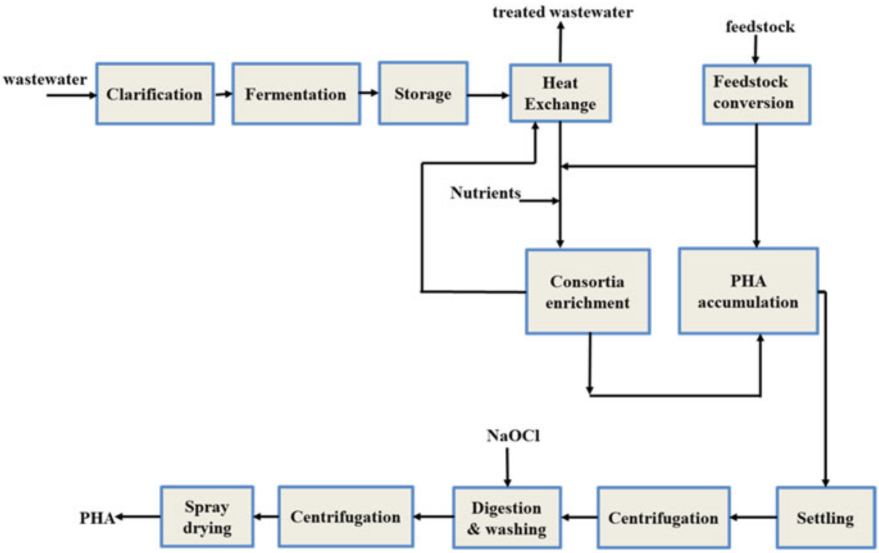

Fig. 1.6 Schematic diagram for a PHA production plant

feeding regime is maintained to promote the growth of PHA-accumulating organisms. The consortia enrichment reactor is on a 12-h cycle (two cycles per day). The treated wastewater is then decanted and used as the coolant in the heat exchanger when required. Approximately 50% of the biomass in the enrichment reactor is then transferred to the PHA accumulation reactor at the end of each cycle, maintaining a sludge age of 6 days. During the start of the next cycle, the enrichment reactor is fed again with wastewater from the storage tank.

The wood sugar- or VFA-containing liquor is then fed to the PHA accumulation reactor as carbon substrate for PHA accumulation. It is worth noting that the wood sugar solution and the volatile fatty acid liquor may produce two different PHA monomeric compositions. The PHA reactor is operated in batch with a batch time of 12 h.

At the end of each batch, the contents are transferred to the settling tank to remove the supernatant. The PHA-containing biomass is further concentrated through centrifugation. Depending on the desired form of the PHA-containing product, the cellular material containing the PHA can either be removed or left as it is for composite product forms. For pure PHA forms, the PHA is extracted from the biomass by NaOCl digestion followed by washing. The washed PHA is centrifuged again and then spray-dried to obtain PHA in powdery form.

1.5.2 PHA Yield and Productivity

A mass balance was carried out for the concept design described above. A simplified process flow diagram with the major mass flows in to and out of the plant is shown in Fig. 1.7. A flowrate of 10,000 T/day of wastewater produced from a pulp mill containing 2 g/L of COD is clarified to remove the primary solids (14 T/day). The clarified wastewater is fermented to produce volatile fatty acids where nearly 75% of the incoming COD is converted into VFAs (Bengtsson et al. 2008a). These VFAs constitute the carbon source for the growth of PHA-producing mixed culture

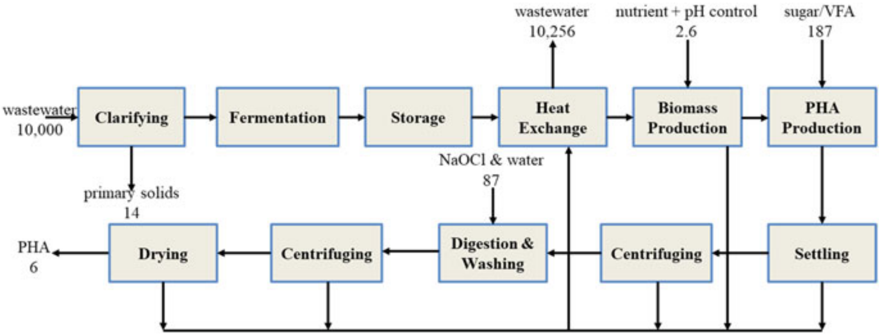

Fig. 1.7 Concept design process flow diagram with mass flow rates in T/day at baseline PHA yield of 0.3 kg PHA/kg COD

Table 1.6 Output parameter variation in high, baseline and low PHA yield scenarios

Output	PHA yield			Units
	High (0.35)	Baseline (0.30)	Low (0.25)	
PHA production	2300 (5600)[a,b]	2000 (5250)[a,b]	1650 (4900)[a,b]	(T/year)
PHA content	39	35	31	(% kg PHA/kg biomass)
Wastewater production	3592 (3539)[a]	3586 (3540)[a]	3579 (3541)[a]	(T/year) × 10^3

[a] Figures within brackets are for un-extracted PHA production

[b] Dry biomass containing relevant % of PHA

organisms with a biomass yield of 0.5 kg TSS/kg COD. The produced VFAs are fully metabolised in the biomass production stage (consortia enrichment), which is reasonable to assume for a 12-h cycle feast-famine operation (Bengtsson et al. 2008a; Wijeyekoon et al. 2018). The produced VFAs reduce the pH and alkali is dosed for pH control. The pulp mill wastewater has a low concentration of N- and P-containing compounds, and therefore supplemental nutrient dosing is required for biomass production (Jiang et al. 2012). These two flow streams are estimated to be 2.6 T/day (Fig. 1.7).

A 20 T COD/day basis is used for PHA production. A total of 90% of this COD is converted into PHA and respiration and for limited cell growth. The PHA accumulation was conservatively estimated as 50% of TSS (Bengtsson et al. 2008a; Jiang et al. 2012). This accumulated PHA after extraction, washing and drying led to 6 T/day of spray-dried material. The digestion and washing process require 87 T/day of NaOCl and water. Overall, the process generated 10,256 T of wastewater containing 1.6 g/L of residual COD produced mostly from the solubilisation of biomass during PHA extraction (Fig. 1.7).

In estimating the PHA production potential, an overall PHA yield of 0.14 kg PHA/kg COD was used for the two-stage process. This is similar to the yield estimated by Bengtsson et al. (2008a), who reported a yield of 0.11 PHA/COD (w/w) for a similar process configuration but with a lower biomass yield of 0.3 gTSS/gCOD and using wastewater with a significantly higher initial COD (8750 mg COD/L) concentration than used here. For the concept design mass balance calculations, the PHA yield for the accumulation stage was taken as 0.30 kg PHA/kg COD (Dionisi et al. 2006) (Table 1.3). The model used this value as the baseline PHA yield taking the design basis as 20 T/day of COD feed to the accumulation stage. The PHA yield on substrate was assumed equal for the two substrates, based on the work of Salehizadeh and Van Loosdrecht (2004).

A sensitivity analysis for PHA yields of 0.25 (low) and 0.35 (high) kg PHA/kg COD (for the accumulation stage) shows the variation of the PHA content of the biomass from 31% (at 0.25) to 39% (at 0.35). Mass balances reveal the PHA production to be in the range of 1650–2300 T/year of purified PHA for PHA yields of 0.25–0.35 kg PHA/kg COD, respectively (Table 1.6). Figures in brackets show corresponding values when PHA is not extracted from the biomass. The PHA production for un-extracted scenario includes the dry biomass containing the PHA.

A 40% PHA content is increasingly feasible considering current state of knowledge in mixed culture PHA production. Several studies have achieved high PHA content in MMCs (Albuquerque et al. 2010b; Jiang et al. 2012; Johnson et al. 2009; Venkateswar Reddy and Venkata Mohan 2012a). These studies have shown the potential to produce PHA accumulation in biomass ranging from 40% to 77% of dry cell weight in laboratory scale. Bowers et al. (2014) investigated PHA production from wood sugars produced by steam explosion of *Pinus radiata* wood chips followed by enzymatic saccharification. PHA yields of 32% (w/w) were obtained with a pure culture strain. There is significant potential to further improve the PHA content through process optimisation.

1.6 PHA Product Concepts

The PHA product concepts are described here at a high level. The product opportunities are described considering PHA processing properties given in literature. The products are conceptualised based on information in literature and PHA production costs.

1.6.1 Global Market Applications for Extracted PHA

There are currently a number of companies selling pure PHA. The combined annual production capacity was reported at more than 66,000 T/year in 2017 (Vandi et al. 2018).

PHAs have the potential to replace some of the petroleum-based plastics due to their biodegradable, biocompatible and compostable properties. These properties enable PHA to be used for biomedical materials in surgical pins, sutures, staples, blood vessel replacements, bone replacements and plates, medical implants and drug delivery devices (Koller and Mukherjee 2022). Amongst the candidates for biodegradable plastics, PHAs have drawn much attention due to their complete biodegradability and the similarity of their material properties to conventional plastics (Luengo et al. 2003). Companies in Europe are producing PHA for use in the automotive, electronics, fibre and food packaging sectors.

The world's large volume PHA manufacturers as of year 2017 are given in Table 1.7. Some of these companies have changed hands and the targeted capacities are yet to be fully realised (e.g. Meridian).

Biomer in Germany (Biomer 2019) produces 1000 T/year of poly (3-hydroxybutyrate) (p-3HB), a monomeric PHA. Since 2013, Biomer have partnered with Newlight to functionalise the PHB. Newlight (Newlight Technologies 2019) currently make a greenhouse gas-derived PHA product called AirCarbon™. They market this for use in film, furniture and automotive parts and

Table 1.7 Large volume manufacturers of polyhydroxyalkanoates as of 2017 (Kourmentza et al. 2017; Vandi et al. 2018)

Polymer	Trade names	Manufacturers	Capacity (T)	Products
PHA	BioMatera	BioMatera Inc. (Canada)	NA	Food packaging, agricultural products, inks, cosmetics and biomedical
PHB, PHBV	Biomer®	Biomer Inc. (Germany)	NA	PHB pellets
P (3HB-co-4HB)	SoGreen™	Tianjin GreenBio Materials, China	10,000	Pellets of blown film, PHA foam pellets for food service ware and industry or electric appliance packaging
PHB, PHBV	MINERV-PHA™	Bio-On Srl., Italy	10,000	Toys, cosmetics, biomeds
mcl-PHA	Nodax™	Danimer Scientific, USA	13,600	Coatings, lamination, resins, oil well polymers
PHBH	AONILEX®	Kaneka Corporation, Japan	3500	Construction materials, garden utensils
PHB	AirCarbon™	Newlight Technologies LLC, USA	23,000	Extrusion, blown film, cast film, thermoforming and injection moulding applications
PHB, PHBV	Biocycle®	PHB Industrial Company (Brazil)	3000	Packaging
PHB	VersaMer™	PolyFerm, Canada	<10	Adhesives, sealants, plastic additives, inks, toners, paints, coatings, medical devices
PHA	AmBio®	Shenzhen Ecomann Biotechnology Co. Ltd., China	5000	Packaging, resins
Mirel PHB	Mirel™	Yield10 Bioscience	50,000	Performance additives, film and bag applications, functional biodegradation
PHB, PHBV	ENMAT™	TianAn Biologic Materials Co. Ltd., China	10,000	Thermoplastics
P (3,4HB)	Sogreen®	Tianjin GreenBio Material Co., China	10,000	Resins, pellets, films

NA not available

storage containers. Newlight is in California, which has a strong local “green/low-carbon” consumer base with legislation that supports the use of biomaterials.

Danimer Scientific (formerly Meridian Holdings Group) (Danimer Scientific 2019) in the USA produces mcl-PHAs (Nodax™) and has approval for food contact—this is a pure culture and genetically engineered system. Four Chinese companies collectively produce 35,000 T/year and sell into Europe as there is currently not a big market for biodegradable materials in China.

A potential future market for PHA could be in the wood plastic composites (WPC) sector with a market size of USD 4.7 billion in 2019 and exhibiting a compounded annual growth rate of 8.6% up to 2027 (Fortunebusinessinsights 2020). The mechanical properties of PHA are particularly suitable for the manufacture of WPC. Initial developments of wood-PHA composites have shown promise with specific mechanical properties comparable to commercially available WPC containing polyethylene and polypropylene plastics (Vandi et al. 2018). However, further developments are required to improve the strain-at failure and impact strength. The use of PHA as a substitute for fossil-based plastics in WPC could help alleviate growing issue of end-of-life disposal of WPC products. A WPC product with PHA could significantly lower the cost of the product compared to the cost of its neat PHA counterpart (Vandi et al. 2018).

1.6.2 Market Applications for Mixed Culture Un-Extracted PHAs

Currently, there are no known commercial products manufactured with PHA-containing cellular material. However, research is being directed towards developing composite products with un-extracted PHA-containing cellular matter (biomass), as this eliminates the few costly steps in the bioplastic manufacturing process. A report for the US Department of Energy describes the work in producing wood fibre-reinforced thermoplastic composites (WFRTC) using pulp mill effluent-derived PHA-containing biomass (Thompson et al. 2010). WFRTC is a growing area in the USA, with applications in decking, siding and fencing. Mechanical testing of the PHA-containing composites has shown high stiffness compared to polypropylene/wood fibre (PP/WF) and comparable stiffness to polystyrene/wood fibre (PS/WF) composites. The strength has been comparable to PP/WF composite. The report concludes that there is significant energy saving, waste reduction and environmental benefits in producing bio-based WFRTC.

Without knowing specific material properties or costs for a commodity material market, it is very difficult to suggest potential applications for an un-extracted PHA material. However, based on product requirements, some markets can be eliminated to leave some potential applications. The authors acknowledge that inclusion of cellular material will result in a product that is not hygienic and could potentially contain some darkened colour and odour when processed at or near 150 °C. Mechanical properties are also likely to be variable without any purification and separation. Large and variable quantities of cellular matter are likely to result in low elongation at break and give a relatively inelastic material. It is unlikely to be able to be blown into a film.

This eliminates the following applications:

- Direct or indirect food packaging
- Medical applications
- Toys or child-accessible products
- Interior consumer goods
- Plastic bags or thin film

A prime area to investigate further for a material from un-extracted MMC-PHA would be horticultural products where degradation is useful. This could include:

- Horticultural ground cover film (cast film)
- Trunk/growth protection
- Horticultural clips or ties
- Bait stations or pest control devices
- Plant pots
- Controlled release of agrichemicals

These products are of high volume and require a limited life span. They align well with biodegradable products that contain levels of nitrogen, phosphorus and other trace elements required for degradation.

1.7 Conclusion

PHA production as a wood processing industry biorefinery opportunity is feasible considering current knowledge on feedstock conversion and PHA production. Developments in biomass conversion technologies in the biofuels sector, MMC-PHA production from waste and increasing market opportunities will accelerate progress of PHA production from biomass. Conversion of wood residues and wastewaters to PHA would make a transformational change to the forest industry in particular and contribute towards a low-carbon circular economy.

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2 Biomass Polysaccharides to Building Blocks: Obtaining Renewable Organic Acids

Izaskun Dávila, Ander Martín, and Itziar Egüés

Abbreviations

2-FA	2-Furaldehyde
AGR	Annual growth rate
AMIMCl	1-Allyl-3-methylimidazolium chloride
BMIMCl	1-Butyl-3-methylimidazolium chloride
[C_4mim]Cl	1-Butyl-3-methylimidazolium chloride
CAGR	Compound annual growth rate
DMF	2,5-Dimethylfuran
DPA	Diphenolic acid
[DPDIm]I	1,3-Dipropyl-2-(2-propoxyphenyl)-4,5-diphenylimidazolium iodide
FA	Formic acid
GVL	γ-Valerolactone
HAc	Acetic acid
HMF	Hydroxymethyl furfural
ILs	Ionic liquids
LA	Lactic acid
LEA	Levulinic acid
MD-CIB	Mechanocatalytically depolymerized citric acid impregnated biomass
PA	Propionic acid

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PLA	Polylactic acid
PVA	Polyvinyl acetate
PVC	Polyvinyl chloride
PVOH	Polyvinyl alcohol
SA	Succinic acid

2.1 Introduction

The oil depletion, the price of fossil resources, and the environmental pollution are major issues of serious concern for the actual society. In fact, the depletion of fossil resources and the effects of pollution on the climate change are already a reality. Therefore, there is a global necessity to find new renewable resources, where the whole process of the resource extraction, the production of goods (fuels, heat, chemicals, and materials), and the degradation of the products must be sustainable, efficient, and environmentally friendly. In this context, in the latest years, the biobased economy has gained interest since it would allow the replacement of petrochemical-derived goods of great interest for industrial applications by their biobased counterparts (Kumar and Verma 2021). The transition of the actual fuel-based economy to a novel biobased economy could be promoted by the production of chemical platforms that could be employed in many fields such as materials science, biotechnology, food science, pharmaceuticals, medicine, environmental technology, etc. Thus, the advances in the sustainable production of these platform chemicals, also denoted as "building blocks," from renewable resources will play an important role in the future sustainability (Moutousidi and Kookos 2021).

Building blocks are intermediate molecules with a structure capable of producing a variety of valuable derivatives with diverse final application. Within building blocks, the sugar-based platforms obtained from biomass (Takkellapati et al. 2018) could be extensive renewable chemical interesting precursors adequate to create new environment-friendly goods and to develop innovative technology (Zhou et al. 2021). Organic acids such as lactic acid, levulinic acid, formic acid, propionic acid, fumaric acid, itaconic acid, glyceric acid, citric acid, oxalic acid, etc. are some important and interesting derived sugar precursors useful for obtaining many industrial products: plastics, biofuels, surfactants, coatings, etc. Therefore, there is a huge interest in the production of these organic acids from renewable materials using green novel technologies.

This chapter summarizes the knowledge in the fractionation of biomass polysaccharides and their conversion to some organic acids. Furthermore, the state of the art, the global value, and the main production processes of the organic acids with the highest market value (lactic acid, levulinic acid, propionic acid, formic acid, succinic acid, and acetic acids) are also described.

2.1.1 Lignocellulosic Biomass: A Novel Renewable Resource

The biorefinery is a refinery that converts biomass into different biobased products, among them chemicals, materials, and bioenergy (biofuels, power, and/or heat). This is commonly achieved through the fractionation of biomass in its components and their conversion into high-added value products in selectivity rates good enough to attract the industry and the markets. Over the years and together with the advances in the biorefinery industry, the production of chemicals from biomass resources has experimented a huge impulse.

Biomass is the most abundant renewable resource in the Earth. It is estimated that the amount of vegetable biomass in the world is about 10^{12} tons, from which 10^{11} tons are renewed annually. Biomass can be classified based on its source and its characteristic, i.e., vegetable biomass (derived from agricultural residues, energy crops, and wood industry), animal biomass (aquatic and marine biomass), and food industry, among others. Within lignocellulosic biomass, agricultural and forestry activities produce annually large quantities of agroforestry waste (such as straw, stems, leaves, pruning, etc.). Consequently, due to its availability and renewable character, lignocellulosic materials possess an important potential to be used as a source of added-value compounds that could replace a substantial portion of the petrochemical products (Bodachivskyi et al. 2018).

Lignocellulosic biomass is formed by three main constituents: cellulose (30–50%), hemicelluloses (20–30%), and lignin (20–30%). The main linkage between these components is hydrogen and covalent bonds providing recalcitrance to the biomass structure and making it difficult to extract each fraction separately. Within the lignocellulosic biomass, cellulose is the main constituent and it consists of hundreds to thousands of $\beta(1 \rightarrow 4)$ linearly linked glucose sugars units (Fig. 2.1a). The hydrogen bonds that are generated between the hydroxyl groups of the cellulose confer it a rigid crystalline structure that makes it cellulose insoluble in water and in the most commonly used organic solvents. Furthermore, this crystallinity also increases the difficulties of extracting, manipulating, and processing the cellulose, and consequently, its fractionation has always been a challenge and it is under constant study. Another fraction of the lignocellulosic biomass are the hemicelluloses, which are mainly constituted by different monomeric sugars, such as xylose, glucose, arabinose, mannose, and galactose, whose composition and polymerization degree can change depending on their source (Fig. 2.1b–d). Compared with the cellulose, the hemicelluloses are completely amorphous and therefore they can be easily fractionated. After cellulose and hemicelluloses, lignin is the most abundant natural polymer on Earth. It is composed of phenolic cross-links of three monolignol monomers: sinapyl alcohol, coniferyl alcohol and *p*-coumaryl alcohol. The compositional ratios of these three moieties depend strongly on the biomass and on the extraction procedure.

Although all the constituents of the lignocellulosic biomass could be used to obtain different building blocks, this chapter is focused on the valorization of polysaccharide fractions.

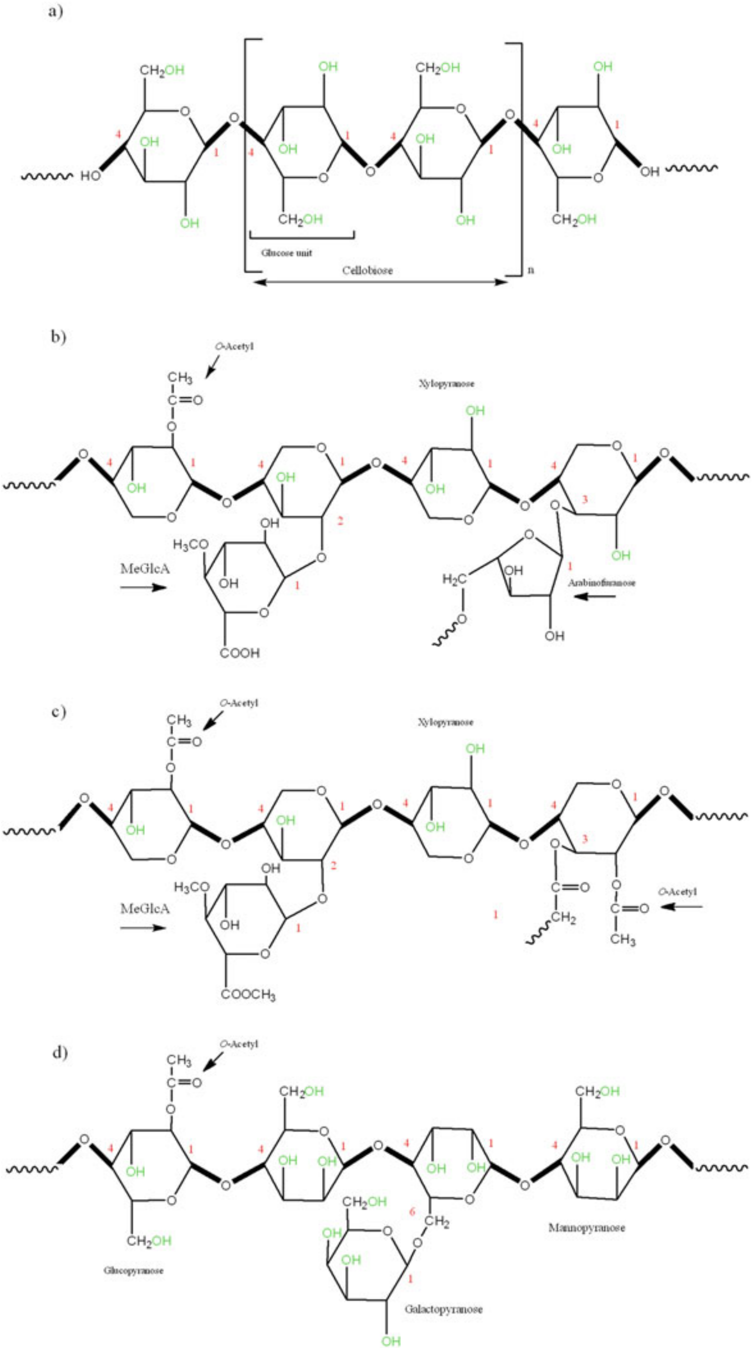

Fig. 2.1 Polysaccharides from lignocellulosic materials: (**a**) cellulose and its glucose monomers, (**b**) hemicellulose in (**b**) arabinoxylan in annual plants, (**c**) hardwood xylan (*O*-acetyl-4 methyl-glucuronoxylan), and (**d**) softwood xylan (*O*-acetyl galactoglucomannan)

2.1.2 Biomass Fractionation and Reducing Sugar Extraction Strategies

As it will be highlighted along the chapter, building blocks, such as organic acids, are attractive compounds able to offer the production of multitude of molecules. Numerous organic acids with great commercial value can be obtained from lignocellulosic polysaccharides using different chemical and biotechnological routes, as it will be reviewed. However, the production of these compounds from renewable resource is still a challenge, since to implement successfully the production of these goods some technological difficulties must be overcome. The main challenge is to design a process that efficiently fractionates the biomass for the polysaccharide extraction and converts them into valuable chemicals. Specifically to produce the sugar-based building blocks, the polysaccharides present in the lignocellulosic biomass must be extracted as monomeric sugars.

An example of a biochemical pathway that could be carried out to extract polysaccharides and reducing sugars from lignocellulosic biomass, is shown in Fig. 2.2. As it can be seen in this pathway, the first step is to prepare the lignocellulosic biomass (milling, drying, etc.), and then commonly a hydrolysis is carried out using high temperature and pressure to swell the material and solubilize water-soluble hemicellulosic polysaccharides and sugars. In many articles, this process is catalyzed by heterogeneous catalysts due to their advantages. The most important benefit of the heterogeneous catalysts is their easy recovery by filtration. After this treatment, the obtained solid is rich in lignin and holocellulose (constituted by cellulose and the hemicelluloses that were not solubilized in the previous stage). With the aim to valorize cellulosic fraction and extract more polysaccharide sugars from this solid, a delignification process is commonly carried out to remove the lignin fraction, and then, the cellulose and the remaining hemicelluloses could be converted into monomeric reducing sugars, such as xylose, arabinose, glucose, galactose, and mannose, via chemical or microbial depolymerization.

In this conventional fractionation process (also shown in Fig. 2.4, Route A), the first step is the fractionation (typically catalyzed hydrolysis) of polysaccharides into sugar monomers followed by their conversion into different organic acids. In the case of cellulose, its insolubility in the most commonly employed solvents makes its fractionation and effective utilization difficult. To solve this, in the literature, strong acid catalysts (H_2SO_4, HCl) are used at moderate-high concentrations to hydrolyze cellulose into glucose. This harsh reaction condition can produce acidic wastewater causing corrosion damages in the equipment (Bodachivskyi et al. 2018). Afterward, the produced glucose could be isomerized into fructose or undergo a retro-aldol reaction producing low-molecular-weight acids or esters. In case of the hemicellulosic-derived reducing sugars, among which xylose or arabinose is the most abundant one, they can be converted into furfural, lactic acid, and levulinic acid, among others, depending on the employed procedure (Fig. 2.3). As De Cárdenas and De Cárdenas (2020) demonstrated, these conversion processes are commonly carried out using enzymes, bacteria, and other biological mechanisms instead of chemical processes, since they produce lower consumption of raw

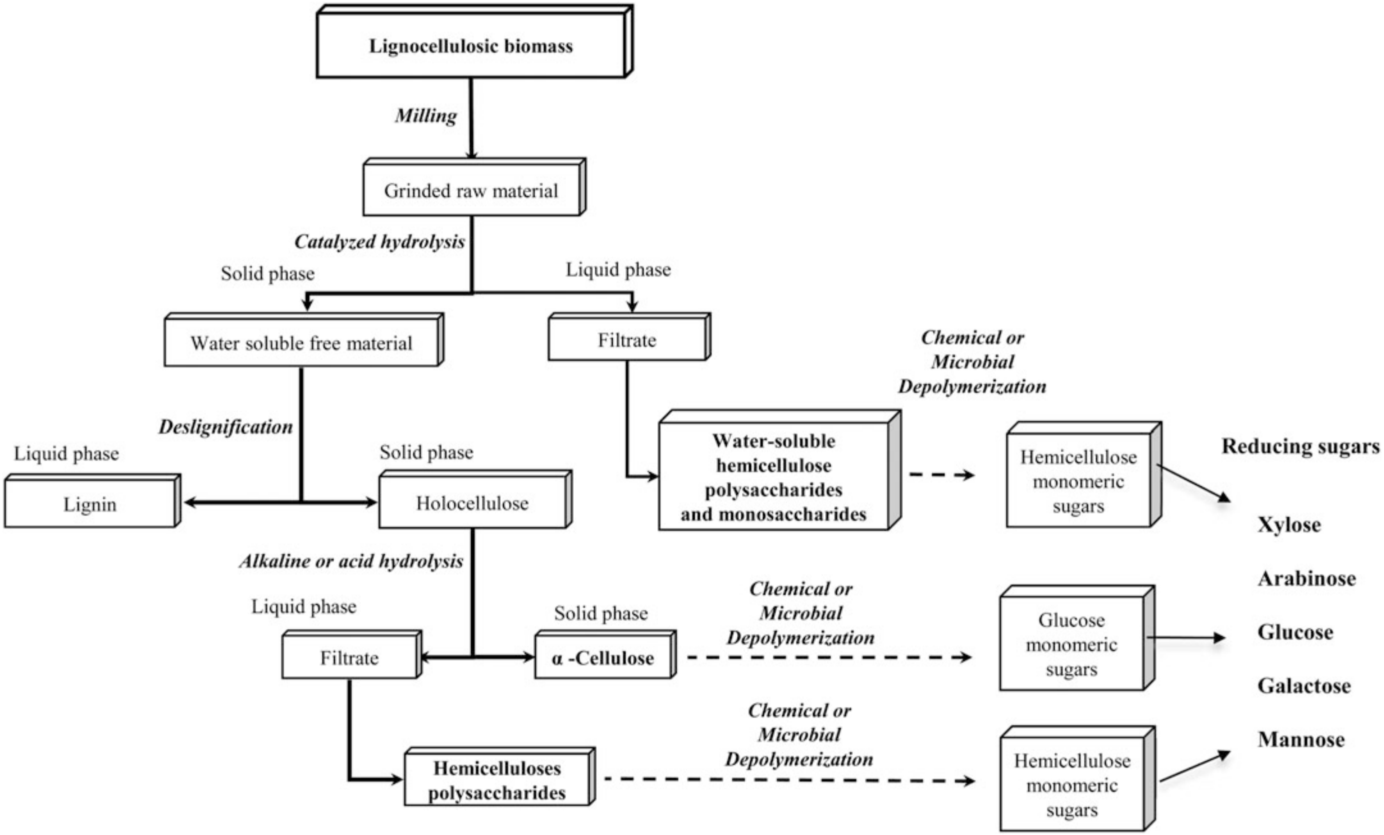

Fig. 2.2 An example of lignocellulosic biomass fractionation pathway for the extraction of reducing sugars

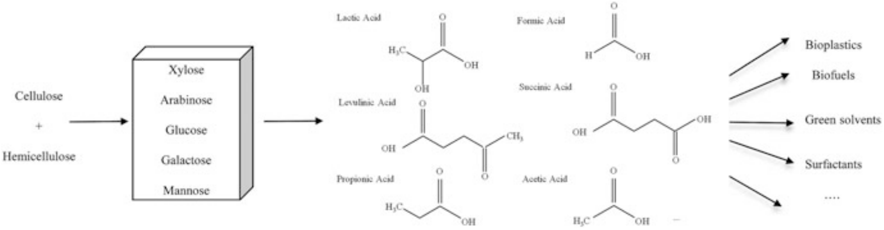

Fig. 2.3 Some sugar-based organic acid building blocks able to be transformed into high added-value products

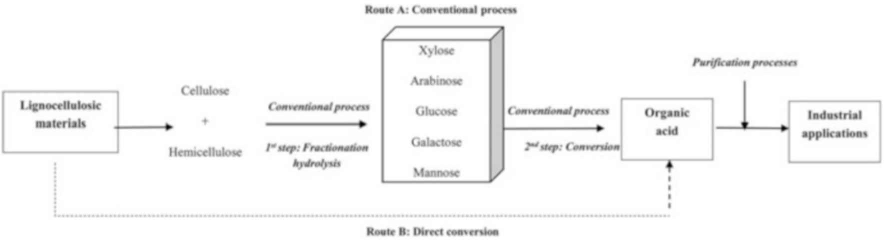

Fig. 2.4 Conversion of lignocellulosic material to organic acids. Route A: conventional process with hydrolysis of polysaccharides into monomeric sugars and further conversion. Route B: direct fractionation and conversion in a single step

materials and generate lower amounts of sub-products and residues. Nevertheless, other authors, such as Li et al. (2015), preferred chemical processes to biological transformations, due to the higher cost of the latest ones.

In the described conventional route (Fig. 2.4, Route A), it is necessary to decrease the number of the steps used to obtain renewable organic acids in order to make their production efficient at competitive cost. Thus, in the latest years, the direct transformation of biomass into organic acids by one-pot reactions has become a promising innovative process (Li et al. 2018; Matson et al. 2011; Xu et al. 2016). This process allows the simultaneous extraction and conversion of the sugars present in the lignocellulosic biomass within a unique reaction (Fig. 2.4, Route B). This process could reduce the number of the steps and it would make the process more efficient and economically competitive. However, these one-pot reactions usually involve harsh conditions, low final product selectivity, and lower conversion rates in comparison with common pretreatment and treatment procedures.

Some examples of direct conversion of cellulose into organic acids can be found in literature. Lei et al. (2014) reported that cellulose could be directly converted in a unique reaction into lactic acid when $ErCl_3$ is used as catalyst, with a maximum yield of 91.1%. De et al. (2012) converted lignocellulosic and algal biomass into 2,5-dimethylfuran fuel (DMF) in a one-pot reaction using a multicomponent catalytic system and they achieved a total yield of 32% DMF in 1 h. Li et al. (2012) also converted cellulose and the hemicellulosic fraction of raw wood biomass into ethylene glycol and its derivates using Ni-W_2C as catalyst and they achieved a yield of 75.6%. Furthermore, they observed that the direct conversion of untreated lignocellulosic biomass using one-pot catalytic hydrocracking was more suitable for scaling up and for producing chemicals from biomass.

On the other hand, with the aim of improving the fractionation of biomass and the conversion of cellulose and hemicellulose into organic acids, the application of intensification techniques, such as ultrasound or microwave technologies, has gained attention, since they could increase the process yield and the selectivity of the reactions. In the literature, it has been reported that microwave (a rapid and uniform heating method) and ultrasound heating processes (transmission of shock waves with cavitation effect) could improve the release of simple sugars and their conversion into different products (Mussatto 2016). Besides that, these intensification technologies could allow to minimize the reaction times, as Sánchez et al. (2013) observed during the production of furfural from corncobs autohydrolysis liquors using a microwave-assisted acid hydrolysis. Maiti et al. (2018) produced levulinic acid from agricultural wastes through microwave-assisted heating one-pot conversion using concentrated hydrochloric acid as catalyst.

Another interesting approach that could increase the efficiency of the one-pot conversions is the use of novel selective solvents to dissolve the polysaccharides and converted them directly into monomeric sugars and chemicals. In this area, ionic liquids (ILs) are good green selective solvents constituted by organic and inorganic ions that act similar to acid-based catalysts. Among the benefits of the ILs are its recyclability, its effectiveness, and its lesser side reactions than in common water catalytic systems. All of this could allow the production of building blocks in a more selective way and using milder conditions (Bodachivskyi et al. 2018). Several studies reported highly efficient catalytic production of glucose in 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) (Bodachivskyi et al. 2018). Therefore, the use of ILs could result also in a very interesting approach to improve the yield production of the monomeric sugar as well as to improve the selectivity of the reaction toward the production of a specific organic acid.

Photocatalysis could be another green potential technology that could be employed for the production of organic acids from biomass. This process involves a chemical reaction promoted by the absorption of light by the reacting species. Photocatalysis is a simple, clean, energy-saving, environmentally friendly, and low-cost process, since it could be efficiently carried out under solar irradiation, ambient temperature, and mild conditions. The catalyst used in this process is solid semiconductors, such as TiO_2, ZnO, NiO, ZrO_2, SnO_2, SiC, Fe_3O_4, CdS, ZnS, etc. Among them, TiO_2 showed excellent photocatalytic activity and oxidizing ability, and it also demonstrated good chemical stability, and nontoxicity and has a low price. Some works have reported the production of different organic acids from glucose using photocatalytic technology (Payormhorm et al. 2017a). These catalytic processes may be scalable with the development of improved process design.

2.1.3 Purification Treatments

Finally, after the extraction and conversion processes, purification processes are needed to separate, to purify, and to concentrate the desired building blocks by removing unreacted sugars, unreacted chemicals, or by-products, as it can be seen in Fig. 2.4. Therefore, purification strategies could also be a key factor for industrial application, since the separation and purification of organic acids could be a challenging task. The most commonly used purification techniques are adsorption, solvent extraction, ionic exchange, and precipitation (Li et al. 2015). At industrial scale, lactic acid is commonly separated by distillation, esterification, and crystallization (Payormhorm et al. 2017b), while at laboratory scale, it has been purified by membrane nanotechnology (Blanc et al. 2015). Another purification process carried out for the recovery of organic acids from a bulk of fermentation broths was the precipitation technique using calcium (Umpuch et al. 2010). The purification of organic acids (lactic, succinic, and citric acids) from glucose has been also carried out by chromatography system, using strong anionic and cationic ion exchangers (Payormhorm et al. 2017b). Especially, the chromatography resins have a good selectivity for organic acids and involve low-energy consumption. Furthermore, ILs have been also used for the removal of L-lactic, L-malic, and succinic acid from aqueous medium (Umpuch et al. 2010). In general, a combination of different purification processes is needed.

2.2 Global Value and Applications of Some Organic Acids

The compound annual growth rate (CAGR) of some organic acids and their main potential applications are summarized in Table 2.1. In general, the global market for carboxylic acids is going to grow from $11.2 billion (2017) to $13.6 billion (2022). In this period of time (2017–2022), the CAGR rate is expected to be 3.9% (Carboxylic Acids 2018).

In 2015, the global demand for lactic acid (LA) and polylactic acid (PLA) and its derivatives reached approximately 200,000 tons, and it was mainly used by food and personal care industries (Lactic Acid Market 2020). In the future, lactic acid global market is estimated to grow as a consequence of its rising demand from its end-use applications. PLA plastic production market is growing due to more strict rules around environmental care. In this context, its market envelops more than 35% of bioplastics. Other PLA markets include automotive industry, electronics, textiles, and others. LA has a great potential to provide also green ester solvents, acrylic acid, and propylene glycol (Dusselier et al. 2013). According to recent market research reports, both LA and PLA markets duplicated the revenue of their market in the last 5 years, reaching a market in 2020 of $3.82 and $5.16, respectively, and showing a 18.6% and 20.9% CAGR in the last forecast period. It is estimated that their production capacity will rise to 950,000 tons/year. The biggest LA consumers for PLA production are North America and Europe; however, the compound annual

Table 2.1 Annual growth rate and potential applications of some organic acids

Product	Compound annual growth rate (CAGR, %)	Industrial potential applications	Reference
Acetic acid	6.0	Textiles, food and beverage, pharmaceuticals, polymers industries, etc.	Acetic Acid Market (2016)
Formic acid	4.9	Food, polymers, catalyst industries, etc.	Formic Acid Market (2021)
Propionic acid	3.5	Cosmetics, drugs, pesticides, polymer, solvent industries, etc.	Propionic Acid Market (2020)
Lactic acid	20.9	Polymer, automotive, electronics, textiles, solvent industries, etc.	Lactic Acid Market (2020)
Levulinic acid	8.9	Pharmaceuticals, agrochemicals, chemicals, flavors and fragrances, personal care, food additives, polymers, solvents, fuel additives and biofuels, etc.	Levulinic Acid Market (2022)
Succinic acid	6.8	Food and beverage, chemicals, biopolymers, personal care, pharmaceutical industries, etc.	Succinic Acid Market (2018)

growth rate for both LA and PLA is higher at the Asia-Pacific region, so it could become an important consumer in the upcoming years (Lactic Acid Market 2020).

In case of levulinic acid (LEA), it reached $28.3 million value in 2021, and it is expected to grow until $34.5 million by 2024, with a CAGR of 8.9% during the following years (2021–2026) (Levulinic Acid Market 2022). North America is the main consumer due to its application as fuel additives, cosmetics, agricultural products, and precursor for other chemicals. LEA is the precursor for large number of products applicable in diverse industries such as pharmaceuticals, agrochemicals, chemicals, flavors and fragrances, personal care products, food additives, resins and coatings, plasticizers, solvents, fuel additives, and biofuels. The production of green solvents, pesticide alternatives, and biopolymers is gaining more attention expanding the levulinic acid market. In this line, the production of gamma valerolactone and caprolactone from LEA is also leading the trend due to their application such as green solvents and in the biobased polymer synthesis. Nowadays, levulinic acid is available on the market; however, there are few production plants, which is reflected in its high cost. However, in the future, due to its increasing demand and the production growth, a decrease of its price is expected, making it more attractive.

Regarding propionic acid (PA), during 2018, its market size was $1.2 billion and a production of 192.000 tones was recorded (Propionic Acid Market 2020). It is estimated that its price will grow by $1.6 billion in 2026, presenting a CAGR of 3.5%. It is mainly used in food industry as food preservative and for animal feeding. PA experienced a growth of interest as building block for the manufacturing of many commodities such as cosmetics, drugs, and pesticides. It is also used in food packaging due to its antibacterial and preservation properties. Furthermore, several esters can be synthesized from propionic acid, which are demanded in paint, resins, and solvent industry.

On the other hand, worldwide formic acid (FA) biggest manufacturers are Europe and Asia. The estimated production worldwide is about 740 kilotons/year. According to recent analysis, formic acid market is projected to generate a revenue of 4.9% CAGR from 2017 to 2027 (Formic Acid Market 2021). The FA market was valued at $290.64 million in 2019 and is projected to reach $328.97 million by 2027. As most of organic acids, it is commonly used in food industry, especially in animal diet for an improvement of meat quality. Besides the food industry, FA is found to be useful in polymer industry for the amalgamation of latex during production of rubber sheets, in textile industries as leather tanning, and in pharmaceutical industries for the production of organic-based esters or drugs. FA has been also a potential candidate for the production of hydrogen (Caiti et al. 2019).

Succinic acid (SA) has attracted much interest as a precursor in food, beverage, chemicals, biopolymers, and pharmaceutical industries. Personal care and food industries are the main consumers of this organic acid. Reports from 2018 attributed a market size of $131.7 million to succinic acid, and it is expected to grow by $182.8 million by 2023, presenting a CAGR of 6.8% (Succinic Acid Market 2018). New trends in environmental-friendly materials lead SA to be the substitute for adipic acid during polyurethane production, which is expected to promote the succinic acid industry.

The market size of acetic acid (HAc) reached $10.9 billion in 2016, and it is expected a 6.0% CAGR for each forecast year until 2024, when the production is estimated to reach $17.9 billion (Acetic Acid Market 2016). Sixty percent of the market is held in the Asia-Pacific region, according to the data of 2016, due to its huge market in textiles. Within its applications, food and beverage industries envelop most part of acetic acid applications/markets. However, it is being used in many other areas with a constant growth due to environmental concern. HAc is also used in pharmaceuticals and is being broadly studied in polymer industry as precursor of various chemicals used in the polymer industry. It is the precursor of several monomers used for the manufacturing of diverse biobased polymers, and it is used as precursor for other chemicals that can be found in electronics, coatings, construction, and packaging, among other applications. In polymer industry, it is mainly used to produce vinyl acetate monomer, which is often polymerized to synthesize polyvinyl acetate (PVA) and polyvinyl alcohol (PVOH). These products are experiencing a substantial demand growth. Therefore, industry is fulfilling investing on acetic acid production infrastructure.

2.3 Production of Organic Acids from Biomass Polysaccharides

2.3.1 Lactic Acid (LA)

Lactic acid is an alpha-hydroxy acid, with a hydroxyl group near to the carboxyl group, which presents two optical isomers: L and D (Fig. 2.5). This organic acid has been identified as one of the highest potential sugar-based platforms from lignocellulosic biomass. As commented in Sect. 2.2, LA is a commodity highly employed by

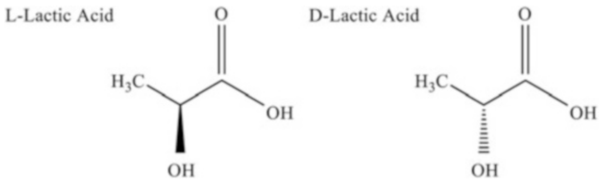

Fig. 2.5 The L- and D-isomers of lactic acid

the food and pharmaceutical industries and also in the manufacture of biodegradable plastics such as polylactic acid, which is an environmental-friendly biobased polymer broadly used in packaging (Onda et al. 2008).

At industrial scale, LA production is based mainly on the conversion of hexose and pentose sugars extracted from any sugar resources, like starch (glucose), sucrose, beet juice, etc. However, to avoid market competition, biomass wastes are starting to be exploited to produce lactic acid, which will change the value of the biomass wastes from trash to valuable resources. Among the different sugar resources, actually, glucose is the most used monosaccharide for the production of LA via either fermentative or chemical pathways. Both techniques present advantages and drawbacks. Fermentation technology implies high cost, long fermentation times, and restricted large-scale operation, and it cannot be directly used with untreated cellulose. Nevertheless, the fermentative process presents a high stereoselectivity, being possible to control the production of one of the isomers with an accuracy of around 95%. In general through chemical synthesis, the obtained selectivity is lower, resulting in racemic mixtures of the L- and D-isomers, with ratios around 60 and 40, respectively. Consequently, nowadays, the fermentation synthesis of lactic acid seems to represent the better way for its production.

The fermentation process for obtaining lactic acid from sugars is commonly carried out in anaerobic conditions, which means that the sugars are directly converted into LA without the generation of undesired by-products, such as water and CO_2. The type of microorganism used to perform the fermentation of the sugars will depend on its ability to ferment disaccharides, hexoses, or pentoses, and consequently depending on the employed microorganism, the yield of the process could vary. To ferment polysaccharides instead of monosaccharides, the use of an additional enzyme as β-amylase is needed to depolymerize the polysaccharides. This enzyme catalyzes the hydrolysis of the (1–4)-alpha-D-glucosidic linkages of the polysaccharides. In the case of the fermentation of the polysaccharides, the enzymatic hydrolysis and the fermentation could be carried out separately (SHF) or simultaneously (SSF). In the latest case, as the monosaccharides are released to the fermentation media by the enzymatic hydrolysis, they are converted in organic acids by the microorganisms. Maslova et al. (2019), for instance, carried out the fermentation of the sugar extracted from different biomass materials (among them pine sawdust and rice straw) for obtaining different organic acids such as LA, succinic acid, and fumaric acid. They carried out a SHF and a SSF observing that the SSF not only allowed the reduction of the number of processes but also permitted the achievement of a higher productivity.

Regarding the chemical production of LA, it could be performed mainly by three different routes, as it is shown in Table 2.2, depending on the selected catalyst: bases, metal heterogeneous catalyst, and zeolites. Raharja et al. (1997) reported one of the first chemical conversions of monomeric sugars to lactic acid. They transformed different monomeric sugars (glucose, xylose, arabinose, mannose, and galactose) into different carboxylic acids (lactic, formic, glyceric, and acetic acid) using an alkaline medium (2 N NaOH, 40 °C). They observed that by increasing NaOH concentration (until 6 N) and the temperature (100 °C), the formation of LA was favored, reaching a maximum conversion yield of 54%, using xylose as starting material, and of 52%, when arabinose was used as starting material. Li et al. (2017) converted glucose into lactic acid with a 95.6% yield using $Ba(OH)_2$ and an inert atmosphere and at room temperature for 48 h. While Sánchez et al. (2012) employed $Ca(OH)_2$ (0.7 M) as the basic medium for the direct production of lactic acid from corn cobs, achieving a yield of 44.76% of LA when they carried the alkaline treatment at 300 °C for 30 min.

Regarding the metal heterogeneous catalysts, apart from the ones shown in Table 2.2, it has been seen that $Er(OTf)_3$ or $ErCl_3$ could be used for the direct conversion of cellulose into lactic acid. For instance, Lei et al. (2014) were able to convert directly by a single reaction into LA with a maximum yield of 91.1% when $ErCl_3$ was used as catalyst. Nevertheless, the use of metal heterogeneous catalyst implicates high temperatures and pressures and is performed in small scales due to its novel state.

Apart from the homogeneous and the metal heterogenous catalysts, zeolites have also gained attention for obtaining lactic acid from mono- and polysaccharides, due to their high surface area and high porosity, tailoring, and volume. For instance, Dong et al. (2016) employed Zn-Sn-beta zeolites to convert sucrose into lactic acid. During this work, they observed that the employment of zeolites promoted the conversion of sucrose into lactic acid, achieving a 99% of sucrose conversion with a LA yield of 54% (2 h at 190 °C). Furthermore, Xia et al. (2019) demonstrated the feasibility to convert *Miscanthus* lignocellulosic material directly to LA using Cr-Sn-Beta as catalyst. When they carried out the process at 240 °C for 1 h, they achieved a yield of 33.4% and a selectivity of 53.2%. Holm et al. (2010) obtained a 100% glucose and sucrose conversion when they used Sn and Pb zeolites with a selectivity of 44%, while Wang et al. (2017) directly converted cellulose into lactic acid with a 57.9% selectivity using Er/deAlβ-2 zeolites. In the same line, Murillo et al. (2016) performed sugar extraction using zeolitic imidazolate frameworks reporting a 42% methyl lactate yield.

In the recent work, Li et al. (2021) performed a deep analysis of different lignocellulosic lactic acid biorefinery strategies for lactic acid production from lignocellulosic feedstocks via techno-economic analysis and life cycle assessment, observing the potential of some strategies for sustainable LA production.

Table 2.2 Chemical synthesis of lactic acid from biomass

Type of catalyst	Catalyst	Substrate	Reaction conditions	Product distribution (%)	Reference
Bases	$Ba(OH)_2$ (0.25 M)	Cellulose	25 °C, 48 h under nitrogen atmosphere of 1 bar (in a previous step, the cellulose is hydrolyzed with HCl 0.08 M at 180 °C for 1 h)	Lactic acid (42.2%), glyceraldehyde (11.1%), fructose (1.2%), and glucose (1.5%)	Li et al. (2017)
	$Ca(OH)_2$ (0.7 M)	Corn cobs	300 °C, 30 min	Lactic acid (44.7%), formic acid (8.3%), acetic acid (10.8%), acrylic acid (1.4%), and ethanol (2.9%)	Sánchez et al. (2012)
	$Ca(OH)_2$ (0.5 M)	Bread residues	300 °C, 30 min	Lactic acid (35.4%), formic acid (4%), acetic acid (3.1%), acrylic acid (1.1%), ethanol (1.2%), arabinose (1.2%), and xylitol (0.8%)	Sánchez et al. (2014)
	NaOH (0.1 M)	Glucose	80 °C, 2 h	Lactic acid (55.0%), glycolic acid (1.7%), formic acid (2.5%), acetic acid (2.7%)	Onda et al. (2008)
Metal heterogeneous catalysts	$YNbO_4$ (0.02 g/mL)	Glucose	140 °C, 5 h	Lactic acid (19.6%) and HMF (8.3%)	Kim et al. (2019)
	ZrO_2 (0.8:1 g catalyst: g substrate)	Xylose	200 °C, 40 min under nitrogen atmosphere of 2.4 MPa and pH 14	Lactic acid (73.7%^{a}), formic acid (39.3%^{a}), glycolic acid (28.4%^{a}), acetic acid (7.6%^{a}), acrylic (0.3%^{a}), and oxalic acid (0.9%^{a})	Yang et al. (2015)

(continued)

Table 2.2 (continued)

Type of catalyst	Catalyst	Substrate	Reaction conditions	Product distribution (%)	Reference
	ZrO_2 (4 g/g substrate)	Xylan from beechwood (>90%)	200 °C, 90 min under nitrogen atmosphere of 2.4 MPa	Lactic acid (25.0%[a]), formic acid (7.5%[a]), furfural (4.0%[a]), and glycolic acid (4.0%[a])	Yang et al. (2015)
	MgO (0.8:1 g catalyst: g substrate)	Xylose	200 °C, 40 min under nitrogen atmosphere of 2.4 MPa and pH 14	Lactic acid (73.8%[a]), formic acid (41.7%[a]), glycolic acid (29.1%[a]), acetic acid (7.9%[a]), acrylic (0.3%[a]), and oxalic acid (0.4%[a])	Yang et al. (2015)
Zeolites	Pb-Sn-beta (0.3 mmol/g)	Glucose	190 °C, 2 h	Lactic acid (52.0%), HMF[b] (6.4%), acetic acid (2.8%), formic acid (4.8%), and glycolic acid (1.2%)	Xia et al. (2018)
	Zn-Sn-beta (16 mg/mL)	Glucose	190 °C, 2 h	Lactic acid (48.0%), formic acid (2.0%), acetic acid (1.8%), levulinic acid (5.2%), acetol (1.3%), and HMF (7.9%)	Dong et al. (2016)
	Er/deAlβ-2 (0.33:1 g catalyst: g substrate)	Cellulose	240 °C, 30 min under nitrogen atmosphere of 2 MPa	Lactic acid (57.9%), formic acid (2.8%), acetol (4.5%), HMF (4.4%), glyceraldehyde (2.6%), and glucose (8.4%)	Wang et al. (2017)
	Cr-Sn-beta (1.5:1 g catalyst: g substrate)	*Miscanthus*	240 °C, 1 h	Lactic acid (33.4%), formic acid (2.8%), acetic acid (4.1%), and glycolic acid (5.4%)	Xia et al. (2019)

[a] The yield is expressed as molar yields
[b] *HMF* 5-hydroxymethylfurfural

2.3.2 Levulinic Acid (LEA)

Among the organic acid family, levulinic acid, which is a short fatty acid with the following formula $CH_3C(O)CH_2CH_2CO_2H$, is identified as one of the key building blocks for a sustainable future. Its structure is composed by five carbon groups including two functional groups, a ketone carbonyl group and an acidic carbonyl group. These functional groups make the LEA a highly reactive chemical that can be used as a precursor for the production of a high variety of bioproducts (Hayes and Becer 2020). Among the different products that can be obtained from the LEA, obtaining diphenolic acid (DPA), levulinic ketals, or γ-valerolactone (GVL) by a biorefinery process has gained interest in the latest years. DPA could be used to produce environmentally friendlier resins and biobased polycarbonates instead of using petroleum-based bisphenol A. DPA could be produced by the reaction between LEA and phenol through a catalyzed chemical process (Shen et al. 2014). Apart from DPA, levulinic ketals could be obtained by reacting LEA with components rich in hydroxyl groups. These ketals are interesting as plasticizer to produce polyvinyl chloride (PVC) and polyurethanes (Leibig et al. 2011). Moreover, levulinic acid can be catalytically reduced to GVL, which could be used to synthesize acrylic compounds, as a fuel extender, solvent, or food additive (Liu et al. 2020).

Right now, the entire commercial levulinic acid production is carried out by the petrochemical industry using chemicals such as furfuryl alcohol or anhydride furfuryl alcohol; however, this organic acid could be also obtained by the conversion of glucose and xylose. In the case of glucose, first, 5-hydroxymethylfurfural (HMF) was generated by the dehydration of glucose, and then it was converted into levulinic acid (Zhang et al. 2015, 2016). Thus, in order to produce levulinic acid from polysaccharides, their efficient hydrolysis is a critical factor. Therefore, to produce LEA from sugars, cellulosic materials should be fractionated using acid-catalyzed reactions, using, for example, Bronsted acids (Rackemman and Doherty 2011). At industrial scale, the hydrolysis of cellulose is commonly carried out using strong mineral acids, such as H_2SO_4, and HCl, among others, due to their efficiency and their low price. For instance, Pileidis and Titirici (2016) patented the *Biofine* process, in which a two-stage acid hydrolysis is carried out at high temperatures and using sulfuric acid as a catalyst, for obtaining levulinic acid and furfural as the main products. After different purification and separation processes (filtration, distillation, and steam stripping) of the reaction medium, they were able to obtain LEA with a purity of 95–97% (Pileidis and Titirici 2016). Nevertheless, this process has its drawbacks, for example, the corrosion and damage caused in the equipment due to the employment of acid conditions or the difficult recovery of the employed homogeneous catalysts (Pileidis and Titirici 2016).

To avoid these problems in the latest years, the use of heterogeneous catalysts, such as Lewis acids, has gained attention, due to their selectivity, lower corrosion problems, and higher recyclability. For instance, there are multiple studies in which heterogeneous catalysts have been used to obtain levulinic acid from saccharides and directly from the biomass (Dos Santos et al. 2021), as it can be seen in Table 2.3. One of these studies is the one carried out by Taghavi et al. (2021), who employed silica-

Table 2.3 Chemical synthesis of levulinic acid from polysaccharides and biomass

Type of catalyst	Catalyst	Substrate	Reaction conditions	Product distribution (%)	Reference
Homogeneous catalyst	*p*-Toluenesulfonic acid (PTSA) (1.5 M)	Glucose	175 °C, 120 min in MIBK/H_2O 3.5/1.5 (v/v)	Formic acid (40.0%), levulinic acid (37.5%), humins (10.0%), and HMF[a] (2.5%)	Bounoukta et al. (2022)
	HCl (0.045 M)	Coconut residues	180 °C, 180 min	Levulinic acid (43.8%)	Junior et al. (2021)
	H_2SO_4 (0.5 M)	Newspaper	180 °C, 5 min using a maximum microwave power of 1.9 kW	Levulinic acid (45.0%), formic acid (10.0%), and furfural (20.0%)	Dutta et al. (2022)
	Methanesulfonic acid (0.2 M)	Chitosan	200 °C, 30 min	Levulinic acid (28.2%)	Kim et al. (2018)
Heterogeneous catalyst	$FeCl_3$ (0.5 M)	Newspaper	180 °C, 5 min using a maximum microwave power of 1.9 kW	Levulinic acid (35.0%), furfural (18.0%), formic acid (15.0%), and C6 and C5 sugars (<5.0%)	Dutta et al. (2022)
	$FeCl_3$ (0.24 M)	Corn cob hydrolysis residue	170 °C, 30 min using a solution containing 30 wt.% of KCl	Levulinic acid (54.5%), glucose (5.0%), HMF (0.5%)	Wang et al. (2019)
	Na-BEA zeolite (0.1 g)	Glucose	200 °C, 5 h	Levulinic acid (100.0%)	Sobús and Czekaj (2022)
	Silica-aluminosilicate-based composites	Cellulose	230 °C, 5 h under nitrogen atmosphere of 10 bars	Levulinic acid (30.0%) and formic acid (15.0%)	Taghavi et al. (2021)
Ionic liquids	3-Dipropyl-2-(2-propoxyphenyl)-4,5-diphenylimidazolium based ionic liquid ([DPDIm]I) (0.25 g/mL H_2O)	Cellulose	140 °C, 2 h	Levulinic acid (62.0%) and formic acid (12.0%)	Zunita et al. (2020)
	4-Bis(3-methylimidazolium-1-yl) butane based ionic liquid ([$C_4(Mim)_2$]	Bamboo	110 °C, 60 min	Levulinic acid (35.1%)	Khan et al. (2018)

(continued)

Table 2.3 (continued)

Type of catalyst	Catalyst	Substrate	Reaction conditions	Product distribution (%)	Reference
	[(2HSO$_4$)(H$_2$SO$_4$)) (0.00125 mol/mL H$_2$O)				
	1-Methyl-3-(3-sulfopropyl) imidazolium based ionic liquid ([C$_3$SO$_3$Hmim]HSO$_4$) (0.55 mmnol/g H$_2$O)	Chitin	180 °C, 5 h	Levulinic acid (56.0%)	Hou et al. (2020)

[a] *HMF* hydroxymethylfurfural

aluminosilicate-based zeolites as catalysts for sugar conversion to LEA. Among this type of zeolites, they observed that CuZ(60%)@H zeolite provided the highest conversion yield of glucose and cellulose to levulinic acid of 45% and 30%, respectively.

Apart from the use of homogeneous and heterogeneous catalysts, the employment of novel and potential technology, such as the use of biphasic media, supercritical fluids, or ionic liquids, is gaining attention due to their promising results (Kumar et al. 2018). Zunita et al. (2020), for instance, used 1,3-dipropyl-2-(2-propoxyphenyl)-4,5-diphenylimidazolium iodide ([DPDIm]I)-based ionic liquid as a potential solvent and catalyst for the conversion of cellulose to levulinic acid. They observed that by carrying out the treatment at low temperature, they achieved a conversion of 94% of the cellulose and that they could reuse the ionic liquid five times. Another example of the employment of IL for obtaining levulinic acid, apart from the ones collected in Table 2.3, is the research performed by Hou et al. (2020) who converted levulinic acid from chitin with a yield of 67% using 1-methyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate ($[C_3SO_3Hmim]HSO_4$) as the catalyst.

In order to make the conversion process environmentally more sustainable and less time consuming, intensification processes, such as the microwaves, have been used to carry out the production of levulinic acid. The use of the microwaves could reduce the heating time, improve the energy transference, and consequently allow the employment of mild reaction conditions (Aliko et al. 2020). Qin et al. (2016), for instance, compared the conversion of wheat straw to levulinic acid with and without the assistance of the microwave irradiation. They observed that the time needed to obtain levulinic acid with a yield of 12.5 mol% reduced from 3 h to 45 min when the microwave irradiation is employed.

2.3.3 Propionic Acid (PA)

Propionic acid is a three-carbon monocarboxylic organic acid that presents the following chemical formula: $H_3CH_2CO_2H$. Nowadays, as most of the chemicals, it is mainly produced by petrochemical industries by one of the following processes, among which the carbonylation of ethylene is the most common one:

1. Carbonylation of ethylene with carbon monoxide and water. In this process, ethylene reacts with carbon monoxide in an aqueous media (Olah and Molnár 2003). Overall, this process gives high yields and high conversion, has no workup complications, and has a low price.
2. Oxidation of propanal (Du et al. 2015). This is a two-step process in which firstly propanal is formed during the production of propanol and afterward propanal is oxidized.
3. Direct oxidation of hydrocarbons. It is the most complex process nowadays, and the composition of the final product depends on reaction conditions, such as the temperature, the pressure, the reactor type, and the reaction time, among others.

However, in the latest years, more environmentally sustainable procedures for obtaining biobased propionic acid are under development, being most of them based on the fermentation of sugars. Ramsay et al. (1998), for instance, carried out the biological conversion of hemicelluloses to propionic acid using *Propionibacterium acidipropionici* by a separated enzymatic hydrolysis and fermentation (SHF). Prior to the fermentation, they hydrolyzed the hemicelluloses extracted from *Populus tremuloides* using a mixture of *endo*- and *exoxylanases* obtaining a hydrolyzate with a xylose concentration of 29.6 g/L. The maximum specific PA production rate that could be achieved from this hydrolyzate was 0.23 g/g h. They also observed that the proper propionic acid inhibits the activity of the microorganisms being not possible to obtain a propionic concentration higher than 2 g/L. Recently, Teles et al. (2019) were able to produce 0.79 g PA/g of substrate using a *Propionibacterium acidipropionici* culture and the sugars present in corn steep liquors as the substrate. Apart from *Propionibacterium acidipropionici*, Gonzalez-Garcia et al. (2017) also observed that *Escherichia coli* in anaerobic conditions could produce propionic acid from glucose when the fermentation media is complemented with methylmalonyl-CoA epimerase via an amino acid degradation. Furthermore, Feng et al. (2010) produced propionic acid using molasses as feedstock in the presence of *Propionibacterium freudenreichii* bacteria, producing 14.58 g/L of propionic acid. However, the use of the fermentation to produce propionic acid has also some drawbacks, as it is not cost-effective due to the low product yield or low productivity. It has also been reported that the presence of by-products such as HAc and SA in the fermentation media could make the fermentation more difficult and more expensive (Vidra and Németh 2018).

2.3.4 Formic Acid (FA)

Formic acid or methanoic acid is the simplest organic acid, as it is formed by a unique carboxylic group and its chemical formula is H_2CO_2. Although the petrochemical industry is the main FA producer commonly through the carbonylation of methanol, it is also a by-product generated during the pulping process carried out by biorefinery industries. Nevertheless, the quantity of formic acid produced by this environmentally sustainable process is not big enough to fill the demand of this organic acid. Thus, investments in new processes are being done by diverse associations like European Union to boost green formic acid production. According to the literature, the most common process to produce formic acid consists of the dehydrogenation of CO_2 in the presence of a noble metal catalyst and using a base and a polar solvent, since it permitted the achievement of selectivies close to 100% under certain conditions. Nevertheless, although the results obtained by this process are successful, the difficulties that could present in the scaling up make it unattractive.

In this context, as an alternative to the dehydration of CO_2, obtaining formic acid by oxidation of saccharides has gained attention. Shen et al. (2022), for instance, reported a facile cascade conversion of cellulose into FA using heteropolyacid-derived temperature-responsive catalysts, such as ChnH$_4$-nPMo$_{11}$VO$_{40}$, achieving a conversion of 49.5% of the cellulose. Another catalyst that has been studied for the conversion of cellulose into formic acid is the vanadium (V(V))-contained catalyst (Lu et al. 2018). Lu et al. (2018) observed that the addition of a second metal, as Mg (II), Ca(II), Al(III), Cr(III), Mo(VI), Mn(II), Cu(II), or Fe(III), into V(V)-contained catalyst system improved the oxidation of cellulose favoring the formation of formic acid. Among the different combinations that they tested, the addition of Fe(III) to V (V)-contained catalysts exhibited the best performance achieving a cellulose conversion of 66.8%, which was higher than the conversion yield obtained when only FeCl$_3$ (48.4%) or NaVO$_3$ (57.6%) was used. Zhang et al. (2014) also employed vanadium-based catalysts, but in this case, they employed a Keggin-type vanadium-substituted phosphomolybdic acid catalyst (H$_4$PVMo$_{11}$O$_{40}$), achieving a cellulose conversion of 67.8% when the experiment was carried out under the optimum conditions. Furthermore, Wölfel et al. (2011) also reported the conversion of different biomass to FA through oxidation in an aqueous media using, in this case, a Keggin-type H$_5$PV$_2$Mo$_{10}$O$_{40}$ polyoxometalate catalyst. They observed that direct conversion 19 wt% of the cellulose present in the poplar wood could be transformed into formic acid. Gromov et al. (2016) obtained formic acid from activated cellulose by one-pot hydrolytic oxidation, using Mo-V-P heteropoly acids as bifunctional (acidic and oxidizing) catalysts. In this study, they obtained a formic acid yield equal to 66 mol%, working in a temperature range between 150 and 160 °C. In order to improve the oxidation of the saccharides, Park et al. (2021), impregnated lignocellulosic biomass with citric acid (CIB), and then subjected it to a mechanocatalytic depolymerization treatment (MD) using dimethyl sulfoxide and hydrogen peroxide to improve the contact between the substrate and catalysts. By the hydrolysis-oxidation process that they carried out, they were able to produce formic acid with a yield of 50.03%.

2.3.5 Succinic Acid (SA)

Succinic acid, which has a chemical formula of (CH$_2$)$_2$(CO$_2$H)$_2$, is one of the organic acids with the shortest chains, as it presents two carboxylic groups with a total of four carbons. At industrial scale, this organic acid is commonly produced by the catalytic hydrogenation of maleic acid derived from butanes and butenes, while in the biorefinery industry, it is produced either by fermentation processes or by chemical routes.

Among the last two routes, the fermentation processes have been more investigated, due to their high selectivity toward the formation of succinic acid. There are a wide variety of microorganisms, such as *Anaerobiospirillum succiniciproducens*, *Mannheimia succiniciproducens*, *Actinobacillus succinogenes*, or *Propionibacterium acidipropionici*, that can convert monosaccharides to bio-succinate. Among the sources from which these monosaccharides could be extracted, the main investigation has been focused on raw biomass such as corn straw, sugarcane bagasse, oak wood, etc. (Kumar et al. 2016). Nishida et al. (2021), for instance, performed the thermochemical conversion of soybean hull into fermentable sugars using imidazole as pretreatment agent. Afterward, the obtained solid residue, containing mainly glucan (57.1 wt.%) but also xylan (16.3 wt.%), was subjected to an enzymatic hydrolysis for obtaining a hydrolyzate rich in glucose (34 g/L) and xylose (10 g/L) due to the complete conversion of glucan and xylan present in the solid. The monosaccharides present in the hydrolyzate were fermented by *Saccharomyces cerevisiae* for obtaining succinic acid together with bioethanol. They estimated that from 1 ton of soybean of 36.5 kg of SA and 124.0 kg of bioethanol could be produced. Vallecilla-Yepez et al. (2021) demonstrated the potential use of corn fiber for the bio-production of succinic acid using the microorganism *Actinobacillus succinogenes*. Nevertheless, in this case, the corn fiber was also pretreated by a liquid hot water process and an enzymatic hydrolysis for obtaining a hydrolyzate in monosaccharides, which was afterward fermented. They observed that the CO_2 availability and pH were critical factors in the fermentation of glucose by *Actinobacillus succinogenes*. Filippi et al. (2021), for instance, carried out the fermentation of glucose obtained from grape pomace and grape stalks by *Actinobacillus succinogenes*. Prior to carrying out the fermentation, the grape pomace was subjected to a water extraction for the extraction of the monosaccharides. Then, the obtained solid residue was mixed with the grape stalks, and the solid mixture was subjected to an alkaline extraction with NaOH (1%, w/v) in order to remove lignin. Finally, the delignified residues were submitted to acidic treatment (H_2SO_4, 3–10%, v/v) followed by an enzymatic hydrolysis using *cellulases* and *β-glucosidases.* As a result, a hydrolyzate containing 22.7 g glucose/100 g remaining solids (48% cellulose hydrolysis) was obtained, and it was fermented by *Actinobacillus succinogenes* producing 40.2 g/L of SA, which corresponded with a yield of 0.67 g/g. Filippi et al. (2022) employed the same microorganism to produce this organic acid from the monosaccharides extracted from apple pomace by an enzymatic hydrolysis of the apple pomace. They observed that from 1 kg of apple pomace, they could produce 157.8 g of succinic acid which corresponded with a concentration of 37.2 g/L. As it can be seen, to produce SA from the biomass, this material must be pretreated which make obtaining the procedure not competitive enough to overcome petroleum refineries in a short period.

Besides the fermentation paths, chemical processes are also being investigated to convert biomass into SA; however, results are yet far from being attractive enough. As it occurred in the fermentation paths, firstly monosaccharides such as sucrose, glycerol, galactose, sorbitol, cellobiose, and maleic acid must be extracted from lignocellulose and converted into succinic acid. Choudhary et al. (2013), for instance, obtained succinic acid through the oxidative cleavage of furan carbonyls, which can be obtained from xylose, using a solid acid catalyst and H_2O_2. This work demonstrated that it is possible to produce SA through a metal-free catalytic way. On the other hand, Muzumdar et al. (2004) converted biobased maleic acid into SA catalyzed by a titanium cathode and they achieved a 92% yield.

2.3.6 Acetic Acid (HAc)

Acetic acid, also known as glacial acetic acid or ethanoic acid, is considered one of the most important carboxylic acids and its formula is CH_3COOH. It is composed by a methyl group attached to a carboxylic group conforming one of the simplest organic acids. Right now, most of acetic acid production processes are related to petroleum refinery, and it is commonly produced by the wet oxidation of natural gas. Today, it is mainly used in pharmaceutical synthesis, the leather tanning, and dyeing industries (Jung and Oh 2021). However, nowadays, in the biorefinery industries, it is still in a novel situation in plant scale; however, there are plants manufacturing HAc as a secondary product. In general, acetic acid is formed by hydrolysis of acetyl group of hemicelluloses (Kumar et al. 2016).

In literature, Ehsanipour et al. (2016) conducted a bioconversion of four different water-soluble monosaccharides extracted from different lignocellulosic residues by *Moorella thermoacetica* (strain ATCC 39073) to acetic acid. They observed that *M. thermoacetica* was able to ferment efficiently xylose and glucose contained in hydrolyzates obtained from the different biomass. Among the different tested biomass, the sugarcane straw permitted the most effective production of acetic acid since 71% of the sugars present in the hydrolyzate were fermented.

Brownell and Nakas (1991) used *Clostridium thermoaceticum* with the aim of converting the sugars extracted from hybrid poplar. The authors concluded that the best condition for the maximum extraction of sugars was using dilute sulfuric acid (at 100 °C for 60 min). *Clostridium thermoaceticum* was grown in non-pH-controlled batch culture at 55 °C, and it produced 14 g/L of HAc after 48 h of fermentation. On the other hand, they observed that in fed-batch fermentations, the same microorganism produced 42 g/L of acetic acid after 116 h of fermentation.

In hydrothermal chemical process, acid-/base-catalyzed reactions and oxidation reactions were employed for the production of acetic acid, as it can be seen in Table 2.4. The addition of alkali or acid and the use of high temperatures enhance high yields of desired products, and hydrogen peroxide (H_2O_2) is often used as an oxidant. In this context, Jin and Enomoto (2011) were able to achieve conversion yields of 11.7% and 9.7% (conversion of the carbon of initial material), by the hydrothermal oxidation rice hulls and sawdust, respectively. Furthermore, Jin et al. (2005) showed the possibility to produce HAc from carbohydrates via oxidation of dehydration products of aldoses, such as furan. For that, two-step hydrothermal process was proposed. The first treatment was focused on the formation of 5-hydroxymethyl-2-furaldehyde, 2-furaldehyde, and lactic acid. Then, an oxidation reaction was performed for the conversion of furans and LA into acetic acid. The HAc obtained by the two-step process had not only a high yield but also better purity.

Another chemical process carried out for the production of acetic acid consisted of the employment of supercritical fluids; however, in general low yields are obtained. In this context, Calvo and Vallejo (2002) used cellulose (among other feedstocks) for the production of HAc, together with formic, glycolic, and lactic acid. They carried out batch tests at fixed conditions of 400 °C, 27.6 MPa, and 5 min

Table 2.4 Chemical synthesis of acetic acid from lignocellulosic biomass

Type of reaction	Oxidant and catalyst	Substrate	Conditions	Acetic acid yield (%)[a]	Reference
One-step hydrothermal oxidation	70–80% of oxygen (H_2O_2)	Rice hulls	300 °C, 120 s	11.7	Ehsanipour et al. (2016)
		Sawdust		9.7	
		Cellulose		9.0	
		Lignin		6.3	
Two-step hydrothermal oxidation	70% of oxygen (H_2O_2)	HMF[b] + 2FA[c] + LA extracted from rice hulls	300 °C, 1 min	21.7	Jin et al. (2005)
Hydrothermal oxidation (sub-supercritical water)	– 2000% of oxygen (H_2O_2)	Cellulose	400 °C, 5 min	10.5	Calvo and Vallejo (2002)
	– 50% of oxygen (H_2O_2) + 0.1 g/L TiO_2 as catalyst			10.6	
	– 25% of oxygen (H_2O_2) + NaOH 5 g/L	Glucose	400 °C, 43 s	16.8	
Catalytic oxidative conversion	–0.1 mmol H4PVMo11O40 catalyst +20 mL water +2 MPa oxygen	Cellulose	180 °C, 3 h	16.0	Zhang et al. (2014)
	–0.1 mmol H4PVMo11O40 catalyst +20 mL water + 0.5 MPa oxygen	Bagasse		20.3	
Hydrothermal oxidation	70–80% of oxygen (H_2O_2)	Rice hulls	300 °C, 120 s	11.7	Jin et al. (2007)
		Sawdust		9.7	
Acidic hydrolysis	0.25 wt.% of H_2SO_4	Hemicellulose hydrolyzate extracted from pinewood	190 °C, 1: 8 solid-liquid ratio	4 g/L	Jung and Oh (2021)

[a] wt%, yield based on the contents of initial material carbons
[b] *HMF* 5-hydroxymethyl-2-furaldehyde
[c] *2-FA* 2-furaldehyde

of reaction time and using H_2O_2 as oxidant. Less than 15% of the initial total organic carbon was converted to acid. However, if NaOH was added to the reaction media (at 250 °C and 27.6 MPa), 77% of glucose was transformed to HAc. In fact, in general, alkali was used to improve the conversion of cellulose-derived carbohydrates into acetic acid. In recent works, Jung and Oh (2021) applied low-acid hydrothermal fractionation for hemicellulose extraction from pinewood. They used pinewood as raw material for hemicellulose sugar extraction. For that, the raw material was first fractionated at 190 °C, in acidic medium with 0.5 wt.% of sulfuric acid for 10 min. Then, further acid hydrolysis was carried out with zinc chloride, and finally liquid-liquid extraction was applied (using ethyl acetate) for furfural and acetic acid recovery from hydrolyzate. Overall, the obtained HAc yield was about 62.3%.

2.4 Concluding Remarks and Future Trends

In this work, the description of lignocellulosic polysaccharides, their extraction processes, and some conversion strategies into renewable organic acid production is showed. Their renewability and biodegradability character make them an interesting alternative to replace petroleum-based organic acids by its organic counterparts. The different research lines performed until today, via chemical or fermentation processes, showed different potential and possibilities. Besides the influence of different process parameters, such as catalyst or microorganism type, concentration, temperature, process time, and so on, the used feedstock characteristics (polysaccharide type) should be also taken into account. However, most of them are still in early stages of research and development. In the near future, for a sustainable and scale-up production process, advancements in technology and its optimization are needed at industrial scale.

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Biochemical and Chemical Catalytic Routes for the Production of Biochemicals from Biomass: Current Status and Future Perspectives

3

Shivali Banerjee and Vijay Singh

Abbreviations

2,5-DMF	2,5-Dimethyl furan
2,5-FDCA	2,5-Furandicarboxylic acid
3-HP	3-Hydroxypropionic acid
FPU	Filter paper unit
HMFs	Hydroxymethylfurfurals
MVL	Mevalonolactone
PEG	Polyethylene glycol
SDGs	Sustainable Development Goals
SSF	Solid-state fermentation
TAL	Triacetic acid lactone

3.1 Introduction

Industrialization and rising population have led to the depletion of fossil-based resources and the alarming challenges of the energy crisis. The overexploitation of fossil-based resources has also resulted in greenhouse gas emissions which lead to climate change and global warming (Mukherjee et al. 2019; Nanda et al. 2016c). Greenhouse gas emissions can be reduced by mitigating the reliability on fossil fuels via sustainable utilization of biomass as renewable feedstocks for the production of

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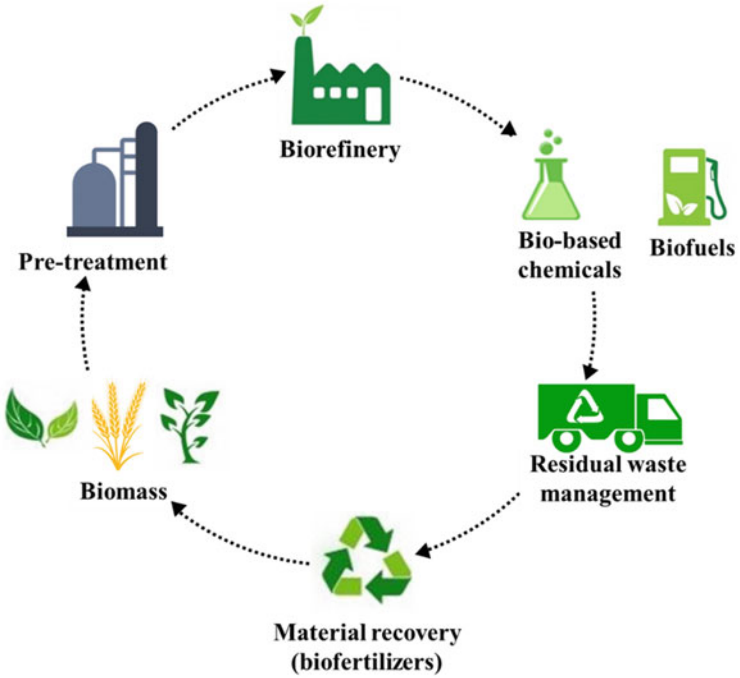

Fig. 3.1 A generalized schematic of the circular bio-based value chain

bio-based chemicals in a circular economy (Nanda et al. 2015, 2016a; Zhou et al. 2011). A bio-based economy is one of the many different routes that could achieve a circular economy. To attain the goal of sustainable, technological, and socioeconomic development, the principles of both circular economy and bio-based economy work together (Hennig et al. 2016). In terms of current targets for sustainable growth, both bio-based and circular economy have the potential to directly contribute to at least 10 out of the 17 United Nations' Sustainable Development Goals (SDGs), the most important one being SDG 12 which is responsible for sustainable consumption and production. In a bio-based value chain (Fig. 3.1), the feedstocks could be biomass drawn from an existing primary production route (e.g., agricultural and forest residues), or of a novel (e.g., microalgae) or secondary origin (e.g., sludge, industrial wastewater, and household organic waste) (Hennig et al. 2016; Lokesh et al. 2018). Agricultural residues, forest residues, and energy crops are among the chief sources of lignocellulosic biomass comprising cellulose (30–60 wt%), hemicellulose (20–40 wt%), and lignin (15–25 wt%) (Nanda et al. 2013, 2014a; Okolie et al. 2021b). Cellulose is a polymer made up of glucose units and hemicellulose comprises pentose and hexose sugars (Kim 2018; Nanda et al. 2014b). Lignin is a macromolecule comprising phenyl propane units joined together by ester bonds and acts as an adhesive for binding cellulose and hemicellulose together (Fougere et al. 2016).

The lignocellulosic biomass could be converted into biofuels and biochemicals by the biochemical, chemical, or thermochemical routes (Cai et al. 2017; Okolie et al. 2019). Biochemical routes mainly comprise fermentation where microorganisms and enzymes convert the biomass into biofuels and biochemicals, while the thermochemical route uses heat and chemical processes for converting biomass into sustainable fuels and biochemicals (Cai et al. 2017). Pyrolysis (Azargohar et al. 2014; Mohanty et al. 2013), gasification (Azargohar et al. 2019; Nanda et al. 2016b), liquefaction (Chand et al. 2019; Ma et al. 2019), and carbonization (Kang et al. 2019) are among the major thermochemical conversion routes. The current state-of-the-art technologies for the production of biofuels have been reviewed elsewhere (Antzela Fivga et al. 2019; Long et al. 2021; Rizwanul Fattah et al. 2020; Ruhul et al. 2015; Vasudevan and Briggs 2008).

This chapter covers the state-of-the-art technologies for the production of industrially relevant biochemicals from renewable biomass resources. Figure 3.2 represents biochemical and chemical catalytic routes for the conversion of biomass into industrially relevant biochemicals. Additionally, the current status, challenges, and future perspectives on the production of biochemicals from renewable feedstocks have been outlined.

3.2 Biochemical Conversion Route for the Production of Biochemicals

Biochemical conversion is based on enzymatic hydrolysis of lignocellulosic biomass into sugars, which are subsequently fermented to produced biofuels or bio-based chemicals. Biochemical conversion routes have the advantage of low processing temperatures and high selectivity of products generated. However, they normally require preprocessing in the form of pretreatment to reduce the complexity of the biomass. The crystalline cellulose present in the microstructure of lignocellulosic biomass is known for its recalcitrant nature toward enzymatic degradation, while lignin is another physical barrier that restricts the enzymatic hydrolysis of biomass (Amoah et al. 2019; Chen et al. 2018b). Hence, pretreatment of biomass plays an important role in overcoming the issue of recalcitrance. The cross-linked fraction of lignocellulosic biomass gets strongly disintegrated by the pretreatment process, which is known to enhance the enzymatic accessibility of cellulose and hemicellulose (Fig. 3.3) (Soltanian et al. 2020). Pretreatment is thus an integral part of the state-of-the-art technologies for the production of both biofuels and biochemicals.

3.2.1 Pretreatment Approaches

Pretreatment of biomass comprises physical, chemical, biochemical, or physicochemical methods (Bilal et al. 2017). Milling, microwave, extrusion, and freezing are among the physical pretreatment methods, while acid, alkaline, organosolv, oxidative, and ionic liquid are among the major chemical pretreatment methods

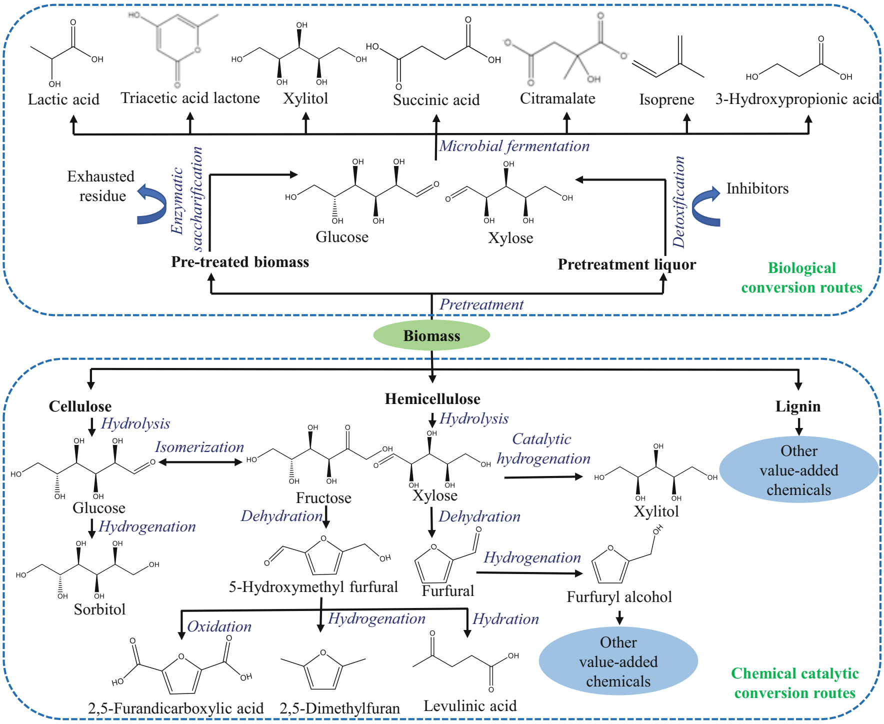

Fig. 3.2 Schematic of the biochemical and chemical catalytic route for conversion of biomass into industrially relevant biochemicals

which improve the enzymatic digestibility of lignocellulosic biomass. Steam explosion, wet oxidation, ammonia fiber explosion, ultrasonication, liquid hot water, and CO_2 explosion are among the physicochemical pretreatment methods (Soltanian et al. 2020). The recent advances in the pretreatment of biomass have been reviewed elsewhere in detail (Baruah et al. 2018; Mankar et al. 2021; Das et al. 2021; Galbe and Wallberg 2019; Kumar and Sharma 2017). Some of the most commonly studied pretreatment methods and their effect on the cellulosic content of the biomass have been summarized in Table 3.1.

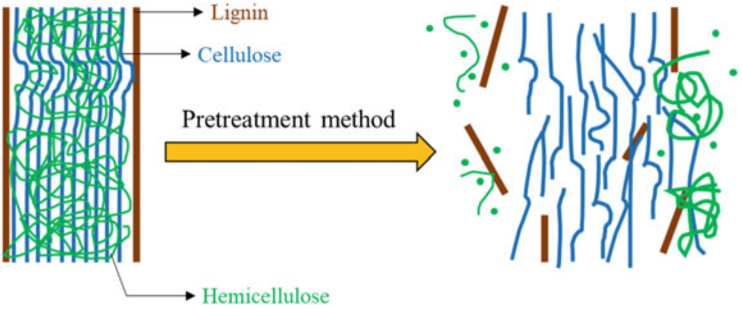

Fig. 3.3 Schematic representation of disintegration of lignocellulosic biomass after pretreatment

3.2.2 Enzymatic Saccharification

Enzymatic saccharification is one of the most important steps in the biochemical route of the production of biochemicals (Abdou Alio et al. 2020). The efficient conversion of carbohydrates into monomeric sugars can be achieved by the optimization of operational parameters such as solid loading, enzyme loading, time of hydrolysis, shaking speed, and additives for enhancing enzymatic saccharification (Zhang et al. 2018).

3.2.2.1 Solid Loading

Solid loading plays an important role in enzymatic hydrolysis for obtaining an increased concentration of sugar monomers. On an industrial scale, the enzymatic hydrolysis of biomass needs to be conducted at higher solid loadings (over 15% w/w) which leads to increased concentration of sugar monomers, improvements in the capital, and operational costs making the process economically more feasible (da Silva et al. 2020). However, the enzymatic hydrolysis at higher solid loadings often creates technical difficulties which affect the process efficiency. This is often known as the “high solids effect” that leads to viscous systems, impaired mixing along with mass, and heat transfer which affects the action of the enzymes. A recent study on the enzymatic hydrolysis of 7.5% w/v pretreated sawdust reported a decrease in the glucose conversion yield from 80% at 5.2% w/v to 59% at 7.5% w/v substrate proportion which could be possible due to the high viscosity of the larger substrate suspension that slows down the mass transfer phenomena (Abdou Alio et al. 2020).

3.2.2.2 Enzyme Loading

Enzyme loading is another important parameter that controls the conversion of biomass carbohydrates into sugar monomers along with the economics of the overall biochemical conversion route for the production of biochemicals. A recent study reported that the enzymatic hydrolysis of pretreated rice straw at 5% solid loading indicated that the glucose yield at 10 filter paper unit (FPU)/g enzyme dosage reached 95.4% after 48 h, while 74% glucose yield was obtained at an enzyme

Table 3.1 Summary of effect of different pretreatments on the cellulosic content of commonly studied lignocellulosic biomass

Type of pretreatment	Raw material	Method	Cellulose content (%)		References
			Raw biomass	Pretreated biomass	
Alkali-assisted	Grass waste	1% w/v sodium hydroxide	31	43	Yan et al. (2020)
	Hemp stems	1% w/v sodium hydroxide	40	74	Zhao et al. (2020)
	Corn stalk	2% w/v sodium hydroxide	36	47	Zhao et al. (2019)
	Sugarcane bagasse	2% w/v sodium hydroxide	35	54	Fan et al. (2020)
	Corncob	1.6% w/v calcium hydroxide	41	49	Chen et al. (2010)
	Grass waste	1% w/v sodium hydroxide supplemented with 2% w/v hydrogen peroxide	31	51	Yan et al. (2020)
Oxidative	Grass waste	2% w/v hydrogen peroxide	31	35	Yan et al. (2020)
	Wheat straw	1.18% w/v sodium chlorite	35	40	Chen et al. (2018b)
Organosolv	Sawmill mixed feedstock	Microwave-assisted water/ethanol organosolv	44	71	Abdou Alio et al. (2020)
	Spruce wood chips	52% w/w ethanol	38	70	Matsakas et al. (2019)
Water-based	Wood	Steam explosion	41	44	Schneider et al. (2020)
	Sugarcane straw	Liquid hot water	34	55	Pratto et al. (2020)
	Poplar wood	Liquid hot water	43	61	Tian et al. (2020)
	Hemp stems	Liquid hot water	40	54	Zhao et al. (2020)
Acid-assisted	Corncob	1% v/v sulfuric acid	41	72	Chen et al. (2010)
	Rapeseed straw	1% w/w sulfuric acid	30	53	Tan et al. (2020)
	Hemp stems	1% w/w sulfuric acid	40	62	Zhao et al. (2020)
	Sugarcane bagasse	0.2% w/v sulfuric acid	37	46	Ko et al. (2018)
	Wheat straw	0.5% w/v sulfuric acid	35	54	Chen et al. (2018b)

(continued)

Table 3.1 (continued)

Type of pretreatment	Raw material	Method	Cellulose content (%)		References
			Raw biomass	Pretreated biomass	
	Spruce wood chips	Acid-catalyzed steam explosion	38	38	Matsakas et al. (2019)

dosage of 5 FPU/g (Tang et al. 2019). Similarly, lower or insufficient enzyme loadings for saccharification of sugar beet pulp led to a 50-fold drop in hydrolysis (Berlowska et al. 2018). Another study reports the increase in saccharification efficiency from 22.5% to 66.7% on increasing the enzyme loading from 2.5 to 20 FPU/g glucan, respectively (Ko et al. 2018).

3.2.2.3 Shaking Speed

Lower shaking speed often results in lower yields of sugar monomers which could be attributed to poor mixing of the substrate with the enzyme, while high shaking speed often leads to the deactivation of the enzymes due to the shearing force and results in decreased saccharification of the enzyme. The shaking speed of 150 rpm is often reported to obtain the highest enzymatic digestibility of cellulose (Chen et al. 2018a, b).

3.2.2.4 Additives

Additives such as PEG-based polymer (PEG 600), surfactant Tween 80, and protein BSA have been found to improve the enzymatic saccharification of pretreated corn stover in terms of enhanced glucose yield (Wei et al. 2019). The improvement in the enzymatic saccharification could be attributed to the properties of these additives to increase positive interactions between the substrate and enzyme (Zhou et al. 2015). A similar study reports that these additives could reduce the enzyme loading (up to 50%) and also shorten the duration of hydrolysis from 72 to 12 h. The enzymatic saccharification of pretreated *P. juliflora* was enhanced in the presence of additives such as Tween 40 (39.2%), PEG 4000 (43.8%), and Tween 80 (47.5%) compared to the control (without any additives) (Gupta et al. 2009). However, the additives such as cetyltrimethylammonium bromide and sodium dodecyl sulfate led to a decline in the yields of sugars upon saccharification.

3.2.3 Fermentation

The monomeric sugars obtained after saccharification could be fermented by microbes for the production of a wide range of biofuels and biochemicals. For the commercial production of the desired biochemical, an ideal microbe is screened that should be capable of utilizing the maximum amount of sugar monomers and can give higher yields of the targeted biochemical (Talebnia et al. 2010). In the case of ethanol production, the microbes are genetically modified to ferment both pentose and hexose sugars leading to higher yields of ethanol. Similarly, the bioprocessing of other biomass resources such as fruit and vegetable wastes has been a potential method for the production of biochemicals and bioproducts. These novel biochemicals are also known as secondary metabolites synthesized by the microbes after the growth phase (Kumar et al. 2021). These metabolites are not required for the growth and reproduction of the microorganism but could be utilized for other secondary needs. These microbial compounds find potential applications in the cosmetic, pharmaceutical, and food sectors, specifically. Recent studies have suggested the application of secondary metabolites to heal various health diseases in humans (Gertsch 2016; Singh et al. 2019). The secondary metabolites have also found potential applications as biopesticides, plant growth regulators, surfactants, and bio-pigments (Ahluwalia et al. 2015; Yan et al. 2018). Microbial secondary metabolites' production requires a fermentation process followed by the downstream steps to recover and purify secondary metabolites (Kumar et al. 2021). Microbial production of secondary metabolites was found to be economically more beneficial when compared to plant-based extraction or tissue culture approaches. This could be attributed to the faster growth of the microbes and the easy downstream processing (Jiang et al. 2020). In this regard, the pharmaceutical industries have focused on fermentation techniques for the production of secondary metabolites as active ingredients in drug manufacturing (Gupta and Chaturvedi 2019; Jiang et al. 2020). The production of these metabolites can be done via two major kinds of bioprocesses, namely, solid-state fermentation (SSF) and submerged fermentation (SmF) (Thomas et al. 2013). Online monitoring and automation are the key features of SmF, making it a better process for the large-scale production of microbial secondary metabolites. On the other hand, SSF provides a natural environment for the growth of microorganisms by utilizing a solid matrix containing adequate moisture (Singhania et al. 2015; Thomas et al. 2013). This solid matrix could be nutrient-dense biomass such as fruit and vegetable waste (Thomas et al. 2013). Couto has reported that SSF is better when compared to SmF since it does not produce any foam during fermentation and decreases the dependency on parameters such as aeration, pH, and temperature (Rodríguez Couto 2008). Hence, SSF emerges to be an excellent bioprocess for the production of microbial secondary metabolites from agro-industrial wastes (Mekala et al. 2008; Singhania et al. 2015).

Biochemical such as lactic acid is produced via fermentation of carbohydrate sources by different microorganisms (Datta and Henry 2006; Ghaffar et al. 2014; John et al. 2007). To achieve maximum yields of lactic acid and higher productivity, lactic acid bacteria have been evaluated for the production of lactic acid from lignocellulosic biomass via fermentation. Lactic acid bacteria, specifically *Lactobacillus* spp., are known to show significant fermentation capabilities.

Succinic acid is another organic acid that is traditionally synthesized by the hydrogenation of maleic acid (Byun et al. 2019). However, recent studies have reported the production of succinic acid via biochemical fermentation of biorefinery sugar (Lu et al. 2021). Succinic acid can be converted into succinate esters which find potential application as precursors of other value-added chemicals (Delhomme et al. 2009; Luque et al. 2009). The selection or development of a succinic acid-producing microbe is one of the key factors that controls the efficacy of the production of succinic acid via fermentation. *Actinobacillus succinogenes* is one of the widely studied microorganisms showing the best performance in producing succinic acid via fermentation (Ferone et al. 2018; Yan et al. 2014; Zheng et al. 2013).

3-Hydroxypropionic acid (3-HP) has also been identified as a platform chemical that can be upgraded into industrially relevant chemicals such as acrylic acid, methyl acrylate, acrylonitrile, and others (Matsakas et al. 2018; Rathnasingh et al. 2009). 3HP has been produced biochemically by the fermentation of sugars by metabolically engineered *Saccharomyces cerevisiae* (Kildegaard et al. 2015). Fermentation of glycerol using metabolically engineered microbes has also been widely reported for the production of 3HP (Jers et al. 2019; Jiang et al. 2018; Li et al. 2016).

The lignocellulosic hydrolyzate could also be converted into sugar alcohol such as xylitol. The biotechnological route for converting pentose sugar-rich liquor into xylitol is an alternative option to the chemical route (Dasgupta et al. 2017). Studies have reported yeasts as the best strains for producing xylitol due to their high rates of assimilation for pentose and high xylitol productivity (Mohamad et al. 2015). However, most yeasts do not produce xylanolytic enzymes. This has led to an interest in filamentous fungi for producing xylitol since these microbes produce a xylan-degrading enzyme complex that releases xylose from xylan-rich lignocellulosic biomass along with subsequent production of xylitol by the same fungi (Mäkelä et al. 2014). Filamentous fungi such as *Trichoderma reesei* and *Aspergillus oryzae* have been studied for the production of xylitol using xylose or xylan as the substrate (Hong et al. 2014; Mahmud et al. 2013). Meng et al. have recently demonstrated the production of xylitol directly from lignocellulosic biomass by using metabolically engineered *Aspergillus niger* (Meng et al. 2022). However, the selection of biomass substrate based on its composition is important for the direct production of xylitol using engineered filamentous fungi (Meng et al. 2022).

Citramalic acid (citramalate) is another important intermediate molecule produced from biomass-derived glucose via fermentation (Wu et al. 2021). Citramalate thus obtained is diverted toward the production of methacrylic acid via dehydration and decarboxylation. Methacrylic acid is a target molecule in the polymer industry (Darabi Mahboub et al. 2018). Studies have been conducted for optimizing the *E. coli* strains to maximize the yield of citramalate (Webb et al. 2018).

Biomass-derived polyketide such as triacetic acid lactone (TAL) is an attractive building block for the production of upgraded chemicals and polymerization (Sajjad et al. 2020). Chen et al. have recently demonstrated the production of piperidine and δ-lactam from TAL (Chen et al. 2021). Sajjad et al. have reported ring-opening polymerization of β-acetoxy-δ-methylvalerolactone (a derivative of TAL) (Sajjad et al. 2021). TAL is produced by the fermentation of biomass-derived sugars by genetically modified microbes (Li et al. 2018b; Markham et al. 2018; Saunders et al. 2015).

Biochemical routes have also been studied for producing bio-based isoprene, which is currently made from petroleum and is an important platform chemical for the synthesis of oil additives, fragrances, and pesticides along with its important application in the rubber production industry (Li et al. 2018a). The biochemical route includes the biosynthesis of isoprene in engineered microbial cell factories. Microorganisms such as *B. subtilis*, *E. coli*, *S. cerevisiae*, and cyanobacterium *Synechocystis* have been engineered for producing bio-based isoprene (Ye et al. 2016). However, the biochemical production of bio-based isoprene is reported to have low yields as the major limitation. Recently, Heracleous et al. have demonstrated the production of bio-based isoprene through a hybrid bio-/thermochemical process (Heracleous et al. 2020). It combines the fermentation of cellulosic sugars to mevalonolactone (MVL) with the acid-catalyzed decarboxylation of MVL to isoprene.

Downstream processing is another important step that controls the economics of the production of biochemicals. The biochemical route mainly involves the set of strategies for efficient and cost-effective recovery of products from fermentation broth. The downstream processing method depends upon the target product that needs to be recovered. Detailed downstream processing technologies have been reviewed in the literature (Kumar and Murthy 2011; Sarup 2022). This chapter specifically does not cover the strategies for downstream processing.

3.3 Chemical Catalytic Route for the Production of Biochemicals

3.3.1 Acid-Catalyzed Hydrolysis

The selective hydrolysis of cellulose into glucose monomers is a critical step for converting biomass into value-added chemicals. Often this reaction is catalyzed by acids mainly mineral acids such as H_2SO_4, HCl, or HF (Gürbüz et al. 2013; Mäki-Arvela et al. 2011). The performance of solid acid catalysts has also been evaluated for the hydrolysis of cellulose and has recently been reviewed in the literature (Van de Vyver et al. 2011). However, using a high catalyst-to-substrate ratio for increasing the contact between the cellulosic substrate (solid) and the heterogeneous catalyst (solid) creates a problem and hinders progress in this area. The dissolution of cellulose in alkyl-methyl-imidazolium ionic liquids is a recent breakthrough in this respect. Ionic liquid disturbs the hydrogen bonding among the cellulosic fibers and leaves the hydroxyl groups and glycosidic linkages accessible to the attack by acid. Hence, the biomass dissolved in ionic liquids can be easily hydrolyzed using acids (Li et al. 2008; Rinaldi et al. 2008; Swatloski et al. 2002).

3.3.2 Acid-Catalyzed Dehydration

The acid-catalyzed dehydration of hexose and pentose sugars is the most common method for the production of furfurals and hydroxymethylfurfurals (HMFs), respectively (Chheda et al. 2007). These furanic species are flexible platform molecules and are used for the production of higher value-added biochemicals. Hydroxymethylfurfural is currently not produced in bulk quantities because of the high costs of production involved. However, the production of hydroxymethylfurfural is expected to increase in the future due to its potential for conversion into valuable chemicals or as a fuel precursor. HMF can be converted into 2,5-furandicarboxylic acid through selective oxidation, which can then be used in the synthesis of biodegradable polyesters (Deshan et al. 2020; Gandini et al. 2009). Acidic hydrolysis of HMF results in the production of levulinic acid (Girisuta et al. 2006; Pyo et al. 2020). Levulinic acid has been identified as a valuable platform chemical that can be used for the production of fine chemicals and fuel additives. Similarly, the pentose sugars (mainly xylose) present in hemicellulose can be converted into furfurals which could be upgraded into value-added chemicals (Lange et al. 2012; Mamman et al. 2008). Further, the role of heterogeneous catalysis has been reviewed elsewhere for the production of bio-based monomers such as furfuryl alcohol, 2,5-furandicarboxylic acid, and levulinic acid from furfural and hydroxymethylfurfural (Yang et al. 2021).

3.3.3 Catalytic Hydrogenation

The catalytic hydrogenation of sugar monomers has been reported for the industrial production of sugar alcohols such as sorbitol, xylitol, mannitol, and others (Bonnin et al. 2021; Carvalho et al. 2021; Marques et al. 2016; Zada et al. 2017). Nickel-based catalysts were first studied and used at an industrial scale for the production of sugar alcohols via hydrogenation of sugar monomers (Zada et al. 2017). However, the high temperature and pressure conditions required for the hydrogenation reaction often lead to side reactions due to the degradation of sugars which results in lower selectivity of products in the presence of nickel-based catalysts. Also, nickel-based catalysts lack stability and metal leaching is one of the major issues associated with these catalysts. To avoid this, noble metal catalysts specifically Ru- and Pt-based have been investigated (Ahmed and Hameed 2019; Liu et al. 2017). The studies showed that ruthenium was the most efficient in the selective hydrogenation of carbonyl to the corresponding alcohol (Bonnin et al. 2021; Esposito et al. 2019; Sanz-Moral et al. 2018; Xu et al. 2020).

Further, catalytic hydrogenation is also used for the production of 2,5-dimethyl furan (DMF) from 5-HMF (Esen et al. 2019; Saha and Abu-Omar 2015). DMF is an important chemical that has characteristics similar to gasoline for internal combustion engines (Somers et al. 2013).

3.3.4 Catalytic Oxidation

Catalytic oxidation is another important industrial route for upgrading platform chemicals such as 5-HMF into biochemicals like 2,5-furandicarboxylic acid (FDCA) (Yi et al. 2014; Zhang and Deng 2015). One-pot oxidation of 5-HMF to

FDCA is reported in water under continuous flow conditions with a heterogeneous resin-supported Pt catalyst (Liguori et al. 2019). In another study, the oxidation of 5-HMF into FDCA was carried out over Ru/Al_2O_3 using O_2 aqueous alkaline solutions in a trickle-bed reactor (da Fonseca Ferreira et al. 2019). Further, the catalytic conversion of biomass into HMF followed by its oxidation into FDCA is reviewed in the literature (Cong et al. 2021). Table 3.2 represents the summary of the global market size of industrially relevant biochemicals along with the conversion technologies for their production from biomass.

3.4 Current Status and Future Perspectives

The successful transition from a fossil-based economy to a sustainable bioeconomy depends upon the establishment of biorefineries that could utilize biomass for the production of biofuels and biochemicals through green and cost-effective conversion technologies. Among the different types of biomasses, lignocellulosic biomass is the most widely available. To successfully run these lignocellulosic biorefineries, a major investment needs to be done in the improvement and advancement of efficient conversion technologies. Advanced biorefineries based on lignocellulosic biomass can be integrated with the existing industries such as paper mills and chemical production industries. Such integration could help in achieving synergies in terms of logistics, product development, and raw material market. Most of such advanced biorefineries have not been commercialized yet, and their development widely depends upon the efficiency and cost-effectiveness of the conversion technologies. The high cost of pretreatment, lower costs of conventional fossil-derived chemicals, and the problems associated with conversion technologies are the major challenges encountered. The problems associated with conversion technologies majorly include the cost of enzymes, high operational temperature and pressure, and recovery and reusability of metal catalysts and enzymes. The current focus is to develop effective pretreatment strategies, increase the efficiency of conversion technologies, and conduct techno-economic and life cycle assessments (Calicioglu et al. 2021; Kumar and Verma 2021; Ögmundarson et al. 2020; Okolie et al. 2021a; Silveira et al. 2015). Future efforts are required for developing strategies for biomass collection ensuring continuous feedstock supply and improving the efficiency and cost-effectiveness of the conversion technologies with the major focus being on sustainable pretreatment approaches along with the development of inexpensive, environmentally friendly, and efficient catalysts. These advanced biorefineries would lead to sustainable utilization of biomass along with the creation of new business opportunities when developed at a commercial scale. Further implementation of long-term planning and policies is required to facilitate the efficient valorization of biomass.

Table 3.2 Summary of conversion technologies for the production of selective biochemicals from biomass

Biochemical	Type of production technology	Method of production	Scale	Global market size	References
Lactic acid	Biochemical route	Fermentation	Commercial	Valued at USD 2.7 billion in 2020; expected to grow at a CAGR of 8% from 2021 to 2028	Abedi and Hashemi (2020), Grand View Research (2021b)
Furfural	Chemical catalytic route	Acid-catalyzed dehydration of xylose	Commercial	Valued at USD 494.1 million in 2020; expected to grow at a CAGR of 6.5% from 2020 to 2028	Grand View Research (2021a), Gravitis et al. (2001)
Hydroxymethylfurfural	Chemical catalytic route	Acid-catalyzed dehydration of fructose	Commercial	Valued at USD 55.8 million in 2018; expected to grow at a CAGR of 1.45% from 2018 to 2025	Market Research (2018), Verma et al. (2017)
Levulinic acid	Chemical catalytic route	Acid-catalyzed dehydration of lignocellulosic feedstock	Commercial	Valued at USD 20.3 million in 2020; expected to grow at a CAGR of 5.3% from 2021 to 2028	Rose and Palkovits (2011), Verified Market Research (2021)
Sorbitol	Chemical catalytic route	High-pressure catalytic hydrogenation of glucose	Commercial	Valued at USD 1.47 billion in 2020; expected to grow at a CAGR of 6.5% from 2021 to 2028	Grand View Research (2021c), Zhang et al. (2013)
Xylitol	Biochemical route	Fermentation of xylose	–	Expected to reach USD 738.18 million by 2028	Carneiro et al. (2019), Grand View Research (2021d)
	Chemical catalytic route	Hydrogenation of xylose	Commercial		Delgado Arcaño et al. (2020)
Succinic acid	Biochemical route	Fermentation	Commercial	Valued at USD 141 million in 2020; expected to grow at a	PR Newswire (2021), Zheng et al. (2009)

(continued)

Table 3.2 (continued)

Biochemical	Type of production technology	Method of production	Scale	Global market size	References
				CAGR of 5.5% during 2021–2027	
2,5-Furandicarboxylic acid	Chemical route	Oxidation of HMF	Commercial	Valued at USD 264.1 million in 2020; expected to grow at a CAGR of 4% in 2022–2027	Ait Rass et al. (2013); Chatterjee et al. (2015); Market Reports World (2021); van Putten et al. (2013)
3-Hydroxypropionic acid	Biochemical route	Fermentation of sugars by metabolically engineered *Saccharomyces cerevisiae*	–	–	Jers et al. (2019), Kildegaard et al. (2015)
Bio-based isoprene	Biochemical route	Produced by metabolically engineered microbial cell factories such as *Escherichia coli*	–	Expected to grow at a CAGR of 5.47% during 2020–2026 and reach USD 890.23 million by 2026	Li et al. (2018a), Market Research (2020), Ye et al. (2016)
Citramalate	Biochemical route	Produced from biomass-derived glucose via fermentation	–	–	Wu et al. (2021)
Triacetic acid lactone (TAL)	Biochemical route	Fermentation of biomass-derived sugars by genetically modified microbes	–	–	Li et al. (2018b); Markham et al. 2018)

3.5 Conclusion

Lignocellulosic biomass is an important feedstock for the production of valuable biochemicals via biochemical and chemical catalytic conversion technologies. However, the major drawback in the conversion of biomass into biochemicals is the high cost of production contributed by the cost of biomass, pretreatment methods, downstream processing cost, and lower product yields. Though the product yields could be maximized by different catalysts, selection of the suitable catalysts and the cost associated with its regeneration are the major challenges that need to be addressed. Biofuels such as bioethanol and biogas have already been produced on an industrial scale from biomass. The industrial production of biochemicals is expected to increase in the future. An integrated biorefinery producing biofuels, biochemicals, and bioproducts would be an advanced approach to the sustainable valorization of biomass. These bio-based products from biorefineries should have an existing market demand that would ensure the economic sustainability of their production. Further, bio-based chemicals can significantly reduce greenhouse gas emissions and would stimulate innovative advancement in the domain of biorefining. An environmentally sustainable industrial sector for the production of biofuels and biochemicals is expected upon the expansion of the bio-based economy.

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Challenges in Biobutanol Fermentation and Separation

4

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Abbreviations

ABE	Acetone butanol ethanol
ATPS	Aqueous two-phase system
CMC	Critical micellar concentration
CPE	Cloud point extraction
GHG	Greenhouse gas
HLB	Hydrophilic-lipophilic balance
LCB	Lignocellulosic biomass

4.1 Introduction

Recent worries about global warming, rising fossil fuel prices and legal restrictions on the usage of nonrenewable sources of energy have fuelled attention towards studying biotechnological pathways for biofuel production. Worldwide petroleum consumption and other fossil-based liquid fuels increased by 14% in 2020 as compared to 2008 (86×10^6 barrels/d). It is projected to further rise to 112×10^6 barrels/d in 2035 (Sarangi and Nanda 2018; Okolie et al. 2021). A major global goal

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is to use renewable resources for fuel, electricity and heat. Woody biomass is a renewable, nonfood plant material that can be used to produce biofuel and reduce dependence on the fossil fuels. In general, there are many other options for producing biomass-based transportation fuels as an alternative.

Although the emerging energy industry faces many challenges, global production of biofuel from first generation has grown exponentially over the past decade. Furthermore, first-generation biofuels (bioethanol derived from food sources) have raised number of issues in the fuel versus food debate, providing a stronger case for the waste to energy scenario (Hijosa-Valsero et al. 2020). Thus, second-generation biofuel technologies are more in demand due to socially and environmentally acceptable life cycle. Second-generation biofuels required the higher capital cost compared to that of first-generation biofuels due to the complicated and expensive processing equipment (Mat Aron et al. 2020).

Wood-based feedstocks also known as lignocellulosic biomass (LCB) (including forestry and agricultural residues), sewage sludge and municipal solid wastes have remarkable potential to enhance biofuel production, thereby ensuring reduction in greenhouse gas (GHG) emissions and energy security achievements (Nanda et al. 2014b, 2015). LCB is widely available in the nature worldwide and an inexpensive resource; thus, it has an implausible potential to supplement the alternative biofuel production. At present, about 1.3 billion tons of LCB is derived from agricultural biomass, 3.7 billion tons from grasslands and less than 1 billion tons from dedicated crops (Banu et al. 2021). The advantage of LCB is its nonfood properties; thus, their bioprocessing grants the least threat to national as well as global security of food, in contrast to food-based raw materials (Nanda et al. 2015).

The biological way for butanol production is via acetone-butanol-ethanol (ABE) fermentation. This route was commercialized due to excessive demand for acetone (used for cordite production) during World War I. C. Weizmann, a Russian scientist, invented ABE fermentation in Manchester University in 1912. ABE fermentation was primarily employed in the military to increase acetone output. Butanol has recently gained popularity as a liquid renewable fuel (Dürre 2007). The main obstacles in the economical manufacture of butanol by ABE fermentation are the high substrate cost, low concentration of butanol and high separation cost. Hence, over the past two decades, global research is exploring alternative inexpensive renewable raw materials for butanol production which mainly include agricultural wastes (Sarangi and Nanda 2018).

4.2 Butanol: A Biofuel

Biobutanol is considered a superior biofuel over ethanol and can replace ethanol in gasoline due to its superior fuel properties. Butanol (33.1 MJ/kg) has 30% more calorific value than ethanol and low freezing point (−114 °C) which makes butanol a better fuel than ethanol. Also, butanol is a cleaner burning biofuel (results in less smoke density) compared to ethanol which helps protect the environment. In addition, it is less volatile, less hazardous, less corrosive, less flammable and less hygroscopic than ethanol (Nanda et al. 2014a). Further, it can be processed and transported through the existing supply lines for gasoline without incurring further costs on infrastructure development unlike ethanol. Butanol can be used as a feedstock in the chemical industry, as fuel for fuel cells and in the cosmetics industry and manufacturing processes owing to its clean burning (Pattnaik et al. 2021). Also, butanol can be blended in any proportion with gasoline or utilized as a fuel additive in current automotive engines. As a result, butanol is more easily integrated into current gasoline-powered transportation systems. Butanol can be used in place of gasoline without requiring any further engine changes (Lee et al. 2008).

4.3 ABE Fermentative Pathway of *Clostridium* Bacteria

n-Butanol can be obtained by bacterial fermentation from sugars. The most used strain for *n*-butanol production is *Clostridium* which includes *C. acetobutylicum*, *C. saccharobutylicum*, *C. beijerinckii* and *C. saccharoperbutylacetonicum.* The ABE fermentation process uses a variety of fermentation techniques, including batch, fed-batch and continuous fermentation using wild-type and modified strains.

The genus *Clostridium* is divided into heterogeneous gram-positive, obligate anaerobes, spore-forming, rod-shaped and non-sulphate-reducing bacteria (Montoya et al. 2000). Recently, the solvent-generating bacterium *Clostridia* has received a lot of attention because of its potential to produce industrially significant compounds like acetone and butanol.

Clostridium fermentation has two successive stages: the acidogenic stage (acid generation) and solventogenic stage (solvent generation). Acidogenic stage is the first step that occurs during fermentation, which leads to the formation of butyric acid (butyrate) and acetic acid (acetate) along with carbon dioxide and hydrogen. Acid production decreases the pH of the fermentation medium resulting in cessation of the cell's activity. Clostridial bacteria have to maintain a balance of NADH and NAD+ because they cannot use the electron transport system to generate ATP. This is because the conversion of glucose to ABE is the only way to regenerate NAD+; all other end products yield NADH. Acetoacetyl-CoA is converted to acetoacetate and then to acetone during solventogenic stage. Glycolysis is the fermentation step where most of the ATP is produced (Tashiro et al. 2007). Most of the acetyl-CoA is converted to acids and solvents, while some are used for the synthesis and growth of lipids.

Immediate death is tricked into a major metabolic change towards the end of the log phase. It is also a sign of the end of the acidogenic stage and the start of the solventogenic stage. Generated acid during acidogenic stage is used by bacteria with the help of CoA and converted into solvents such as acetone, ethanol and butanol. This uptake is a detoxifying biological response that prevents inhibitory action of organic acids for cell growth (Gheshlaghi et al. 2009). A phenomenon of acid crash caused because of excess acid accumulation in the system inhibits bacterial growth and reaches a stationary phase (Yang et al. 2013). Acid crash may result from low initial substrate concentrations and/or excess concentration of nutrients (Zverlov et al. 2006). Under the condition of acid crash, conversion from acidogenic stage to solventogenic stage does not take place, and fermentation stops abruptly due to excessive acid production. However, optimal sugar concentration and butyrate together have shown promising results for biobutanol production (Tashiro et al. 2007). Therefore, if butyrate remains in the reactor (hydrogen producing) after fermentation, a significant amount of butanol may be produced provided there is proper blending with the right amount of sugar.

During solventogenesis, pH of the media will increase again keeping bacterial cells active for a longer time. However, after attaining a particular concentration, solvents may additionally start killing microorganism as butanol is extremely toxic. Maximum concentration of solvent achieved during fermentation is about 2% (w/w) (Dürre 2008). During fermentation, other than ABE, other desirable products that include acetic acid and butyric acid are produced. However, formation of a few undesirable by-products consumes available carbon and subsequently reduce yield.

4.4 Microbes Used for ABE Fermentation

A large variety of *Clostridium* cultures are capable of producing acetone, butanol, isopropanol and ethanol, with varying yields and proportions (Khandeparker and Sani 2018). Bacteria from genus *Clostridium* include different butanol-producing species such as *C. saccaroperbutylacetonicum*, *C. pasteurianum*, *C. acetobutylicum*, *C. beijerinckii*, *C. sporogenes*, *C. saccharoacetobutylicum*, *C. aurantibutyricum*, *C. cadaveris* and *C. tetanomorphum*. During the first half of the last century, *Clostridium acetobutylicum* was the first bacterium to be used in industrial butanol production from sugar and starch. It is a gram-positive, strict anaerobe that forms spore and is believed to be a highest butanol-producing bacteria at that time (Johnson et al. 1997). However, butanol yields were substantially greater in *C. beijerinckii*, *C. acetobutylicum*, *C. saccharoacetobutylicum*, and *C. saccaroperbutylacetonicum* (Huang et al. 2010; Li et al. 2020). DNA fingerprinting and 16S rRNA sequencing was used to compare different strains of these species (Johnson et al. 1997; Dürre 2008; Keis et al. 2001; Winzer et al. 2000). Gutierrez et al. (1998) studied various strains of *C. beijerinckii* and *C. acetobutylicum* that produced butanol from potato. *C. acetobutylicum* DSM 1731, according to Gutierrez et al., is the strain that produces the most butanol, with a productivity of 0.24 g/L h. Besides *C. acetobutylicum*, competence of other clostridial species which are able to produce butanol was investigated on the basis of raw materials and their ability of producing solvents in a particular ratio. On the same path, Qureshi and Blaschek (2000) and Qureshi et al. (2008a, b, 2010a, b) reported almost equal solvent ratio with higher butanol concentration of 18.0–25.0 g/L by cultivating *C. beijerinckii* compared to *C. acetobutylicum* (10.0–16.0 g/L) (Jones and Woods 1986; Qureshi et al. 2001) using various waste cellulosic materials. Apart from this, *C. aurantibutyricum* was investigated to produce acetone and isopropanol along with butanol (Somrutai et al. 1996). Its efficiency was examined using palm oil mill discharge as substrate in ABE fermentation. The list of some of the important strains and the substrate employed in ABE fermentation are abridged in Table 4.1.

Instead of using only anaerobic microorganisms, aerobic bacteria (*Bacillus subtilis* TISTR 1032) are co-cultured with anaerobic bacteria (*C. butylicum* WD 161) to investigate an increase in the total amount of solvent production. Desaccharification in the presence of aerobic microbes leads to high amylase activity and thus enhanced solvent production. In fact, cultivating aerobic and anaerobic organisms together helped in skipping the usage of expensive reducing agents specially used to maintain anaerobic conditions during the ABE fermentation (Jones and Woods 1986; Tran et al. 2010). An increase in the number of co-cultivation stages may result in infection of organisms with bacteriophages that may result in a failure of such system. In order to avoid bacteriophage infection to organisms, controlled surgical methods such as immunization of resistant strain, decontamination, sterilization and disinfection were performed.

In addition, the selection of butanol-producing strains depends on various factors such as nutrient requirements, type of substrate or raw material, resistance to bacteriophage infection, determined productivity and resistance to solvent toxicity. Researchers should focus on increasing butanol tolerance capacity of organisms by molecular biology and genetic engineering techniques. Also, focus should be given on isolation of novel species, which has more desired characteristics.

4.5 Substrates Used for ABE Fermentation

Demand for butanol increased tremendously after World War I (Birgen et al. 2019). During this period, numerous other butanol fermentation plants were installed worldwide that used substrates from starch and sugar. However, it was later realized that the cost of the substrate was continuously increasing that lead to ceasing of many butanol plants (Sarchami and Rehmann 2019). In ABE fermentation, the cost of substrates which is $\geq$70% of the total cost of butanol production plays an important role in economical production of butanol (Gu et al. 2011). Researcher suggested that using cheap and renewable feedstock like lignocellulosic material will significantly reduce the cost of butanol production. Butanol production using lignocellulosic raw material is mainly carried out in three major steps as (1) pretreatment of the feedstock, (2) hydrolysis and (3) fermentation (Cheng et al. 2012). A variety of substrates used for butanol fermentation are reported in Table 4.2. Butanol can be produced from molasses without any treatment of molasses. However, molasses is more expensive than agricultural waste. Therefore, debating on which raw material is cheaper for ABE fermentation becomes very difficult. Analysis of energy efficiency and economics of butanol production using sugar molasses was reported by Van der Merwe et al. (2013).

The availability of raw materials throughout the year is also an important factor to be considered. Agricultural wastes such as wood, corn fibre, rice straw, bagasse, straw and waste paper (Qureshi et al. 2007), sweet sorghum and annual recurring crops are the main sources to be used as a substrate for the production of biobutanol.

Table 4.1 List of substrate and *Clostridium* species used in ABE fermentation

Sr. no.	Microorganism	Year	Substrate	Yield	Yield/productivity	Reference
1	*C. beijerinckii* P260	2007	Wheat straw	42%	–	Qureshi et al. (2007)
2	*C. beijerinckii* P260	2010	Barley straw	43%	26.64 g/L total solvents	Liu et al. (2010)
3	*C. beijerinckii* P260	2010	Switch grass	37%	8.91 g/L total solvents	Qureshi et al. (2010a)
4	*C. beijerinckii* P260	2010	Corn stover	43%	18.04 g/L total solvents	Qureshi et al. (2010a)
5	*C. beijerinckii* P260	2011	Glucose	–	17.52 g/L butanol	Mariano et al. (2011a)
6	*C. acetobutylicum* CICC 8008	2011	Corn straw		6.20 g/L butanol	Lin et al. (2011)
7	*C. beijerinckii* NCIMB 8052	2011	Tropical maize stalk juice	–	0.27 g-butanol/g-sugar	Wang and Blaschek (2011)
8	*C. beijerinckii*	2011	Cassava flour	–	23.98 g/L butanol	Lépiz-Aguilar et al. (2011)
9	*C. saccharoperbutylacetonicum* N1-4	2012	Rice bran	57%		Al-Shorgani et al. (2012)
10	*C. acetobutylicum*	2012	Cassava bagasse	32%	76.4 g/L butanol	Lu et al. (2012)
11	*C. beijerinckii* NCIMB 8052	2012	Corncob	–	8.2 g/L butanol	Zhang et al. (2012)
12	*C. sporogenes* BE01	2013	Rice straw	–	3.49 g/L butanol 5.32 g/L total solvents	Gottumukkala et al. (2013)
13	*C. pasteurianum*	2013	Glycerol	0.35 g/g	8.8 g/L butanol	Khanna et al. (2013)
14	*C. beijerinckii* MCMB 581	2014	Glucose	–	15.3 g/L butanol	Singh et al. (2016)
15	*C. sporogenes*	2015	Glucose	–	12 g/L butanol	Dhamole et al. (2015)

Table 4.2 Different feedstocks used for butanol production

Sr. no.	Bacteria/*Clostridium* species	Substrate	Total ABE concentration	Reference
1.	*C. beijerinckii* P260	Barley straw	26.64 g/L	Qureshi et al. (2010b)
2.	*C. beijerinckii* P260	Wheat straw	21.42 g/L	Qureshi et al. (2007)
3.	*C. beijerinckii* P260	Corn fibre	9.3 ± 0.5 g/L	Qureshi et al. (2008b)
4.	*C. beijerinckii* P260	Switch grass	14.6 g/L	Qureshi et al. (2010a)
5.	*C. acetobutylicum* DSM 1731	Domestic organic waste	9.3 ± 0.5 g/L	Claassen et al. (2000)
6.	*C. saccharoperbutylacetonicum* DSM 13864	Sago starch	9.10 g/L	Liew et al. (2006)
7.	*C. acetobutylicum* P262	De-fibrated sweet potato slurry	7.73 g/L	Badr et al. (2001)
8.	*C. beijerinckii* BA101	De-germed corn	14.28 g/L	Ezeji et al. (2007b)
9.	*C. beijerinckii*	Liquefied corn	18.4 g/L	Ezeji et al. (2007a)
10.	*C. acetobutylicum*	Whey permeates	3–4 g/L h	Qureshi and Maddox (2005)

These substances mainly consist of three polymers that include cellulose, hemicelluloses and lignin. Cellulose makes up about 50% of the wood mass. It is an ordered linear glucose polymer that breaks down into monomers during hydrolysis. Hemicellulose is a short, branched heterogeneous polymer, also known as polyose. It consists of xylose, α-galactose, mannose, β-glucose, arabinose and sometimes uronic acid. Lignin is an organic complex polymer supporting tissue of vascular plants. It contains phenylpropanoid units drawn from *p*-hydroxyquinol alcohols. Lignin is hydrophobic in nature and has high resistance to chemical and biological degradation (Adsul et al. 2011).

Pretreatment leads to generation of several inhibitory compounds such as hydroxymethylfurfural, salts, ferulic acid, furfural and para-coumaric acid that can inhibit cell growth and negatively affect fermentation. Furthermore, fermentation with lignocellulosic substrate needs to be added with nutritional supplements.

Table 4.2 shows some of the important organisms and the substrates used with them for ABE fermentation. According to Qureshi et al., *C. beijerinckii* P260 produced 26.64, 9.30 ± 5, 26.27 and 14.6 g/L of total solvents using barley straw, corn fibre, corn stover and switch grass, respectively (Qureshi et al. 2008a, b, 2010b). With sago starch, total solvent of 9.1 g/L has been reported using *C. saccharoperbutylacetonicum* DSM 13864 by Liew et al. (2006). Using a mixed culture (*B. subtilis* and *C. actobutylicum*) on cassava starch, total solvent production enhanced by 6.5-fold than pure culture of *C. butylicum* (Tran et al. 2010). Mixed culture produced 7.40 g/L ABE, whereas *C. butylicum* TISTE 1032 produced 1.13 g/L ABE (Tran et al. 2010). Badr et al. have reported 7.73 g/L of ABE using *C. acetobutylicum* P262 with de-fibrated sweet potato slurry as a substrate (Badr et al. 2001). 14.28 and 18.4 g/L of ABE have been reported using *C. beijerinckii* BA101 and *C. beijerinckii* with de-germed corn and liquefied corn, respectively (Ezeji et al. 2007a, b). Qureshi and Maddox (1995) have reported ABE productivity of 3–4 g/L h with *C. acetobutylicum* using whey permeate as a feedstock. 5–15% higher butanol concentration has been reported by Lin and Blaschek (1983) with *C. acetobutylicum* ATCC 824 using extruded corn.

4.6 Challenges in ABE Fermentation

Butanol has a number of advantages over ethanol as discussed in Sect. 4.1. However, butanol production by fermentation is not economically feasible. In ABE fermentation, butanol production is affected by butanol toxicity. Due to the low butanol titre in the fermentation broth, subsequent processing of biobutanol recovery and purification is similarly energy intensive (Mariano et al. 2011a, 2012; Matsumura et al. 1988). Since the use of food/crop for biofuel production is prohibited, there is a need for a cheap raw material that provides the maximum butanol yield with minimum processing. Therefore, there are two interrelated challenges in butanol fermentation as explained schematically in Fig. 4.1:

1. Butanol toxicity
2. Separation of butanol (due to low concentration)

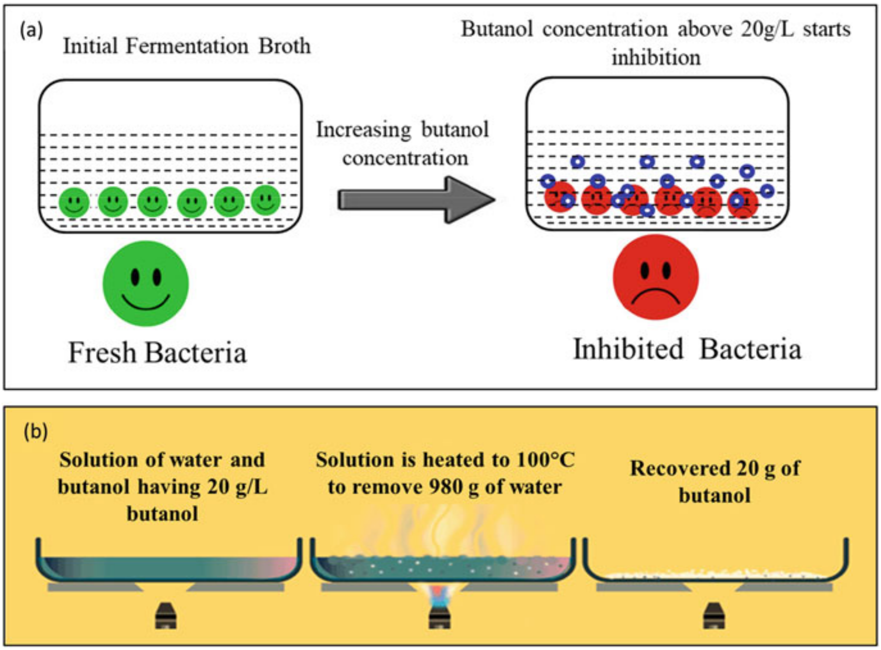

Fig. 4.1 Challenges in butanol fermentation

Butanol concentrations more than 20 g/L are harmful to butanol-producing microbes; thus, biobutanol production is considered as an example of product inhibition (Fig. 4.1a). It disrupts the membrane cell wall thus inhibiting the growth and subsequently hinders butanol production (Awang et al. 1988). Low butanol concentration and productivity makes its separation a serious challenge (Fig. 4.1b). Various methods have been reported in order to relieve butanol toxicity which includes gas stripping (Ezeji et al. 2003, 2007; Setlhaku et al. 2013), pervaporation (Setlhaku et al. 2013; Qureshi et al. 2001; Tong et al. 2010), membrane-assisted solvent extraction (Jeon and Lee 1987; Tanaka et al. 2012; Qureshi and Maddox 2005), adsorption (Qureshi and Maddox 2005; Xue et al. 2016) and liquid-liquid extraction (Dadgar and Foutch 1988; Ha et al. 2010). However, majority of these methods were focused only on separation of butanol as it is generated. None of the method focused on improving the butanol concentration that decrease its separation cost.

4.7 Biobutanol Fermentation

Biobutanol fermentation can be done in a variety of ways, including batch, fed-batch and continuous fermentation, using various feed materials such as starch and lignocellulosic substance. The batch fermentation process is a straightforward, time-tested and widely researched fermentation method for butanol production. The conventional output ratio of ABE is about 3:6:1 (15.0–50.0 g/L) which is attained during 2–6 days of fermentation (Mariano et al. 2012). Several issues need to be addressed in the butanol fermentation process, including low yield (~20% w/w), product toxicity, fermentable sugar limitation (<60 g/L) and diluted product stream (productivity ~0.5–0.6 g/L h). Further the cost of utilities in a butanol-producing plant is almost threefold than that of an ethanol-producing unit of same capacity (Visioli et al. 2014). New mutant strains for the subsequent butanol removal from the fermenter have been produced to overcome butanol toxicity. As a result of this improvement, product inhibition was reduced, and productivity was increased (Mariano et al. 2012) (Fig. 4.1).

In fed-batch fermentation, initially, a low amount of substrate is added and more substrate is added as it is consumed. This will keep the fermentation process moving forwards ensuring that the substrate concentration does not reach a point where it becomes harmful. Fed-batch is used in situations when excessive feed concentrations are inhibitory to the culture (Li et al. 2011). *C. saccharoperbutylacetonium* was fed with butyric acid to produce biobutanol in a pH stat fed-batch fermentation process, resulting in a butanol titre of 16.59 g/L. *C. beijerinckii* P260 has been found to produce 16.59 g/L butanol using wheat straw hydrolysate (Qureshi and Ezeji 2008). In fed-batch studies, highest productivity using gas stripping was 1.16 g/L h and pervaporation was 0.98 g/L h which was significantly higher than batch fermentation (0.6 g/L h).

One time addition of inoculum is sufficient in a continuous butanol fermentation process. Thus, a continuous process will minimize sterilization and inoculation time consequently enhancing the productivity. As butanol toxicity prevents fermentation from entering the stationary phase, the continuous culture technique was used to analyse the physiology of culture in exponential phase. *C. beijerinckii* BA101 has shown a maximum butanol productivity of 1.74 g/L h (Ezeji et al. 2004).

Continuous culture has certain major drawbacks, such as the instability of solvent production over long periods of time and simultaneous increase in acid concentration. In a single-stage continuous fermentation system, high productivity may come at the expense of low product concentration as compared to batch processes. As a result of this complexity, industrial-scale utilization of a single-stage continuous reactor is not feasible, and two or more multistage continuous systems have been examined. The butanol concentration in a two-stage system using *C. acetobutylicum* DSM 1731 was 18.2 g/L, which was comparable to the solvent concentration in a batch process (Ezeji et al. 2004). Acidogenesis was obtained using *Butyribacterium methylotrophicum*, and solventogenesis was achieved using *Butyribacterium acetobutylicum* in a two-stage continuous investigation. It was discovered that the pH affects the ultimate concentration of products (Kumar and Gayen 2011). In addition, end-product toxicity, reinoculations, low productivity in the fermentation broth and bioreactor sterilization consumption can all impair ABE fermentation.

Table 4.3 shows some of the batch fermentation studies for ABE production. According to Qureshi et al., *C. beijerinckii* P260 produced 26.64 g/L of ABE using barley straw as a substrate (Qureshi et al. 2008a). With corncob residue hydrolysate, total solvents of 9.90 g/L have been reported using *C. beijerinckii* NCIMB 8052 by Zhang et al. (2012). Using *C. beijerinckii* BA101 culture on corn fibre, total ABE production obtained was 9.3 g/L (Qureshi et al. 2001). Singh et al. (2017) have reported 18.3 g/L of ABE using *C. beijerinckii* MCMB 581 with glucose as a substrate. 18.54 and 11.70 g/L of ABE have been reported using *C. acetobutylicum* ATCC 824 and *C. saccharobutylicum* DSM 13864 with corn stover and corn stover hydrolysate, respectively (He and Chen 2013; Ding et al. 2016). Chen et al. (2013) have reported ABE yield of 8.10 g/L with *C. saccharoperbutylacetonicum* N1-4 using rice bran hydrolysate as a feedstock. Using a mixed culture (*C. beijerinckii* 10132 and *C. cellulovorans* 35296) with wheat straw, total ABE production of 23.30 g/L was obtained. However, mixed culture of *C. acetobutylicum* ATCC and *B. subtilis* DSM 4451 with spoilage date palm, total ABE yield obtained was 21.56 g/L. Komonkiat and Cheirsilp (2013) have reported ABE productivity of 15.69 and 18 g/L with *C. acetobutylicum* DSM 1731 *and C. beijerinckii* TISTR 1461, respectively, using felled oil palm trunk as a substrate.

4.8 Extractive Fermentation of Butanol

Aqueous two-phase system (ATPS) is a liquid-liquid method of extraction which forms two phases on addition of various components in water. On the basis of the components used to form two-phase systems, ATPS is classified into different types: polymer-polymer, polymer-salt, short-chain alcohol-salt, ionic liquid-based ATPS

Table 4.3 Butanol production by batch fermentation

Sr. no.	Microorganism	Substrate	Yield	Reference
1	*C. beijerinckii* P260	Barley straw	26.64 g/L ABE	Qureshi et al. (2010b)
2	*C. beijerinckii* NCIMB 8052	Corncob residue hydrolysate	9.90 g/L ABE	Zhang et al. (2012)
3	*C. beijerinckii* BA101	Corn fibre	9.3 g/L ABE	Qureshi et al. (2008b)
4	*C. beijerinckii* P260	Corn stover:switch grass (1:1)	21.06 g/L ABE	Qureshi et al. (2010a)
5	*C. beijerinckii* MCMB 581	Glucose	18.3 g/L ABE	Singh et al. (2017)
6	*C. acetobutylicum* ATCC 824	Corn stover	18.54 g/L ABE	He and Chen (2013)
7	*C. saccharobutylicum* DSM 13864	Corn stover hydrolysate	11.70 g/L ABE	Ding et al. (2016)
8	*C. saccharoperbutylacetonicum* N1-4	Rice bran hydrolysate	8.10 g/L ABE	Chen et al. (2013)
9	*C. beijerinckii* 10132 + *C. cellulovorans* 35296	Wheat straw	23.30 g/L ABE	Valdez-Vazquez et al. (2015)
10	*C. acetobutylicum* ATCC + *B. subtilis* DSM 4451	Spoilage date palm	21.56 g/L ABE	Abd-Alla and El-Enany (2012)
11	*C. acetobutylicum* ATCC 824	Oil palm frond juice	15.69 g/L ABE	Nasrah et al. (2016)
12	*C. acetobutylicum* DSM 1731	Felled oil palm trunk (sap)	18 g/L ABE	Komonkiat and Cheirsilp (2013)
13	*C. beijerinckii* TISTR 1461	Felled oil palm trunk (hydrolysate)	14.10 g/L ABE	Komonkiat and Cheirsilp (2013)
14	*C. acetobutylicum* NCIM 2877	Orange peel waste	19.50 g/L butanol	Joshi et al. (2015)
15	*C. acetobutylicum* NRRL B-527	Peapod waste 120	5.94 g/L ABE	Nimbalkar et al. (2018)
16	*C. acetobutylicum* DSM 792	Apple peel waste	20 g/L ABE	Raganati et al. (2016)
17	*C. bifermentans* (SBI 4) + *B. coagulans*	Sago waste	9.01 g/L ABE	Johnravindar et al. (2017)
18	*C. beijerinckii* ATCC 55025-E604	Bamboo	6.45 g/L butanol	Kumar et al. (2017)
19	*C. beijerinckii*	Apple pomace	12.92 g/L ABE	Hijosa-Valsero et al. (2017)

and surfactant-based ATPS. Surfactant-based ATPS provide a variety of unique and desired qualities for biomolecule purification when compared to other ATPS.

Extractive microbial fermentation of organic components in a liquid-liquid two-phase system is a promising approach to overcome the problems of microbial fermentation in aqueous solution such as inhibition of substrates and/or products, low substrate solubility and degradation of products (Wang and Dai 2010). Surfactants are the surface-active agents, which are amphiphilic molecules that contain both polar and apolar part with an ability to interact with interfaces. The hydrophilic part of surfactant is highly polar moiety which is responsible for some water solubility to the whole molecule. Surfactants are classified into anionic, cationic, zwitterionic (amphoteric) and non-ionic based on its hydrophilic and hydrophobic moieties. The surfactant can provide biomolecules with both hydrophobic and hydrophilic environments at the same time. This is the major advantage of surfactant-based ATPS as it allows selective partitioning based on biomolecule hydrophobicity.

The hydrophilic-lipophilic balance (HLB) is the main parameter for determining polarity and solubility of surfactants. Surfactants above the critical micellar concentration (CMC) assemble themselves into various forms as micelles, reverse micelles and liquid crystals as lamellar and hexagonal (Wang and Dai 2010). Above a certain temperature, non-ionic surfactant separates into two phases as the dilute phase and the surfactant-rich phase also known as coacervate phase. This phenomenon distinguishes non-ionic surfactants from ionic surfactants. The temperature at which two phases separates is known as a cloud point and the system is known as a cloud point system (Hinze and Pramauro 1993). The molecular structure of surfactant mainly determines its cloud point.

Entrapment of organic components into micellar structure and separation of phases of non-ionic surfactant and aqueous solution at temperature above its cloud point make cloud point system a capable unique method for extractive microbial fermentation. Schematic representation of the extractive fermentation with surfactant is shown in Fig. 4.2. Many of the extractive microbial fermentation are not accessible to water organic phase two-phase systems to produce toxic products. Being nonvolatile in nature, these polymers also make aqueous two-phase system fulfil green, safety demands of industrial processes. However, troublesome downstream processing and costly phase forming component are vital challenges of this process (Andersson and Hahn-Hägerdal 1990; Sinha et al. 2000; Zijlstra et al. 1998). Cloud point system is a combination of advantages of aqueous-organic solvent two-phase system and aqueous two-phase systems together making this process inexpensive, biocompatible and green.

Some researchers have investigated performance of non-ionic surfactant for butanol separation in an extractive microbial fermentation. Dhamole et al. investigated extractive microbial fermentation using surfactant to separate butanol from simulated broth and real broth. They further studied simultaneous removal of butanol during the fermentation (Dhamole et al. 2012). Extractive fermentation with non-ionic surfactant has shown improved biobutanol production. Further, extraction of product from fermentation systems is carried out using the same surfactant. In L62-water phase butanol partition coefficient was found to be in the range of three to four times. Furthermore, reduction in processing volume was also observed which enhances the butanol concentration by six times in the coacervate phase compared to control. Finally, 95% of the butanol present in coacervate phase was separated by evaporation and the final concentration reached to 106.8 g/L. Surfactant was also

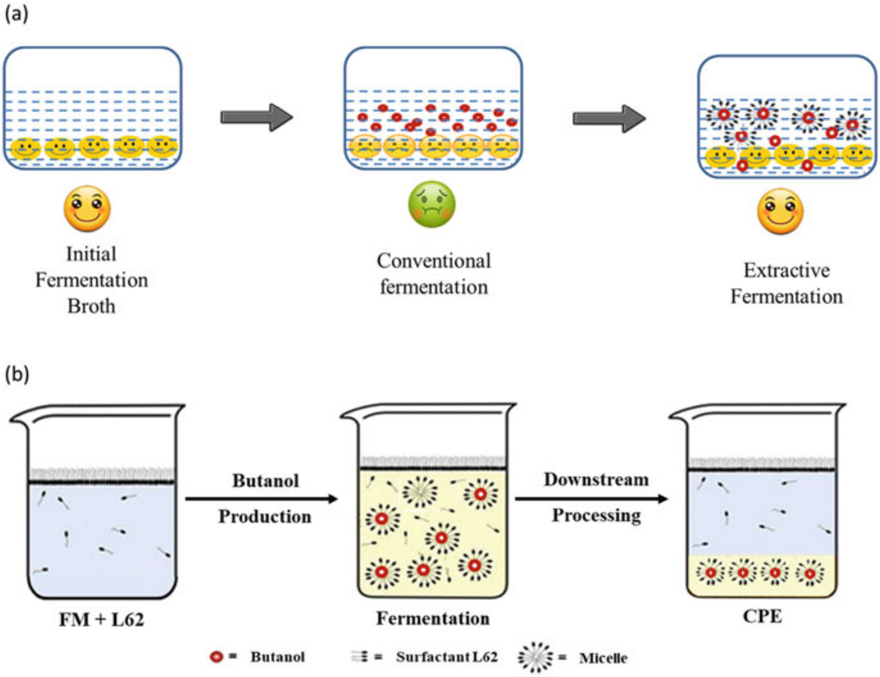

Fig. 4.2 Schematic representation of extractive fermentation with surfactant

studied for its reusability and was successfully reused for three extraction cycles without changing its properties as an extractant and showed same recovery of butanol in each successive cycle (Dhamole et al. 2012). Despite all the advantages of using extractive microbial fermentation using non-ionic surfactants for butanol production, very few researchers have focused on this area.

Butanol fermentation is a complex system and consists of different compounds including substrate, nutrients, intermediate products, products and various by-products. Every component in a fermentation system may affect the cloud point of the surfactant. Hence, it is essential to understand the effect of each component of the fermentation system on surfactant-based ATPS. This will be useful in deciding the temperature range for CPE in fermentation system and extraction of butanol into coacervate phase with high efficiency. The results showed that the cloud point temperature was highly dependent on the surfactant, butanol and glucose concentrations; however, the effects of other components from fermentation system were negligible (Raut et al. 2018a). The coexistence of glucose and butanol had a synergistic effect in lowering the cloud point of surfactant L62.

Subsequently, CPE was used to extract butanol from fermentation system using non-ionic surfactant L62. Raut et al. presented a detailed study on the effect of different operating parameters such as surfactant concentration, initial butanol, temperature and time on the extraction of butanol (Raut et al. 2019). Extraction efficiency was enhanced with surfactant concentration and decreased with increase in temperature and initial butanol present in the broth.

Despite promising results obtained from the CPE of butanol using extractive fermentation, a major challenge to overcome is recovery of butanol from the surfactant-rich phase, recovery and reuse of surfactant. Some research groups studied the back-extraction processes. In these processes, microemulsion systems were used for back-extraction of product, recovering the surfactant, thus enabling its subsequent reuse (Raut et al. 2018b). Shen et al. studied microemulsion systems using different solvents such as petroleum ether, cyclohexane and diethyl ether (Shen et al. 2014). Raut et al. have studied the back-extraction of butanol using Winsor III microemulsion with highly nonpolar hexane as a solvent (Raut et al. 2018b). Winsor III microemulsion represents three-layer system, where the middle layer also known as bi-continuous phase was rich in surfactant and exists in equilibrium with upper phase (organic phase) and lower phase (aqueous phase). Upper phase was rich in hexane and butanol, whereas lower phase was rich in water and butanol.

Gedam et al. explored microemulsion-based butanol extraction from simulated and microbial fermentation broth using C5–C7 alkanes (pentane, hexane and heptane) (Gedam et al. 2019). Extraction efficiency of butanol was reduced in studies with hexane-based Winsor III microemulsions using a two-step approach (coacervation followed by back-extraction). However, when compared to the two-stage method, the single-step method with hexane reduced a step and resulted in four times more butanol extraction (Gedam et al. 2019). Thus, use of surfactant in butanol fermentation improved the butanol concentration and was also used in separation of butanol from the broth.

4.9 Biocompatibility of Surfactants

Cell growth (cell count) method was used to study the biocompatibility of *C. beijerinckii* MCMB 581 in the presence of surfactants L62 and L62D. All flasks containing PYG (peptone, yeast extract, glucose) medium were inoculated with 1 mL of inoculum containing 10^6 cells and supplemented with various surfactant concentrations ranging from 1% to 10% (v/v). The number of cells increased with respect to the initial cell number for all surfactant concentrations. However, in the presence of surfactants, the cell number was slightly lower than in the absence (7×10^8). A slight decrease in cell count (6×10^8 to 3×10^8) was observed as surfactant concentration increased (1–10% v/v). Cell growth was observed to be delayed but not inhibited in the presence of surfactants. It could be attributed to late adaptation of cells to the surfactant-contained medium. It was also difficult to observe cells under a microscope because the presence of surfactant was a hindrance, which could have resulted in low nutrient availability to the microbial cells at the start. Based on the cell count, it can be predicted that cells will take some time to adapt to the surfactant-containing medium, resulting in delayed growth. Both surfactants, L62 and L62D, were found to be biocompatible.

4.10 Downstream Processing

Downstream processing of biomolecules generally involves four steps: recovery, isolation, purification and polishing. Out of these four steps, only purification step contributes more than 70% of the entire cost of downstream processing. The traditional strategies of biomolecule purification involve numerous steps of unit operations and consequently are generally expensive. In every step, a little quantity of target biomolecule is dissipated ensuing in a huge overall loss. Hence, to invent an effective technique for separation of biobutanol either at the completion of fermentation or simultaneous extraction, all through the fermentation was main focus of many researchers. Several methods have been proposed for the separation of butanol from fermented broth, including distillation, gas stripping, adsorption, solvent extraction, pervaporation and perstraction.

4.10.1 Distillation

Aqueous mixture of ABE is a complicated system, wherein water-organic azeotropes can form throughout the process of distillation. Aqueous *n*-butanol forms a heterogeneous azeotrope, and a simple two-column distillation system can be used without the need to add additional compounds to the mixture to be separated. In conventional distillation, to recover the products of ABE fermentation from the batch fermenter, the mixture of ABE is heated to 100 °C and is recovered as a vapour stream (Roffler et al. 1987). The vapour produced contains approximately 70% (w/w) water and 30% (w/w) acetone, butanol and ethanol. The condensate is then sequentially separated in a distillation column. In the first column operating at a pressure of 0.7 atm, about 99.5% by weight of acetone is removed, while the residual bottom product of the first column is sent to an ethanol column operating at a pressure of 0.3 atm. Ninety-five percent ethanol is obtained in this step. Thereafter, the bottom product and overhead stream of the ethanol column are redirected to a decanter where water and *n*-butanol are separated. The 9.5 wt% *n*-butanol aqueous phase is sent to the stripper and the *n*-butanol-rich phase (23 wt% water) is sent to the *n*-butanol stripper. In the *n*-butanol stripper, 99.7% by weight of *n*-butanol is obtained (Mariano et al. 2011b; Green 2011; Abdehagh et al. 2014). Currently, the most widely used method in the industry to extract ABE fermented products is distillation. However, this method has several drawbacks such as high cost of investment, low selectivity and high-energy consumption (Oudshoorn et al. 2009). Thus, other methods for extracting the product of fermentation are being studied.

4.10.2 Adsorption

Adsorption is one of the most useful methods for energy-efficient and selective butanol separation from fermented broth. In the adsorption process, butanol is selectively adsorbed to the surface of an appropriate adsorbent. Further, desorption of the product can be obtained in various ways, such as by raising the temperature or using displacers, etc. for getting solution with higher butanol concentrations. Before choosing a proper adsorbent, many factors must be taken into account such as adsorption capacity, selectivity to target product, ease of desorption, rate of adsorption and cost of adsorbent.

The contact time required between the solution containing adsorbent and the adsorbate directly affects the adsorption kinetics. Fast kinetics is required as it allows circulation of adsorbent to the fermentation system and reduces butanol concentration below toxic levels. Bulk adsorbent is required due to slow adsorption rate (Yang et al. 1994). Solid adsorbent, used for adsorption, determines the selectivity, adsorption capacity and ease of desorption. Various adsorbents such as mesoporous carbons (MPC) (Staggs et al. 2017; Levario et al. 2012), zeolites (Faisal et al. 2016; Saravanan et al. 2010; Oudshoorn et al. 2012) and resins (Abdehagh et al. 2015; Nielsen and Prather 2009; Wiehn et al. 2014) have been investigated for adsorption of ethanol and *n*-butanol. The adsorbent used in the adsorption method has a high selectivity for butanol, but has several problems in recovery of ABE fermentation products. One of them is the difficulty in desorbing organic compounds previously adsorbed on the adsorbent, and in order to realize this, various separation methods are required. Bacteria can also stick to the adsorbent and reduce adsorption efficiency, especially if the adsorbent is reused (Regdon et al. 1994, 1998; Takeuchi et al. 1995; Abdehagh et al. 2013; Saravanan et al. 2010).

4.10.3 Gas Stripping

This is one of the simple techniques used to separate butanol from fermentation broth. This method uses oxygen-free nitrogen or gases produced during fermentation. Hydrogen and carbon dioxide are purged through fermentation medium to remove acetone, ethanol and butanol. The stripper gas is passed through the fermenter and retains the solvent and water. The stripping gas is passed through a condenser and the vapour is moderately condensed. Then the reduced gas stream is passed through the fermenter for the next extraction cycle. Due to the toxicity of butanol to microbial cells, gas separation method improves the yield and also the productivity. It was observed the circulation of large amounts of gas does not inhibit the cell but can lead to the formation of foam (Ezeji et al. 2004, 2007; Dürre 2007; Zheng et al. 2009; Qureshi and Ezeji 2008). Gas stripping results depend a lot on gas flow rate, other elements in the broth and antifoaming agents used.

The gas stripping process has several advantages over other separation methods, such as simplicity, low operating cost and no reduction in efficiency due to contamination or contamination due to the presence of biomass. One of the drawbacks is that the small bubbles formed during gas stripping create an excessive amount of foam in the bioreactor. During this process, you need to add an antifoaming agent that can be toxic to the bacteria. This in turn reduces the overall productivity of ABE fermentation.

4.10.4 Liquid-Liquid Extraction

Solvent extraction is one of the popular methods for butanol or ABE removal from microbial fermentation broth. This method uses a solvent having low toxicity to microbes and which is insoluble in water blended with microbial fermentation broth to separate butanol selectively.

As the solvent is immiscible in fermentation broth, the organic phase can be separated easily in order to recuperate butanol as well as other soluble solvents. It is aspired that the extractant should separate butanol without considerably separating other substrates or nutrients (Ezeji et al. 2007; Dürre 2007). Till now solvents with higher distribution coefficients for butanol were investigated and found to be harmful to organisms producing butanol. Compared to other separation methods, it has a large extractant capacity and high selectivity for *n*-butanol/water separation. The main disadvantages of using direct extraction when extracting fermented products are the formation of emulsions and clogging of the extractant (Cichy et al. 2005; Groot et al. 1990). This can cause phase separation problems and consequently some contamination of the water stream with chemicals. Furthermore, in order to resolve some problems of slow mass transfer into solvent, cell growth inhibition and emulsion formation through agitation, it was suggested to carry out ABE fermentation in external columns (Kujawska et al. 2015). With the use of extraction columns, it is potential to utilize a solvent which has more partition coefficient though it is not biocompatible with a condition that common solubility of water and solvent is less.

4.10.5 Pervaporation

Pervaporation is used for situations where the solution is dilute in permeant molecules. In case of butanol separation from fermentation broth, the permeant (butanol) is present in very low concentrations. The feed (fermentation broth containing butanol) is passed through a hydrophobic membrane which will allow butanol to pass through it. On the downstream side (permeate side), butanol is recovered as a vapour using a sweeping gas or vacuum. This permeate vapour is further recovered by condensing in a cold trap. For pervaporation, heat of vaporization is supplied by setting the temperature of the feed or the vacuum applied on the permeate side (Ezeji et al. 2007; Qureshi and Ezeji 2008; Li et al. 2010; Qureshi and Blaschek 1999). The pervaporation process is especially suitable for separation of butanol from fermented broth due to its low-energy consumption, nontoxicity to microbes and no loss of nutrients and substrates (Li et al. 2010; Qureshi and Blaschek 1999; Qureshi et al. 1999).

Pervaporation is highly recommended for separating mixtures that form azeotropes and has almost same boiling point (Wang et al. 2009a). Solute/solvent separation in pervaporation does not depend on volatility, but on diffusivity and solubility. No product contamination, realistic price/performance ratio, high selectivity, modularity and low operating temperature are some of the advantages of pervaporation (Lipnizki et al. 2000). However, being a rate-controlled method, the penetration flux across the membrane is commonly less and huge membrane surface area is obligatory. The interaction of the permeate with the membrane determines a solubility of component, and the diffusion coefficient depends on the size, shape and mass of the molecule. Several factors such as low fluxes, membrane expansion and concentration polarization can limit pervaporation efficiency. Further, it is observed that by decreasing the membrane thickness, the flux increased but the selectivity decreased. Membrane pore size, support, porosity and surface roughness limit the reduction in film thickness (Wang et al. 2009a, b; Fouad and Feng 2008; Huang and Meagher 2001; Vrana et al. 1993).

4.11 Conclusions

Butanol production is hindered by solvent toxicity. The low concentration of butanol in the broth leads to high separation cost. Different methods such as distillation, adsorption, solvent extraction, gas stripping, pervaporation and perstraction can be used to separate butanol. However, they are not able to increase the butanol concentration in the fermentation broth. Extractive fermentation with non-ionic surfactant looks like a promising method as it improves the butanol concentration. In addition, the same surfactant separates the butanol. Overall, an economic analysis of these methods is needed to evaluate performance and decide upon the method.

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State-of-the-Art Technologies for Production of Biochemicals from Lignocellulosic Biomass

5

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Abbreviations

AFEX	Ammonia fibre expansion
BTMAC	Benzyltrimethylammonium
CELF	Co-solvent enhanced lignocellulosic fractionation
ChCl	Choline chloride
COSMO-RS	Conductor-like screening model for real solvents
DES	Deep eutectic solvent
DMSO	Dimethyl sulfoxide
EG	Ethylene glycol
FA	Formic acid
FDCA	Furandicarboxylic acid
GHG	Greenhouse gases
Gly	Glycerol
HBA	Hydrogen bond acceptors
HBD	Hydrogen bond donors
HMF	Hydroxymethylfurfural
IL	Ionic liquid
LA	Lactic acid
Lac	Laccase
LCB	Lignocellulosic biomass

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LiP	Lignin peroxidase
LVA	Levulinic acid
MEA	Monoethanolamine
MnP	Manganese peroxidase
NTP	Nonthermal plasma
OA	Oxalic acid
PB	*p*-Hydroxybenzoic acid
PBA	*p*-Hydroxybenzyl alcohol
PCA	*p*-Coumaric acid
PEG	Poly(ethylene) glycol
PET	Polyethylene terephthalate
PHA	*p*-Hydroxybenzaldehyde
SCFs	Supercritical fluids
SE	Steam explosion
TEBAC	Triethyl benzyl ammonium
XOS	Xylooligosaccharides

5.1 Introduction

At present, there is a great loss of natural resources, and high consumption of energy and chemicals due to the unstoppable employment of fossil fuels as the main resource for today's life (Takkellapati et al. 2018; Usmani et al. 2020). In this sense, in order to fulfil the unavoidable demand for energy and chemicals in the increasing world's population, up to 80% of the energy and 90% of the chemicals are intimately dependent on this nonrenewable resource, leading not only to its depletion but also to a great and negative impact in the environment due to harmful greenhouse gas (GHG) emissions and the production of toxic materials (Takkellapati et al. 2018). This challenging situation drives to seek for natural, more efficient, sustainable and renewable resources as a way to substitute the fossil derivatives (Usmani et al. 2020).

In this scenario, biorefineries play a key role in enabling a more sustainable and environmentally friendly world by converting biomass into valuable products (Solarte-Toro et al. 2018), building the bases of the bioeconomy and achieving the objectives established in the agenda 2030 (Solarte-Toro and Cardona Alzate 2021). Thus, biomass is considered the cheapest and most abundant source that can be employed for that aim, having a great potential for the production of biofuels and high-added-value products (Cho et al. 2020; Yiin et al. 2021). Specifically, lignocellulosic biomass (LCB)—including wood, agricultural residues and energy crops—is a carbon-neutral material with large reserves, reaching productions of up to 200 billion tons per year (Chen et al. 2022; Ashokkumar et al. 2022), which may facilitate the transition to a greener resource utilization (Thoresen et al. 2020) and the

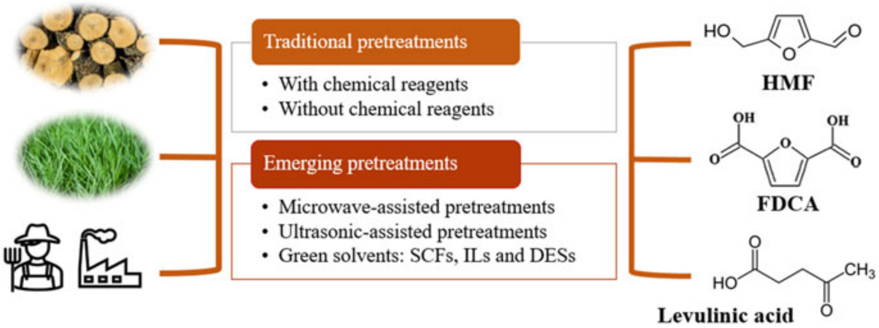

Fig. 5.1 Lignocellulosic biomass pretreatment methods and derived value-added products

mitigation of the carbon emissions and the global climatic issues derived (Usmani et al. 2020).

The LCB possesses a complex three-dimensional matrix structure, composed of a blend of cellulose fibres coated by hemicelluloses and lignin at different proportions depending on the species (Velvizhi et al. 2022). The valorization of LCB cues the production of biofuels and/or green platform chemicals not dependent on fossil resources, although their recalcitrant structure enables the straightforward obtainment of these useful end products. Hence, pretreatments are needed to promote the separation of the main constituents of LCB in separated streams, providing a more efficient valorization (Usmani et al. 2020). This process is a key step for the valorization of LCB since it may account for about 20% of the total cost in a lignocellulosic biorefinery (Fírvida et al. 2021; Saravanan et al. 2022). Although the fractionation processes can be performed using a wide variety of reagents (acid or alkali), the employment of green solvents has appeared as an interesting novel alternative in order to use available at large scale, cheap, recyclable, energy-efficient, low toxicity, biodegradable and, in general, stable solvents (Wang and Lee 2021).

In this sense, the selective fractionation of LCB would allow its conversion into green bio-based platform chemicals. With that aim, the transformation of simple sugars via chemical or biochemical pathways enables the obtainment of valuable building blocks such as those from the furanic-aliphatic family, i.e. hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid (FDCA) and levulinic acid (Rivas et al. 2021). These platform chemicals were highlighted by the US Department of Energy (DoE) as one of the most promising chemicals coming from biomass that may substitute a wide range of valuable products such as polymer materials, pharmaceutical derivatives, fuels or food products (Sajid et al. 2018; Davidson et al. 2021). Figure 5.1 shows a scheme with the different pretreatment methods described in this chapter and the value-added products discussed in it.

Hence, this book chapter aims to display a comprehensive overview of the fractionation processes and the high-added-value products that can be obtained within second-generation biorefinery schemes.

5.2 Composition and Sources of Lignocellulosic Biomass

Lignocellulosic biomass (LCB) is a renewable resource that includes a wide range of feedstock from forestry (hardwoods and softwoods), agricultural or industrial practices, energy crops, etc. (Cai et al. 2017; Rodionova et al. 2022). LCB is mainly constituted of two polymers with saccharide nature (cellulose and hemicelluloses) and one-third polymer with phenolic nature (lignin). Approximately 90% of dry matter in LCB consists of these three polymers (Nanda et al. 2014), whereas the rest comprises minor amounts of other components such as extractives and minerals.

Distribution of cellulose, hemicelluloses and lignin is not uniform within the cell walls of LCB. The quantity and structure of these polymers are variable depending on the species, tissues and maturity of the plant cell wall (Barakat et al. 2013). Thus, the organization of these nonuniform three-dimensional matrices depends on the source of LCB in a highly variable composition as shown in Table 5.1. Related to this structural complex is the following: (a) cellulose has a crystalline fibrous conformation that acts as the main constituent of the plant cell wall and is responsible for the complicated and recalcitrant nature of LCB (Mankar et al. 2021); (b) hemicelluloses are binding agents between lignin and cellulose and add rigidity to the entire biomass complex (Isikgor and Becer 2015; Mankar et al. 2021); and (c) lignin behaves like a glue, filling and strongly binding the gap between hemicelluloses and cellulose. The function of lignin in the LCB is to provide impermeability and resistance against oxidative and microbial attack. Thus, LCB has evolved to resist degradation, thanks to the hydrophobicity of lignin, the recalcitrance of cellulose and the encapsulation of cellulose by the lignin-hemicelluloses complex (Isikgor and Becer 2015).

Cellulose is a linear polymer with around 100,000 average molecular weight and a molecular formula of $(C_6H_{10}O_5)_n$, constituted by D-anhydroglucopyranose units (glucose) bonded by β-(1 → 4) glycosidic links, which form the disaccharide cellobiose. Hydroxyl groups (OH) in the structure of D-anhydroglucopyranose, the primary (C6) and the secondary (C2 and C3), have different polarities that confer them the possibility to participate in intermolecular and intramolecular hydrogen bond interactions (Batista Meneses et al. 2022). In fact, cellulose contains both crystalline (organized) and amorphous (not well organized) regions alternating with each other as microfibrils; this crystalline region is resistant to degradation and the amorphous region is easy to degrade. Because of the fibrous nature and strong hydrogen bonding, cellulose is found to be insoluble in the majority of the solvents (Nanda et al. 2014; Kumar et al. 2016).

Hemicelluloses are branched heteropolymers, mainly constituted by different five and six carbon saccharide units, pentoses (xylose, arabinose) and hexoses (mannose, glucose, galactose) (Bhatia et al. 2020), interlinked via β-1,4 glycosidic linkages. Hemicelluloses also present substituents as acetyl and uronyl groups. Hemicelluloses, unlike cellulose, have a random and amorphous structure, which is composed of several heteropolymers including xylan, galactomannan, glucuronoxylan, arabinoxylan, glucomannan and xyloglucan. Hemicelluloses in

Table 5.1 Composition of different lignocellulosic biomasses expressed as % on dry basis

				Hemicellulose									
Biomass	Acid-soluble lignin	Klason lignin	Cellulose	Total^{a}	Xylan	Galactan	Arabinan	Mannan	Acetyl groups	Uronic groups	Extractives	Ashes	References
Hardwood													
Birch wood (*Betula alba*)		24.2	39.1	32.4	21.5	1.4	0.4	2.1	4.6	2.4	2.8	0.4	Rivas et al. (2017)
Silver birch (*Betula pendula* L.)	4.7	17.7	43.1	26.9	20.9	0.7		1.8	3.5		1.7		Borrega et al. (2011)
Poplar wood	3.2	22.8	41.09	21.0	17.2	0.9	0.6	2.2					Zhou et al. (2021)
Eucalyptus globulus		27.7	44.7	20.1	16.0		1.1		3.0		2.0		Kelbert et al. (2015)
Paulownia elongata × fortunei		20.9	42.2	28.2	17.0		0.8		3.8	6.6	9.5	0.3	del Río et al. (2020)
Sugar maple (*Acer saccharum*)	3.8	22.3	45.5	24.0	15.1	2.1	0.6	2.4	3.8		3.2		Mittal et al. (2009)
Aspen (*Populus tremuloides*)	2.9	20.0	47.5	23.5	14.7	1.2	1.3	2.6	3.7				Mittal et al. (2009)
Poplar (pruning)	14.7		40.5	22.5	14.1	1.0	1.5	3.8	2.1		18.9	2.5	Nitsos et al. (2016)
Softwood													
Pinewood	0.6	26.9	40.5	20.3	9.08 (as arabinoglucuronoxylan)	1.9	0.6	15.79 (galactoglucomannan)			3.0	0.21	Ståhl et al. (2018)
Pinus pinaster wood		34.1	36.7	20.2	4.7	3.2	1.3	9.4	1.2	3.9	4.7	0.3	Rivas et al. (2014)

(continued)

Table 5.1 (continued)

Biomass	Acid-soluble lignin	Klason lignin	Cellulose	Hemicellulose							Extractives	Ashes	References
				Total[a]	Xylan	Galactan	Arabinan	Mannan	Acetyl groups	Uronic groups			
Pinewood (sawdust)	23.9		37.9	19.8		7.2	2.0	9.6	1.1		18.3	0.06	Nitsos et al. (2016)
Spruce	5.0	26.8	44.5	18.3				18.3			5.1	0.28	Pielhop et al. (2015)
Grasses/herbaceous plants													
Miscanthus	0.5	26.0	45.0	25.4	22.5	0.4	2.3	0.2			1.0	2.8	el Hage et al. (2010)
Miscanthus		24.5	40.7	30.5	19.1	2.0	2.5	0.9	3.0	3.0	2.2		Rivas et al. (2019)
Arundo donax		23.0	35.2	28.5	18.2		0.8		3.8	5.5	9.1	3.1	Caparrós et al. (2007)
Switch grass	24.1		42.6	27.3	23.1	0.5	1.5	0.3	1.9		2.0	4	Morales et al. (2021)
Agricultural/agroindustrial wastes													
Vine shoots	3.2	22.2	31.2	19.3	11.7	2.6	0.9	0.9	3.2		3.9	3.4	Rivas et al. (2021)
Vineyard (pruning)	25.3		33.8	18.1	13.2	1.6	0.3		3.0		16.8	3.1	Nitsos et al. (2016)
Rice straw		14.4	40.9	23.9	20.5		3.4				18.5	10.6	Moniz et al. (2014)
Hazelnut shell		38.8	26.3	31.5	22.8		0.3		4.4	4.0		0.6	Pérez-Armada et al. (2019)
Brewers' spent grain		20.4	16.5	26.3	16.8		8.8		0.8			2.1	Michelin and Teixeira (2016)

Corn husk		15.5	32.5	30.4	21.1		6.3		3.0			2.0	Michelin and Teixeira (2016)
Corncob		18.5	35.8	30.7	22.4		4.9		3.5			0.8	Michelin and Teixeira (2016)
Wheat straw	1.0	16.4	34.5	38.6	17.9	1.1	1.7	0.7	14.9	2.3	1.6	2.7	Fu et al. (2010)
Luffa sponge		14.2	55.0	15.4	13.6		1.7		0.2			1.1	Michelin and Teixeira (2016)
Triticale straw	1.1	14.0	32.2	26.6	19.3	1.1	2.3	0.4	2.0	1.5	17.6	4.1	Fu et al. (2010)
Flax shives	0.8	22.4	26.1	21.6	11.8	1.5	0.6	1.3	2.8	3.6	13.5	10.0	Fu et al. (2010)
Bamboo	25.1		48.4	21.8	20.3	0.7	0.8						Yuan and Wen (2017)
Rice husks	0.7	22.7	35.6	15.0	13.6		1.4				6.6	15.7	Kim et al. (2021)
Sunflower hulls	25.3		34.1	25.2	21.2	3.5	0.5				13.2	0.4	Kamireddy et al. (2014)
Sorghum bagasse	13.0		42.6	26.2	22.9		3.3				11.3	3.0	Banerji et al. (2013)
Sugarcane bagasse	2.8	21.7	40.5		22.3	1.4	3.1						Zhang et al. (2018)

[a] Total content of hemicelluloses, as the sum of xylan, galactan, arabinan, mannan, acetyl and uronic groups, in case they were reported

woods differ in composition, since in hardwoods they are mainly constituted by xylan and in softwoods by glucomannans.

Lignin is a three-dimensional polymer made up by aromatic components, unlike the carbon backbones that constitute cellulose and hemicelluloses (Batista Meneses et al. 2022). This complex structure contains methoxyl, phenolic hydroxyl and some terminal aldehyde groups in the side chains. The three monolignols are *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The aromatic rings, which are abundantly present in lignin in the form of the basic phenylpropane units, are responsible for the antioxidant properties. The phenylpropane units are linked by β-O-4, β-5 and β–β′ bonds (Zhang and Naebe 2021). Lignin contains three types of phenylpropanoids, *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), and their nature and quantity are variable according to species, tissues, maturity and spatial localization in the cell. As a general trend, the lignin content is lower in hardwoods than in softwoods. In contrast, hardwoods exhibit a higher amount of holocellulose and extractives than softwoods (Nanda et al. 2014). Related to the particularities of lignin from different LCB, in softwoods it mainly consists of guaiacyl units and minor percentage of *p*-hydroxyphenyl units (HG-lignin), while in hardwoods it is mainly made up by guaiacyl and syringyl units (GS-lignin) (Lourenço and Pereira 2018). Nonwoody LCB contains all the three units; thus, grass lignin belongs to HGS-lignin (Rodionova et al. 2022). It should be noted that H units in grasses are the lowest among the three lignin units, but their proportion is much higher than in hardwood and softwood.

Extractives are nonstructural components of LCB, which can be soluble in water or neutral organic solvents. They include biopolymers such as steroids, terpenoids, resin acids, lipid fats, waxes and phenolic constituents as stilbenes, flavonoids, tannins or lignans (Kumar et al. 2016). Elemental composition in LCB refers to major elements, such as K, Na, Mg, Ca or Si, and minor ones as S, Al, Fe, P or Mn; they can be found in less than 1% by weight in wood or shells, while in husks and straws, they reach up to 25% by weight (Nanda et al. 2014; Kumar et al. 2016).

5.3 Pretreatment Methods

Lignocellulosic pretreatment methods can be classified into traditional and emerging pretreatment technologies (Chen et al. 2022). Traditional methods can be divided into two types depending on whether or not they use chemical reagents. In addition, some traditional pretreatments can be described as fundamental methods, which are necessary as a previous stage to obtain biomass materials that meet the production requirements of the industry (Wang 2021).

5.3.1 Fundamental Pretreatment Methods

Fundamental pretreatment methods include washing, drying and mechanical pretreatment, which are necessary to exclude impurities and obtain shape uniformity

(Wang 2021). Mechanical pretreatment consists of applying shear or compression forces to reduce the size of the raw material (Rezania et al. 2020). The commonly used mechanical pretreatments include grinding, milling and chipping. Chipping is performed during the collection of biomasses to get particles of 10–30 mm, while after milling or grinding, the size achieved is between 0.2 and 2 mm (Mankar et al. 2021). Milling and grinding decrease the biomass crystallinity and reduce polymerization degree improving the enzymatic digestibility (Dalena et al. 2018; Raynie et al. 2020).

Various types of milling instruments have been used so far, such as hammer milling, disk milling, ball milling and vibratory milling (Rezania et al. 2020). The more effective instrument reported is vibrating balls (Raynie et al. 2020). The main disadvantage of this method is that high-power consumption is usually associated with low efficiency. For this reason, the grinding process accounts for a significant part of the operating costs in the whole lignocellulosic biomass pretreatment process (Rezania et al. 2020).

5.3.2 Traditional Pretreatment Methods

5.3.2.1 Pretreatments with Chemical Reagents

Traditional chemical pretreatments include the use of different reagents such as acids, alkalis, oxidizing agents and organic solvents. As shown in Table 5.2, these methods are still being investigated as an alternative to the pretreatment of lignocellulosic biomass.

Acid Pretreatment

Acidic hydrolysis is a traditional pretreatment that has been used to solubilize hemicellulose, precipitate lignin and make cellulose more accessible for enzymatic hydrolysis. Acid reagents can destroy the glycosidic bonds and break all polysaccharide-lignin linkages achieving the recovery of most monomeric sugars (Raynie et al. 2020; Rezania et al. 2020). The liquid phase rich in soluble sugars is usually submitted to a detoxification treatment before the subsequent fermentation. The commonly used reagents include organic acids such as acetic acid and inorganic acids like sulphuric and phosphoric acid (Rezania et al. 2020; Chen et al. 2022) The key parameters in acid pretreatment are temperature, residence time, acid concentration and solid loading. Dilute acid pretreatment reduces acid consumption but requires higher temperatures to achieve a reasonable yield of glucose from cellulose (Rezania et al. 2020). LCB pretreatment is usually applied within the acid concentration of 0–5% (w/w) under 120–215 °C for 1–120 min. The overall fermentable sugar and solid recovery can reach 60–75% and 3565%, respectively (Chen et al. 2022). These variations in the recovery of sugars may be related to the different operating conditions and the type of lignocellulosic materials. Gonzales et al. (2016) evaluated the pretreatment of different biomasses (empty palm fruit bunch, rice husk and pine tree wood pellets) with 5% (v/v) dilute sulphuric acid at 121 °C for 30–90 min, and the sugar recovery yield ranged between 39.7 and 60.7%. Moreover,

Table 5.2 Recent studies of pretreatments of lignocellulosic biomass with chemical reagents: acid, alkaline, oxidative and organosolv pretreatments

Pretreatment	Biomass	Results	Reference
Acid (5% (v/v) H_2SO_4 at 10% (w/v) solid/liquid ratio and 121 °C for 30–90 min)	Agricultural wastes and pine tree wood	When the combined severity factor was at or over 2.01, hydrogen fermentation decreased due to severe 5-HMF and furfural production	Gonzales et al. (2016)
Acid (2.4% H_2SO_4 at 130 °C for 84 min)	Olive tree biomass	Up to 71% solubilization of hemicellulosic sugars achieved under optimized conditions	Martínez-Patiño et al. (2017)
Acid (0.05–0.4% (w/v) H_2SO_4 at 60 °C for 30 min and 180 °C for 40 min)	Wheat straw	A natural surfactant (10 g/L humic acid) was added during acid pretreatment to improve enzymatic hydrolysis efficiency, achieving a yield of 92.9%	Tang et al. (2021)
Acid (7.5% (w/v) gluconic acid at 168 °C for 35 min)	Sorghum straw	The maximum xylooligosaccharide (XOS) yield of 50.3% was achieved under optimum conditions	Dai et al. (2022)
Acid (5% (w/v) acetic acid at 170 °C for 30 min)	Poplar sawdust	A xylooligosaccharide yield of 31.6% was achieved after acetic acid hydrolysis, and a global yield of 36.5% when this process is followed by hydrogen peroxide-acetic acid delignification	Ying et al. (2022)
Alkaline (5% (w/v) NaOH at 120 °C for 30 min)	Cocoa pod husk	Cellulose content increased to 57% after alkaline pretreatment and enzymatic yields of 98.75% were achieved	Hernández-Mendoza et al. (2021)
Alkaline (7.2% NaOH, 80 °C for 30 min)	Chestnut shell	Under the optimal conditions, 92.6% of delignification was achieved and 60.5% of glucan was recovered	Morales et al. (2018)
Alkaline (5% (w/v) NaOH, 121 °C for 40 min)	Coconut husk fibres	20.15% and 31.17% of lignin were removed and an increase in cellulose content of 17% and 20% was achieved for mature and young coconut husk, respectively	Din et al. (2021)
Alkaline (2% NaOH, 105 °C for 10 min)	Barley straw	Under optimal conditions, 84.8% of delignification and 79.5% of hemicellulose removal were achieved	Haque et al. (2012)
Alkaline (2% NaOH at 124 °C for 105 min)	Vine pruning	67.7% of the lignin was removed and the solid obtained had a 69.4% of glucan	Gullón et al. (2017)

(continued)

Table 5.2 (continued)

Pretreatment	Biomass	Results	Reference
Oxidative (20–80 mg H_2O_2/g biomass)	Wheat straw	35.2% and 58.1% of residual lignin were removed with 20 and 40 mg H_2O_2/g biomass for 12 h, respectively. Using 80 mg H_2O_2/g biomass only led to an additional 1.8% lignin removal when reaction time is increased from 6 to 15 h	Yuan et al. (2018)
Oxidative (8.87 g O_3/g biomass)	Wheat straw	The glucose yield on enzymatic hydrolysis increased five times when the treatment time is extended from 2 h to 6 h	Kumar et al. (2020)
Oxidative (50–100 mg O_3/g biomass)	Sugarcane bagasse	Glucose yields of 22.81% and 45.09% were achieved on enzymatic hydrolysis with ozone doses of 50 and 100 mg O_3/g biomass, respectively	Osuna-Laveaga et al. (2020)
Acid oxidative (acetic acid + H_2O_2 (1:1;v/v) at 80 °C for 2 h)	Agricultural wastes and eucalyptus bark	45–75% of lignin was removed and from 2.1- to 20.8-fold the saccharification process was improved for three lignocellulosic raw materials	Mota et al. (2019)
Alkaline oxidative (2% (v/v) NaOH + 2% (v/v) H_2O_2 at 60 °C for 5 h)	Sugarcane bagasse	Cellulose and holocellulose content increase up to 78% and 90%, respectively, after alkali hydrogen peroxide pretreatment with NaOH	Meléndez-Hernández et al. (2021)
Organosolv (50% EtOH at 200 °C for 1 h)	*Paulownia* wood	65% of the lignin was removed	del Río et al. (2020)
Organosolv (60% EtOH + *n*-propylamine at 140 °C for 40 min)	Corn stover	The combination of organic solvents increases lignin removal by 82% compared to a single ethanol treatment	Tang et al. (2017)
Organosolv (70% (w/v) industrial glycerol at 200–240 °C for 1–5 h)	Sugarcane bagasse	Approximately 70% of lignin and hemicellulose are removed from the biomass, producing extraordinarily few fermentation inhibitors	Sun et al. (2016)
Acid organosolv (25% (v/v) butanol + 0.5% H_2SO_4 at 200 °C for 1 h)	Sorghum bagasse	Under optimal high cellulose and low lignin content were achieved (84.9% and 15.3%, respectively)	Teramura et al. (2018)
Acid organosolv (EtOH + H_2SO_4)	Poplar sawdust	Lignin removal was enhanced from 22.23% to 59.87% when acid concentration was raised by 10 to 20 mM	Chu et al. (2021)

the increase of the reaction time from 30 to 90 min provoked a three- to fourfold increase in the concentration of furfural and 5-hydroxymethylfurfural (HMF). The dilute acid pretreatment has been extensively optimized using experimental designs to find the optimal conditions that lead to a high solubilization of sugars (Gonzales et al. 2016). For example, Martínez-Patiño et al. (2017) reported solubilization of hemicellulosic sugars of 71% under 2.4% H_2SO_4, 84 min and 130 °C, when the acid pretreatment was applied to olive tree biomass (Martínez-Patiño et al. 2017).

The main advantage of acidic hydrolysis is the high delignification efficiency (>50%) and removal of hemicellulose (Raynie et al. 2020). On the other hand, the equipment corrosion, the high cost of acid recovery and the formation of inhibitors such as furfural and HMF are some of the drawbacks of this process. Using high concentrated acids can also damage the lignin structure. It is worth knowing that acid pretreatment processes have improved in economic and environmental aspects (Raynie et al. 2020; Rezania et al. 2020; Chen et al. 2022).

Alkaline Pretreatment

Alkaline hydrolysis involves solvation and saponification reactions achieving the cleave of the ester linkages between the hemicellulose with the lignin and cellulose. This method reduces cellulose crystallinity and dissolves lignin and part of the hemicellulose, increasing the accessibility of enzymes (Raynie et al. 2020). The commonly used reagents are NaOH, KOH, NH_3-H_2O, $Ca(OH)_2$, etc. (Chen et al. 2022). $Ca(OH)_2$ is a cheap and safe chemical that can be easily recovered and recycled by washing the biomass with water which can then be saturated with carbon dioxide to form a calcium carbonate precipitate. Therefore, it is preferred to select $Ca(OH)_2$ for lignocellulose pretreatment in the industry (Wang 2021).

Alkaline pretreatment enables the extraction of lignin selectively without losing reducing sugar and carbohydrates and removing acetyl groups in hemicellulose structure (Raynie et al. 2020), enhancing porosity and surface area of biomass and therefore improving enzymatic hydrolysis (Rezania et al. 2020). Besides, it can be applied for a wider temperature range achieving versatile performance even at low temperatures (Chen et al. 2022). The main disadvantage of this method is the longer reaction times compared to other pretreatments (Rezania et al. 2020). Alkaline hydrolysis can also reduce delignification efficiency due to the condensation and redistribution of lignin and make cellulose denser and thermodynamically more stable than its native structure (Raynie et al. 2020).

LCB pretreatment is typically applied within alkali concentration of 2–7% and under 100–200 °C for a short contact time (10–90 min), or a concentration range of 0–2% at 50–100 °C for several hours (Chen et al. 2022). For example, when chestnut shells are treated with 7.2% NaOH at 80 °C for 30 min, a delignification of 92.6% was obtained (Morales et al. 2018). In another study, the alkali treatment of barley straw under optimal conditions (2% NaOH, 10 min and 105 °C) led to maximum lignin and hemicellulose removal of 84.8% and 79.5%, respectively (Haque et al. 2012). Gullón et al. (2017) studied a sequential fractionation of vine pruning based on the first stage of autohydrolysis at 201 °C, to recover hemicellulosic sugars, followed by a delignification of the autohydrolysed solid using 2% NaOH, 124 °C and 105 min. These conditions allowed the removal of 67.7% of the lignin, obtaining a solid with 69.4% of glucan (Gullón et al. 2017).

Oxidative Pretreatment

Oxidative pretreatment involves different chemical reactions such as electrophilic reaction, site chain dislocation and aliphatic-organic bond cleavages. Some common reagents are solutions of per-acids, e.g. hydrogen peroxide, and ozone (Raynie et al. 2020).

The decomposition of hydrogen peroxide into OH^- and O^{2-} contributes to the cleavage of alkyl propylene ether bonds and aromatic nuclei destroying lignin structure without releasing inhibitory by-products. Hydrogen peroxide under alkali conditions is unstable and is decomposed in the presence of transition metals (Chen et al. 2022). Overall, lignin removal rises with increasing H_2O_2 charge and reaction time (Yuan et al. 2018). For example, when treating wheat straw (previously extracted with NaOH) with H_2O_2 loads of 20 and 40 mg H_2O_2/g biomass for 12 h, removal of the residual lignin of about 35.2% and 58.1% was achieved, respectively (Yuan et al. 2018). However, in this same work, the authors reported that when using a high H_2O_2 charge (80 mg H_2O_2/g biomass), the increased reaction time from 6 h to 15 h only led to an additional 1.8% lignin removal.

Ozone can selectively remove lignin and decompose hemicellulose by breaking down the hydrogen bonds (Raynie et al. 2020; Chen et al. 2022). Due to ozonolysis being performed at room temperature, this method does not modify cellulose structure and any toxic by-product is released during the process. The major disadvantage of this method is the high ozone requirements, which makes it more expensive than other pretreatments (Raynie et al. 2020). Several authors have stated that ozone dose, treatment time and pH are key parameters that affect lignin removal (Kumar et al. 2020; Osuna-Laveaga et al. 2020; Chen et al. 2022). Thus, Kumar et al. (2020) applied 8.87 g ozone/g to treat wheat straw and observed that when the treatment time is extended from 2 to 6 h, the glucose yield increased five times (Kumar et al. 2020). Osuna-Laveaga et al. (2020) evaluated the effect of ozone dose on enzymatic hydrolysis of sugarcane bagasse and reported the highest glucose yields for the highest ozone dose (45.09% using 100 mg O_3/g biomass vs 22.81% using 50 mg O_3/g biomass) (Osuna-Laveaga et al. 2020).

Organosolv Pretreatment

The organic solvent pretreatment is employed to degrade lignin and hemicellulose and promote enzymatic hydrolysis of cellulose. Organic solvents can break the α-O-aryl bond and 4-*O*-methyl glucuronic acid ester bonds in lignocellulose (Chen et al. 2022). A wide range of organic solvents has been used for the pretreatment of LCB such as methanol, ethanol, tetrahydrofuran, acetone, ethylene glycol, formaldehyde, dioxane and amines with or without catalyst. Some organic acids and bases are also employed as reagents (Mankar et al. 2021; Chen et al. 2022). The main advantages of this pretreatment are the high efficiency in the fractionation of lignocellulose biomass in cellulose, hemicellulose and lignin with high purity and the easy recovery and reuse of the solvents (Rezania et al. 2020). In some cases, the organic solvents are too expensive, so it is necessary to recover as much as possible, making the process energy-intensive and costly. Besides, the high flammability and volatility of the solvents lead the process to be carried out under controlled conditions (Mankar et al. 2021).

Typically, organosolv pretreatment is performed in the range of 150–220 °C, and below 60 °C may result in lower lignin removal efficiency (Chen et al. 2022).

For instance, *Paulownia* wood treated with 50% ethanol, at 200 °C for 1 h, resulted in a lignin removal of 65%, and when the treatment time was extended to 4 h, only an increase of 6% in lignin removal was achieved (del Río et al. 2020). Chu et al. (2021) evaluated the effect of the addition of an acid catalyst (H_2SO_4) in the ethanol organosolv pretreatment of poplar sawdust. The authors found that when acid concentration was raised from 10 to 20 mM, lignin removal was enhanced from 22.23% to 59.87% (Chu et al. 2021). The combination of different organic solvents can improve the lignin removal efficiency. For example, the mixture of *n*-propylamine (10 mmol/g dry biomass) and 60% ethanol used to treat corn stover (at 140 °C for 40 min) increased lignin removal by 82% compared to single ethanol treatment (Tang et al. 2017).

Ammonia Fibre Expansion (AFEX)

The ammonia fibre expansion (AFEX) pretreatment method is similar to that of the steam explosion pretreatment (Rezania et al. 2020). The process involves anhydrous ammonia (1:1) at mild temperatures of 60–170 °C and high pressures between 15 and 30 bar for a short time (5–60 min) (Mankar et al. 2021).

Due to ammonia and oxyhydrogen ions released from liquid ammonia at high pressure, the ester and ether bonds between lignin and hemicellulose are broken (Chen et al. 2022). Besides, hemicellulose is degraded into oligomeric sugar and is deacetylated, while cellulose crystallinity is reduced by the rearrangement of the hydrogen bonding within its fibres (Rezania et al. 2020; Mankar et al. 2021).

The AFEX method achieves higher accessibility of enzymes for hydrolysis with negligible production of inhibitors, mild temperatures, short residence times and high retention of cellulose/hemicellulose content. The main drawbacks are the high capital cost of the equipment to withstand the high pressure involved in the process, the energy requirements for ammonia recycling and the high cost of this reagent (Rezania et al. 2020; Mankar et al. 2021). In addition, it has been reported that the method is less effective for hardwoods and softwoods with high lignin contents (e.g. 25–30%) compared with the high efficiencies obtained with agricultural residues and herbaceous crops (Zhao et al. 2017; Li et al. 2022).

Kamm et al. (2017) used aqueous ammonia (25% w/v) instead of liquid ammonia to test its influence on sugar concentration and its enzymatic yield. They concluded that conversions of more than 90% can be reached in both cases. Despite modified AFEX pretreatment needing higher temperature, inhibitors were neither produced (Kamm et al. 2017). Zhao et al. (2017) proposed hydrogen peroxide presoaking prior to ammonia fibre expansion (H-AFEX) to treat *Miscanthus*. The authors reported that the addition of 0.5% H_2O_2 (g/g dry biomass) led to an increase in glucose yield of about 10% (Zhao et al. 2017). Other examples of AFEX pretreatment are listed in Table 5.3.

Table 5.3 Recent studies of lignocellulosic biomass pretreatment using autohydrolysis, steam explosion (SE) and ammonia fibre expansion (AFEX)

Pretreatment	Biomass	Results	Reference
Hydrothermal	*Paulownia* wood	The liquor obtained at 205 °C presented a high concentration of xylooligosaccharides (21.33 g/L), and glucose yields close to 70% were obtained by enzymatic hydrolysis in the solid	del Río et al. (2020)
Hydrothermal	Vine shoots	83.1% of xylan was converted into xylooligosaccharides (corresponding to 12.2 g/L) performing at 200 °C, but the solid presented low enzymatic susceptibility	Gullón et al. (2017)
Hydrothermal	Poplar wood	Performing non-isothermal autohydrolysis at 210 °C with a solid ratio of 6 kg/kg, a liquor with a concentration of 28.71 g/L of oligosaccharides was obtained	Rivas et al. (2020)
Hydrothermal	*Eucalyptus globulus* bark	Maximum oligosaccharide concentration (17.5 g/L) was achieved under a non-isothermal regime at a severity of 3.69, corresponding to hemicellulose recovery of 77.03%	Gomes et al. (2021)
Hydrothermal	Elephant grass	4.09 g/kg of xylooligosaccharides are recovered in the liquor at 180 °C for 1 h	Mihiretu et al. (2017)
Steam explosion	*Eucalyptus grandis*	76 kg of xylooligosaccharides per ton of sawdust were obtained at 200 °C for 10 min. High ethanol concentrations (75.6 g/L) and yields (259 L/ton of dry raw sawdust) were obtained by SSF	Rochón et al. (2022)
Steam explosion	Barley straw	SE (180 °C for 30 min) to barley straw to obtain xylooligosaccharides, fermentable sugars and lignin	Álvarez et al. (2021)
Steam explosion and hydrothermal	Olive tree pruning biomass	80.4% of sugar recovery was achieved with the steam explosion at 220 °C, slightly lower than the 92% obtained with hydrothermal pretreatment at 180 °C	Romero-García et al. (2022)
Steam explosion +2.2% (v/v) H_2SO_4	Agricultural banana wastes	An overall glucose yield of 91.0% was achieved at 177 °C for 5 min with 2.2% (v/v) H_2SO_4 as catalyst	Guerrero et al. (2017)
Steam explosion + 0.25% (w/w) H_2SO_4	*Aucoumea klaineana*	Using optimum conditions (210 °C, 5 min), 112 kg of ethanol and 82 kg of lignin of high purity can be recovered from 1 ton of wood	Besserer et al. (2022)
AFEX	Wheat straw	Up to 90% of total sugar conversion is achieved with aqueous ammonia (25% (w/v))	Kamm et al. (2017)
AFEX	Corn stover	Biogas production of anaerobic co-digestion gets enhanced with AFEX treatment	Rojas-Sossa et al. (2019)

(continued)

Table 5.3 (continued)

Pretreatment	Biomass	Results	Reference
AFEX	Sugarcane bagasse	Methane yields of 292–299 (L CH_4)/(kg VS) and 57–59% (v/v) biogas methane content were achieved	Mokomele et al. (2019)
H-AFEX	*Miscanthus*	The addition of 0.5% H_2O_2 (g/g dry biomass) led to an increase in glucose yield of about 10%	Zhao et al. (2017)
H-AFEX	Corn stalk	Glucan and xylan conversions were 88.9% and 86.3% at 130 °C and 0.7 (w/w) H_2O_2 loading, resulting in a total sugar yield of 495.5 g/g dry corn stalk	Zhao et al. (2016)

5.3.2.2 Pretreatments Without Chemical Reagents

Traditional methods that avoid chemical reagents include those pretreatments that only require water as reaction media, such as hydrothermal, steam explosion and biological pretreatments. Some recent studies are listed in Table 5.3, which also includes examples of AFEX pretreatment to compare it with the steam explosion.

Hydrothermal Pretreatment

Hydrothermal pretreatment (also known as liquid hot water, autohydrolysis and hydrothermolysis) involves water with a solid loading rate of 2–30% w/w at temperatures of 160–240 °C and pressures between 6.2 and 33 bar, respectively, during 0–50 min (Rezania et al. 2020; del Río et al. 2022). The high temperatures produce the autoionization of water into hydronium ions (H_3O^+) that interact with the oxygen of the glycosidic bonds and allow the release of hemicellulosic compounds, such as acetyl groups in the form of acetic acid. In turn, this organic acid acts as a mild catalyst that promotes the solubilization of other hemicellulose-derived compounds (Raynie et al. 2020; del Río et al. 2022).

The high selectivity for hemicellulose solubilization as oligosaccharides, which are high value-added products, can make lignocellulosic biorefineries more competitive (del Río et al. 2022). In addition, this method does not use corrosive, expensive and toxic chemical reagents (Bhatia et al. 2020).

Several research works have highlighted the suitability of autohydrolysis as the first stage of a biorefinery, since it enables the selective solubilization of the hemicellulosic fraction in the liquid phase, remaining the cellulose and lignin almost unaltered in the solid fraction (del Río et al. 2020) In this context, Gullón et al. (2017) studied the non-isothermal autohydrolysis treatment of vine shoots to obtain xylooligosaccharides (XOS). When the operation was performed at 200 °C, 83.1% of the xylan was converted into XOS (corresponding to 12.2 g/L). However, the solid obtained under these conditions presented a low enzymatic susceptibility (obtaining 49.5% of total glucan hydrolysis after 96 h) (Gullón et al. 2017). In another study, the hydrothermal processing at 205 °C of *Paulownia* wood allowed obtaining a solution with a high concentration of XOS (21.33 g/L) and a solid with good enzymatic susceptibility (with a glucose yield close to 70%) (del Río et al. 2020).

Despite the advantages, some remaining challenges still must be overcome, such as the high energy and water consumption, the low concentration of sugars, the fermentation inhibitors and the lack of literature that collects studies for the co-production of biofuels and value-added compounds within a multiproduct biorefinery approach (Rezania et al. 2020; del Río et al. 2022).

Steam Explosion Pretreatment

Steam explosion (SE) is an effective, environmental-friendly and industrially scalable pretreatment method that involves two stages: autohydrolysis and instantaneous decompression stage. As described before, hemicellulose is hydrolysed by acetic acid derived from acetyl groups and other acids during the hydrothermal stage. At the same time, cellulose crystallinity is reduced, and lignin depolymerized. The sudden release of pressure in the second stage destroys the structure of fibrous materials, breaking the glycosidic and hydrogen bonds, thereby modifying the biomass both physically and chemically (Yu et al. 2022a).

Steam explosion can be considered an economical approach, due to the process efficiency and the lack of chemicals required (Yu et al. 2022a). Owing to these advantages, it is one of the most used methods to remove hemicellulose and lignin with efficacy. The incomplete lignin removal and the generation of the inhibitory compound are some drawbacks of this method (Rezania et al. 2020; Chen et al. 2022).

SE pretreatment is applied with hot steam at 180–240 °C and high pressure of 1–3.5 MPa, followed by an explosive decompression to atmospheric pressure. Other key parameters are residence time and the selection of catalysts (Yu et al. 2022a). Recently, Álvarez et al. 2021 applied SE (180 °C for 30 min) to barley straw to obtain XOS, fermentable sugars and lignin (Álvarez et al. 2021). Romero-García et al. (2022) compared autohydrolysis and SE of olive tree pruning biomass, and the results showed that both treatments performed similarly, although the former yielded the highest overall sugar recovery, 92%, at lower operation temperature (180 °C) versus 80.4% for SE at 220 °C (Romero-García et al. 2022).

Biological Pretreatment

Biological pretreatment presents various advantages compared with physical and chemical pretreatments such as (1) low operational cost, (2) no need of chemical reagents and (3) lower energy requirements. In addition, another important benefit of biological pretreatment is that compounds that affect subsequent hydrolysis and fermentation are not generated (Sindhu et al. 2016; Chen et al. 2022). However, long incubation times and the loss of carbohydrates are the main disadvantages of this pretreatment (Martínez-Patiño et al. 2018). Biological pretreatment is performed using bacteria, fungi or enzymes to help degrade lignin from LCB (Chen et al. 2022). Fungi such as white-rot fungi, brown-rot fungi and soft-rot fungi are the most effective microorganisms to break down lignin due to the secretion of several oxidative enzymes, namely, lignin peroxidase (LiP), manganese peroxidase

(MnP), laccase (Lac) and versatile peroxidase (VP) (Martínez-Patiño et al. 2018). For example, the treatment of poplar wood using white-rot basidiomycete *Peniophora incarnata* under room temperature for 7 days led to a 70% lignin removal. Enzymatic hydrolysis showed that the maximum yield of glucose reached 33.4% that was improved sevenfold relative to the untreated group (Ma et al. 2021). Martínez-Patiño et al. (2018) screened seven white-rot fungi to treat olive tree biomass. In this study, the authors studied the changes in biomass composition, secretion of ligninolytic enzymes and enzymatic hydrolysis efficiency after 15, 30 and 45 days of solid-state fermentations. The results indicated that the treatment with *Irpex lacteus* for 45 days improved enzyme susceptibility compared with the non-inoculated sample (31% vs 13.5%) (Martínez-Patiño et al. 2018). Xu et al. (2018) applied *Bacillus subtilis* to treat corn stalk for 24 h which resulted in a lignin degradation of 23% and cellulose crystallinity decrease of 4.1% (Xu et al. 2018).

5.3.3 Emerging Methods

In the last decades, greener solvents such as supercritical fluids, ionic liquids and deep eutectic solvents gained interest because they allowed performing under milder conditions, which reduces the release of degradation products and energy consumption, using less toxic and more environmental-friendly chemicals (Raynie et al. 2020; Bhatia et al. 2020). Other emerging methods such as non-thermal plasma (NTP), co-solvent enhanced lignocellulosic fractionation (CELF), microwave and ultrasound pretreatment have been developed recently to decrease the required quantity of harsh chemicals and processing time. Microwave and ultrasound pretreatments are the most extensively studied of these nonconventional methods (Sidana and Yadav 2022).

5.3.3.1 Microwave-Assisted Heating Pretreatment

Microwave heating pretreatment involves the use of non-ionizing electromagnetic radiations typically in the frequency range of 300 MHz–300 GHz with a wavelength of 1 m to 1 mm. LCB and water absorb microwave radiations which produce the alignment of the molecule dipoles. The realignment of polar molecules generates heat, and its propagation is carried out through two mechanisms: ionic conduction and bipolar rotation (Aguilar-Reynosa et al. 2017; Siddique et al. 2022).

The localized heating produced by microwave irradiation disrupts chemical bonds in the lignocellulosic biomass, depolymerizes lignin and releases the hemicellulose fraction (Sidana and Yadav 2022). LCB usually has a low dielectric constant, which reduces the efficiency of pretreatment. However, the microwave absorption capacity can be enhanced by the presence of moisture and inorganic components (Sidana and Yadav 2022).

The main advantage of the method is the reduction of the reaction times to ten times less in comparison with other heating systems, thus decreasing the energy consumption. Due to the short reaction times, the amount of side products is also reduced. Besides, the heat loss is reduced with the use of non-conductor vessels that allows the passage of microwaves without being heated. The main drawback is the formation of hot spots due to the nonhomogeneous properties of the LCB. Besides, some materials have low-energy absorption due to their dielectric properties, and in some cases, these properties can change with temperature (Aguilar-Reynosa et al. 2017).

Microwave-assisted heating is usually performed at 70–230 °C for 5–120 min with microwaves of 2450 MHz and power ranging from 250 to 1000 W (Sidana and Yadav 2022).

Due to the advantages of microwave heating, it has been used to obtain oligosaccharides through hydrothermal treatment from several LCBs. For example, Mihiretu et al. (2017) applied this technology to extract xylan from aspenwood and sugarcane trash with maximal yields of 66% and 50%, respectively (Mihiretu et al. 2017). Using microwave-assisted hydrothermal treatment at 200 °C, Luo et al. (2017) reported a high removal of hemicellulose (more than 95%) from bamboo (Luo et al. 2017). Dávila et al. (2021) solubilized hemicelluloses from vine shoots, under microwave irradiation to evaluate the impact of temperature and time on the production of oligosaccharides. In this same work, the authors compared the extraction of oligosaccharides using autohydrolysis assisted by microwave and by conventional heating. The authors found that operating under conditions that maximize the production of oligosaccharides, the microwave process enabled reducing both extraction time and energy consumption by 2.6 and 3.5 times, respectively, compared to the conventional treatment (Dávila et al. 2021).

5.3.3.2 Ultrasonic-Assisted Heating Pretreatment

Ultrasounds are acoustic waves with frequencies over the hearing range (>20 kHz). Their propagation through low-pressure areas in the medium produces minute gas or vapour bubbles that gradually increase in size until implosion, giving rise to a phenomenon called acoustic cavitation. The implosion of the cavitation bubbles releases a large amount of energy, creating local hot spots with temperatures of 2000–5000 K and pressures up to 1800 atm (Mankar et al. 2021; Sidana and Yadav 2022).

Ultrasonic pretreatment causes physical and chemical changes in the lignocellulosic biomass through thermal effects and shearing forcers developed over implosion, but also due to the oxidative radicals produced for the decomposition of the water molecules. The rupture of hydrogen bonds reduces the cellulose crystallinity. Besides, the ultrasonic method breaks α-O-4 and β-O-4 ether linkages in lignin and increases hemicelluloses solubility (Mankar et al. 2021; Sidana and Yadav 2022).

One of the main advantages, as in the case of microwave-assisted pretreatment, is the reduction of hydrolysis time compared with the conventional hydrothermal method. This advantage, along with low instrumental requirements, high efficiency and reliable repeatability, can make this process more cost-effective (de Carvalho Silvello et al. 2019). Nonetheless, Bundhoo and Mohee (2018) concluded that sonication is energetically inefficient based on the lab-scale studies reviewed. Besides, more studies on pretreatment condition optimization, scale-up and economic and environmental sustainability analysis are needed (Bundhoo and Mohee 2018; Sidana and Yadav 2022).

The pretreatment efficiency does not increase with frequencies greater than 100 kHz. Typically, the sonication method is conducted at 20–80 kHz for 20–150 min (Chen et al. 2022). Other relevant parameters are biomass composition, particle size and reaction configuration geometry (Mankar et al. 2021). Ultrasonic irradiation is usually combined with chemical (acid, alkali, ionic liquid, deep eutectic solvents) or physical methods, achieving higher efficiencies (Sidana and Yadav 2022).

Several works have evaluated the optimization of ultrasonic pretreatment of various biomass feedstock. In this line, Onu Olughu et al. (2021) examined the effect of the operational variables (acoustic power, solid-solvent ratio, hammer mill screen size and sonication time) on the delignification yield. The results revealed that the sonication time was the factor that had the greatest impact on delignification followed by acoustic power. Under optimized extraction conditions (50 min, 1/25 g/mL, 180 W, 3.2 mm), UAE led to a delignification yield of 20.11% (Onu Olughu et al. 2021).

The potential of ultrasonic treatment has also been used to improve the performance in enzymatic saccharification of LCB. For example, de Carvalho Silvello et al. (2019) demonstrated that the application of ultrasonic waves during the enzymatic hydrolysis of sugarcane bagasse led to an 89.37% higher concentration of reducing sugars in comparison to the unsonicated biomass (de Carvalho Silvello et al. 2019).

Table 5.4 gathers selected recent studies of microwave- and ultrasonic-assisted pretreatment of lignocellulosic biomass.

5.3.3.3 Green Solvents

Supercritical Fluids (SCFs)

Supercritical fluids (SCFs) are substances at temperatures and pressures above their vapour-liquid critical point, defined as the endpoint of the liquid-vapour equilibrium curve. The substances exhibit an intermediate behaviour between liquid and gases, presenting high diffusivity and density, and low viscosity at these conditions. These properties allow these nontoxic and relatively low-cost solvents to penetrate the solid material easily due to faster mass transfer (Raynie et al. 2020; Bhatia et al. 2020; Mankar et al. 2021).

Supercritical carbon dioxide (SC-CO_2) is the most widely used supercritical fluid due to its lower critical temperature and pressure (31.1 °C, 73.6 bar) compared with other compounds such as water (374.2 °C, 221.2 bar), ammonia (132.3 °C, 112.8 bar) and methanol (240 °C, 79.6 bar) (Bhatia et al. 2020; Chen et al. 2022). SC-CO_2 reacts with water present in biomass, forming a carbonic acid which works as a catalyst and increases the hydrolysis rate of the lignocellulosic biomass. A higher moisture content improves the reaction rate (Raynie et al. 2020; Mankar et al. 2021). Besides, high pressure and temperature enhance the interaction between the supercritical fluid and lignocellulose because the pore size and the surface area get expanded (Badgujar et al. 2021; Chen et al. 2022).

Table 5.4 Recent studies of microwave- and ultrasonic-assisted pretreatment of lignocellulosic biomass

Pretreatment	Biomass	Results	Reference
Microwave-assisted hydrothermal	*Paulownia* wood	80% of xylan is recovered as xylooligosaccharides, and 95% of cellulose is recovered	del Río et al. (2021)
Microwave-assisted hydrothermal	Vine shoots	Microwaves reduce extraction time and energy consumption by 2.6–3.5 times, respectively, compared to the conventional treatment	Dávila et al. (2021)
Microwave-assisted hydrothermal	Aspen wood sawdust	Maximum xylan extraction yield of 66% and cellulose digestibility of 78% were achieved at 195 °C for 20 min	Mihiretu et al. (2017)
Microwave-assisted hydrothermal	Bamboo powder	More than 95% of hemicellulose in bamboo was dissolved applying hydrothermal pretreatment at 200 °C	Luo et al. (2017)
Microwave-assisted hydrothermal	Brewer's spent grain	43 mg/g BSG of fermentable sugars were recovered (82% of total)	López-Linares et al. (2019)
Ultrasound-assisted hydrothermal	Brewer's spent grain	Under optimal conditions (20% US power, 1 h, 26.3 °C and 17.3% w/v of biomass in water), 2.1-fold increase in reducing sugar yields was achieved	Hassan et al. (2020)
Ultrasound-assisted hydrothermal	Sugarcane bagasse	Sonication led to an 89.37% higher concentration of reducing sugars in comparison to the unsonicated biomass	de Carvalho Silvello et al. (2019)
Ultrasound-assisted alkali (2% (w/v) NaOH)	Orange peel	92% delignification in 4 h using ultrasound-assisted alkaline pretreatment, while the conventional alkaline pretreatment resulted in 86%	Utekar et al. (2021)
Ultrasound-assisted alkali (2% (w/v) NaOH)	Wheat waste biomass	Under optimized conditions (2% NaOH at 100 °C for 30 min and sonication for 1 h), 70% delignification and 84.5% hydrolysis yield were achieved	Saratale et al. (2020)
Ultrasound-assisted acid (4% (v/v) H_2SO_4)	Sugarcane bagasse	Acid pretreatment with 4% v/v H_2SO_4 and ultrasonication (25 min) favour the efficient hydrolysates (85%) of monomeric glucose from the cellulose of sugarcane bagasse	Vasaki et al. (2022)

SC-CO_2 is considered a clean and green solvent. It is nonflammable, nontoxic and non-reactive in nature. The pretreatment is performed under mild conditions, usually below 30 MPa and 200 °C; thus, it does not cause the disintegration of biomass components. It is not necessary a detoxification step before fermentation because SC-CO_2 can be easily separated via depressurization. Furthermore, carbon dioxide liberated during fermentations can be used for pretreatment (Raynie et al. 2020; Badgujar et al. 2021). It has been reported that SC-CO_2 pretreatment at 20–30 MPa for 6–72 h could improve sugar production by 45.4–101.45% (Chen et al. 2022).

The main drawback of supercritical fluid pretreatment is the lack of process evaluation at an industrial scale which needs further investigation. Supercritical fluids have been well studied at a large scale for biomass-derived compound extraction, but there are very few research articles on the scale-up of biomass pretreatment method (Badgujar et al. 2021).

Putrino et al. (2020) evaluated SC-CO_2 pretreatment in different contact time conditions (3 and 5 h) and the addition of various polarity modifiers (NaOH, $NaHSO_4$ and ethanol) to enhance enzymatic hydrolysis of cellulose present in coconut fibres. The authors concluded that the method caused changes in the morphology of the raw material, increasing porosity, and reducing the phenolic compound content. However, there was no significant increase in sugar yield after enzymatic hydrolysis because there is hardly any reduction of the lignin content (Putrino et al. 2020).

Takada et al. (2021) studied the topochemistry of the delignification of the *Fagus crenata* wood using supercritical methanol treatment (270 °C, 27 MPa). After 30 min, more than 70% of the lignin was eluted. The authors observed that the lignin in the secondary wall was easily decomposed and removed, while the middle lamella lignin was initially resistant to the pretreatment method (Takada et al. 2021).

Several studies have evaluated the combination of supercritical fluids with co-solvents and other pretreatment methods. In this line, Silveira et al. (2015) achieve a 41.9% delignification, high carbohydrate recoveries and high enzymatic digestibility by combining SC-CO_2 with the ionic liquid 1-butyl-3-methylimidazolium acetate and ethanol as co-solvents to pretreat sugarcane bagasse (Silveira et al. 2015).

Ionic Liquids (ILs)

Ionic liquids (ILs) are molten salts with a melting point lower than 100 °C, usually composed of organic cations, and organic or inorganic anions (Usmani et al. 2020; Chen et al. 2022). ILs can be classified depending on the cation, being the most used for lignocellulosic biomass pretreatment imidazolium-based ($[(C_3N_2)X_n]^+$), but also ammonium-based ($[NX_4]^+$), pyrrolidinium-based ($[(C_4N)X_n]^+$), pyridinium-based ($[C_5N)X_n]^+$), phosphonium-based ($[PX_4]^+$), sulphonium-based ($[SX_3]^+$) and choline-based have been used widely for this purpose. The most commonly used anions are chloride and acetate (Rezania et al. 2020; Usmani et al. 2020; Chen et al. 2022).

Several semi-empirical and empirical parameters have been used to predict and simulate the solubility of biomass and other biomolecules in ionic liquids. COSMO-RS and the Kamlet-Taft parameters describe polarity, while Hansen parameters quantify the solubility (Usmani et al. 2020). The cellulose dissolving capability can be attributed to the affinity of the anion to hydrogen bonds, which promotes the formation of an electron donor-electron acceptor complex between cellulose and the ionic liquid. On the other hand, the lignin solubility in ILs is attached to the interactions between the aromatic components of lignin and the cations (Usmani et al. 2020; Chen et al. 2022).

ILs are considered a green alternative to volatile organic solvents because they are easy to obtain, do not form hazardous chemicals, selectively remove lignin and hemicelluloses and can be operated in continuous mode with high biomass input (Bhatia et al. 2020; Chen et al. 2022). ILs also have intrinsic and interesting properties such as nonflammability, wide electrochemical windows, broad liquid regions, low vapour pressure, high viscosity, low conductivity and high thermal and chemical stability. The tuneable nature of ILs allows for the design of a solvent with specific properties to perform the required extraction selectivity and capacity (Usmani et al. 2020).

The main drawbacks are related to the recovery and reuse of ILs which is crucial due to the high cost of the solvents (Bhatia et al. 2020). Desirable properties in a solvent such as low vapour pressure, high viscosity and high dissolution capacity for polar molecules become a challenge in its recovery. Distillation is not, in general, an adequate method to remove impurities from ILs, and many polar compounds such as water, inorganic salts or acids tend to accumulate in the solvent. The solutions become viscous and difficult to handle post cellulose extraction, making it challenging to recover hemicellulose and lignin. Besides, some ILs are toxic to microorganisms and enzymes (Usmani et al. 2020).

In the last decade, the solvent and catalytic capacities of ILs for biomass treatment have also attracted much interest. In this context, Asim et al. (2021) using an ionic liquid-based on [PyH] $HSO_4 \cdot (H_2SO_4)_3$ under mild conditions (60 °C, 2 h) reported a high delignification (79%) and lignin recovery (77%) from wheat straw (Asim et al. 2021). In this same line, Portela-Grandío et al. (2021) proposed an organosolv process catalysed with 1-butyl-3-methylimidazolium hydrosulphate for the fractionation of invasive species such as *Acacia dealbata* wood. The authors found that under optimized conditions (190 °C, 60% ethanol, 60 min of reaction time and 0.6 g 1-butyl-3-methylimidazolium hydrosulphate/g wood), this treatment led to high solubilization of lignin and hemicelluloses and cellulose recovery (87.5%, 88.7% and 88.3%, respectively) (Portela-Grandío et al. 2021).

Deep Eutectic Solvents (DESs)

Deep eutectic solvents (DESs) are liquid eutectic mixtures composed of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) at specific molar ratios, with freezing points lower than those of the individual components. They have favourable features similar to ionic liquids, such as low vapour pressure, high thermal stability and tunable physicochemical properties. Moreover, compared with traditional solvents and ionic liquids, DESs are less toxic, more biodegradable, more compatible with enzymes and microorganisms and more cost-effective in the synthesis process than ILs (Chen et al. 2020, 2022; Wang and Lee 2021).

Chlorine-chloride (ChCl) is the most used HBA for biomass pretreatment for its low cost (65 US$/kg) and safe and healthy nature, and it can be derived from biomass (Xu et al. 2020b; Wang and Lee 2021). Other quaternary ammonium salts such as betaine, benzyltrimethylammonium chloride (BTMAC) and triethyl benzyl ammonium chloride (TEBAC) are also used as HBAs in DES (Chen et al. 2020).

DESs can be classified into four groups according to the functional group of HBDs carboxyl acid-based DESs, amine-/amide-based DESs, polyalcohol-/carbohydrate-based DESs and phenolic compound-based DESs (Zhou et al. 2022). Lactic acid (LA), formic acid (FA) and oxalic acid (OA) are some biomass-derived carboxylic acids that have been used as HBDs in DES synthesis. The acid strength, amount of carboxyl groups and molar ratio are closely related to lignin extraction efficiency. The presence of active protons promotes proton-catalysed cleavage of various bonds in biomass (Chen et al. 2020; Zhou et al. 2022).

Amide-based (e.g. urea), amine-based (e.g. monoethanolamine) and imidazole-based compounds are used to synthesize amine-/amide-based DESs. This kind of DESs exhibits alkaline behaviour, which facilitates the selective lignin extraction through deprotonation of phenolic hydroxyl groups in lignin. Polyalcohol-/carbohydrate-based DESs contain chemicals with hydroxyl groups such as polyalcohols (e.g. glycerol (Gly) and ethylene glycol (EG)) and carbohydrates (e.g. glucose) and usually exhibit neutral or near-neutral pH conditions. Polyalcohol-based DESs have been widely used for lignocellulosic pretreatment, being ChCl/Gly the most popular as Gly is a low-cost by-product generated in the biodiesel industry, and high delignification (60–90%) has been reported by several studies. On the other hand, carbohydrate-based DESs generally have a low capability of lignin extraction, being more used as solvents in chemical reactions rather than for biomass pretreatment. More recently, lignin-derived compounds, such as vanillin, *p*-coumaric acid (PCA), catechol, *p*-hydroxybenzyl alcohol (PBA), *p*-hydroxybenzoic acid (PB) or *p*-hydroxybenzaldehyde (PHA), have been used in phenolic-based DESs synthesis, which can aid in the development of a closed-loop biorefinery (Chen et al. 2020; Zhou et al. 2022).

As in the case of ILs (see Sect. 5.3.3.3.2), the Kamlet-Taft parameters are used as a quantitative tool to describe the solvatochromic properties of DESs, thus reducing the efforts to select the appropriate DES for treatment (Wang and Lee 2021; Zhou et al. 2022). DES-based pretreatment can be enhanced manifold by applying microwaves and ultrasound, and also catalysts and co-solvents such as water, acids and metal salts have been tested to boost the performance of lignin extraction. Even though DES solvents are expected to become one of the most popular biomass pretreatments in the future, a deeper understanding of the interactions of DESs with the different biomass fractions is still missing (Raynie et al. 2020; Mankar et al. 2021; Zhou et al. 2022). Besides, further studies are needed to develop effective DESs recycling technologies and understand the properties of different DES lignin to broaden their applications (Chen et al. 2020).

Zhao et al. (2018) studied a series of three ethanolamine-based DESs and three amide- or glycerol-based DESs to treat wheat straw. The authors evaluated the influence of different parameters on the delignification performance such as properties of DESs (pH and viscosity), pretreatment temperature (50, 70, 90, 110, 130 °C) and pretreatment time (1, 6, 9, 12, 24 h). Among all tested DESs, the choline chloride/monoethanolamine (ChCl/MEA (1:6)) system using a liquid/solid ratio of 20:1 during 9 h and 70 °C showed the highest lignin removal (71.4%) while preserving 93.7% of the cellulose. In addition, this solid exhibited good enzymatic digestibility with cellulose and xylan conversion of 89.8% and 62%, respectively (Zhao et al. 2018).

Another work conducted by Mankar et al. (2022) evaluated the ability of four ChCl-carboxylic acid-based eutectic mixtures to be applied combined with microwave-assisted technology for the extraction of lignin from coconut coir. The authors also compared the effect of different heating types (microwave and conventional heating) on the lignin removal efficiency. Under optimum conditions (150 °C for 20 min using ChCl/LA (1:4)), the lignin yield was six times higher using microwave irradiation compared to conventional heating (82% vs 13.5%) (Mankar et al. 2022).

Table 5.5 shows recent studies on supercritical fluids (SCFs), ILs and DESs pretreatment of lignocellulosic pretreatment.

5.3.3.4 Other Emerging Methods

Several advanced treatment methods used in food industries for improving the nutritional quality and shelf-life of ready-to-eat food products have been gaining interest as biomass pretreatment techniques over the last decade. These nonconventional methods have been proved successful at a laboratory scale, but they are in an early research state. Nonthermal plasma (NTP), hydrodynamic cavitation, high hydrostatic pressure homogenization, electron beam irradiation and gamma irradiation are some of the pretreatments discussed by Sidana and Yadav (2022).

Co-solvent enhanced lignocellulosic fractionation (CELF) technique is another novel method where a mixture of tetrahydrofuran (THF) and water is used as a monophasic solvent to simultaneously extract lignin from biomass and transform glucan-rich solid residue into various fuel precursors, 5-hydroxymethyl furfural, furfural and levulinic acids in high yields (Bhatia et al. 2020; Mankar et al. 2021).

5.4 Lignocellulosic Biomass to Value-Added Biochemicals

In recent years, the investigation of the furanic-aliphatic family has substantially increased, such as versatile building blocks derived from renewable resources. For the development of bio-based platform chemicals, simple sugars present in the lignocellulosic materials can be converted by chemical or biochemical processes into value-added building blocks, which contributes to reaching the desired bio-based economy. In this context, the most relevant marketable bio-based chemicals, namely, hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid (FDCA) and levulinic acid that can be obtained in a biorefinery scheme, are approached in this chapter.

5.4.1 Hydroxymethylfurfural (HMF)

Hydroxymethylfurfural or 5-hydroxymethylfurfural (HMF) containing a hydroxymethyl group (an aldehyde group and a furan ring) is one of these platform

Table 5.5 Recent studies of biomass delignification using supercritical fluids (SCFs), ionic liquids (ILs) and deep eutectic solvents (DESs) as green solvents

Green solvent type	Solvent	Biomass	Delignification (%)	Conditions	Reference
Supercritical fluids (SCFs)	SC-CO_2	Coconut fibres	–	70 °C—5 h	Putrino et al. (2020)
	SC-CH_4	*Fagus crenata*	>70	270 °C—30 min	Takada et al. (2021)
	SC-CO_2	Oil palm trunk	–	80–120 °C—1 h	Sohni et al. (2020)
	SC-CO_2 + 75% H_2O/EtOH mixture	Rice husk	90.6	80 °C—10 min	Daza Serna et al. (2016)
	SC-CO_2 + EtOH + Bmin [OAc]	Sugarcane bagasse	41	180 °C—2 h	Silveira et al. (2015)
Ionic liquids (ILs)	[PyH][HSO_4(H_2SO_4)$_3$]	Wheat straw	79	60 °C—2 h	Asim et al. (2021)
	[Bmin][H_2SO_4] + 60% EtOH	*Acacia dealbata*	87.5	190 °C—1 h	Portela-Grandío et al. (2021)
	[Bmin]$MeSO_4$ + H_2O	*Acacia dealbata*	92.4	140 °C—24 h	Almeida et al. (2022)
	[TEA][HSO_4]	Wheat straw	80	130 °C—3 h	Ziaei-Rad et al. (2021)
	[C_2min][OAc]	*Miscanthus*	73.7	160 °C—3 h	Bhatia et al. (2021)
Carboxylic acid-based DESs	ChCl/LA (1:5)	Sugarcane bagasse	81.6	80 °C—12 h	Chourasia et al. (2021)
	ChCl/FA (1:2)	Pinewood	70	130 °C—6 h	Oh et al. (2020)
	ChCl/LA/FA (1:1:1)	Pinewood	72	130 °C—6 h	Oh et al. (2020)
	$ZnCl_2$/LA (1:10)	Poplar sawdust	96.3	120 °C—3 h	Bai et al. (2022)
Polyalcohol-based DESs	ChCl/Gly (1:2)	Sugarcane bagasse	58.1	80 °C—12 h	Chourasia et al. (2021)
	ChCl/EG (1:2)	*Miscanthus*	83.3	110 °C—12 h	Hassan and Mutelet (2022)

Amine-/amide-based DESs	ChCl/urea (1:2)	*Bambusa bambos*	19.4	120 °C—10 h	Ramesh et al. (2020)
	ChCl/MEA (1:6)	Wheat straw	71.4	70 °C—9 h	Zhao et al. (2018)
Phenolic-based DESs	ChCl/PB (3:2)	Poplar	69.0	160 °C—3 h	Wang et al. (2020)
	ChCl/PCA (1:1)	Switch grass	60.8	160 °C—3 h	Kim et al. (2018)
Microwave-assisted lignin extraction with DESs/ILs	ChCl/LA (1:4)	Coconut coir	82	150 °C—20 min	Mankar et al. (2022)
	ChCl/LA (1:2)	Corn stover	79.60	152 °C—45 s	Chen and Wan (2018)
	[Bmin][OAc] + 70% H_2O	Wheat straw	35.3	360 W—10 min	Yu et al. (2022b)

[Bmin], 1-butyl-3-methylimidazolium; [C_2mim], 1-ethyl-3-methylimidazolium; ChCl, choline chloride; EG, ethylene glycol; EtOH, ethanol; FA, formic acid; Gly, glycerol; LA, lactic acid; MEA, monoethanol amine; $MeSO_4$, methyl sulphate; [OAc], acetate; PB, *p*-hydroxybenzoic acid; PCA, *p*-coumaric acid; [PyH], pyridinium; SC, supercritical; [TEA], triethylammonium chemicals. This versatile chemical structure allows its transformation into higher-value derivative compounds (such as levulinic acid, 2,5-dimethylfuran, ɣ-valerolactone, 5-hydroxymethyl-2-furan carboxylic acid, 2,5-diformylfuran, 5-formylfuran carboxylic acid and 2,5-furandicarboxylic acid), with applications in different sectors such as plastic, pharmaceutical, fuels, fragrance and textile industries. For this reason, HMF was identified by the US Department of Energy as one of the most promising bio-derived molecules from lignocellulosic biomass. Accordingly, the global market of HMF is expected to reach $61 million by 2024 (Market Study Report 2019).

HMF is produced by acid dehydration of hexoses or their corresponding polysaccharides obtained from lignocellulosic biomass. Its efficient large-scale production requires deep understanding of dehydration mechanisms using the adequate catalyst and the optimization of the process. Among several processes used for their production, the use of liquid ionic and biphasic systems has been extensively explored (Naz et al. 2021; Yousatit et al. 2022) due to the interesting yields reported (Sousa et al. 2015). More recently, emerging green solvents such as DESs for the sustainable production of HMF have been also considered, taking into account their inherent advantages as solvents (Zuo et al. 2021). Generally, the main strategies used for the HMF production are (1) the heterogonous acid catalysis using catalysts such as zeolites and polymeric resins and (2) homogenous catalysis catalysed by the ionic liquid and organic or mineral acids. HMF production involves a wide range of conditions that can be evaluated (such as extractive solvent, reactive phase and/or water/organic media). The scientific community has devoted huge efforts to develop more efficient and sustainable processes for HMF production. Among several strategies, the use of microwave technology as an alternative to conventional heating systems allows employing lower reaction times and obtaining higher yields. The use of biphasic systems employing soluble solvents (such as dimethyl sulfoxide (DMSO), acetone or poly(ethylene) glycol (PEG)) reduces undesired hydration reactions of HMF compared to aqueous media. In addition, the catalytic process can be combined with an enzymatic reaction in order to improve HMF yields. For instance, immobilized glucose isomerase enzymes can be used for the isomerization of glucose into fructose, being subsequently dehydrated in HMF (Alipour 2016). On the other hand, high-pressure CO_2 has been also evaluated as a low-cost alternative to acid catalysts. One of the main challenges for the advance in the HMF production includes the direct transformation from lignocellulosic biomass within a one-pot approach (Zhao et al. 2011; Xu et al. 2020a).

5.4.2 2,5-Furandicarboxylic Acid (FDCA)

Particularly, 2,5-furandicarboxylic acid (FDCA), obtained by complete oxidation of HMF, has also been identified as one of the top 12 high-potential bio-based products to be obtained from biomass (Bozell and Petersen 2010), and its worldwide market is expected to reach $850 million by 2025 (Acumen Research and Consulting 2022). Its major industrial use is as a substitute for terephthalic acid (TPA), which can be used to synthesize several polyesters such as polyethylene furanoate (PEF). PEF is obtained by the polymerization of FDCA with ethylene glycol to replace the petroleum-derived polyethylene terephthalate plastic (PET) (Gubbels et al. 2013; Motagamwala et al. 2018). The European Union has funded a consortium of 11 companies, known as "PEFerence", in order to develop an innovative production process for FDCA and PEF (https://peference.eu/). FDCA may also be employed as a building block in the production of medicines, plasticizers, thermosets, coatings and polyamides (Hu et al. 2018).

Large-scale production of FDCA requires two key steps: (1) dehydration of hexoses (such as fructose, glucose and C6 polysaccharides/cellulose) to obtain HMF and (2) further catalytic oxidation to produce FDCA (by chemical catalysis, electrocatalysis or enzymatic catalysis). Most studies employ chemical catalysis using a methodology based on a Pt/C catalyst for efficient oxidation. High FDCA yields have been also reported using several types of nanoparticles as catalysts in oxidation conditions (>90%) (Siankevich et al. 2014). Direct conversion of fructose into FDCA was also obtained using a triphasic system achieving a global yield of 78% (Yi et al. 2015). Nevertheless, this typical chemical route implies the generation of by-products, impurities, wastes and the need for downstream processing, which compromises the ecological footprint. In this sense, biocatalysis using enzymes for bioconversion of HMF into FDCA shows several advantages as an alternative route, namely, the mild reaction conditions and the high selectivity of the enzymes (Domínguez de María and Guajardo 2017).

The enzymatic oxidation of HMF includes three consecutive oxidation steps. Some authors have proposed the combination of enzymes with chemocatalysis (Krystof et al. 2013; Qin et al. 2015). Moreover, this biocatalytic reaction can be carried out using whole cells, which entails several advantages such as no need of cofactor regeneration and no tedious purification of enzymes. The first whole-cell biocatalyst reported for FDCA production using HMF as substrate was using a *Pseudomonas putida* S12 strain, which was modified to express the *hmfH* gene from *Cupriavidus basilensis* (encoding an HMF/furfural oxidoreductase) (Koopman et al. 2010).

Alternatively, furfural was also employed as a more sustainable and economical substrate for FDCA production. Furfural can be industrially obtained by acid-catalysed thermohydrolysis of the hemicellulose process. The biocatalytic conversion was also reported using a recombinant *Escherichia coli* expressing two enzymes (oxidase and carboxylase) to convert furfural into 2-furoic acid and subsequently furoic acid into FDCA, respectively (Kawanabe et al. 2021). The increase of industrial patent application shows the interest in this approach for FDCA production (de Bont et al. 2018). Nevertheless, higher productivities should be obtained to validate this strategy at an industrial level.

5.4.3 Levulinic Acid (LVA)

Levulinic acid (LVA), also known as 4-oxopentanoic acid, is a low molecular weight carboxylic acid also included in the top 12 bio-based platform chemicals due to a wide range of applications, namely, personal care, adsorbents, lubricants, drug delivery and as a precursor for the production of biofuels, chemicals and polymers. The global market size for LVA is projected to achieve US $5.02 billion by 2028 (Grand View Research 2021). LVA is produced from HMF by acid degradation of cellulose in an aqueous medium and subsequent rehydration of HMF in an acidic medium. In this reaction, formic acid is also formed in equimolar quantities, which is also beneficial since formic acid can be used as plasticizers, rubbers, formaldehyde, textiles and drugs. Furfural has been also employed for LVA conversion via hydrogenation to furfuryl alcohol and subsequent ethanolysis (Dutta and Bhat 2021). LVA production by desirable one-pot conversion has been reported using simple sugars such as glucose and polysaccharides such as cellulose, as well as directly from biomass (Mukherjee et al. 2015; Morone et al. 2015). Reaction conditions for LVA production are harsher than for cellulose or HMF conversion. Generally, low LVA yields are related to side reactions that are derived in the formation of dark and coloured solid denominated humins.

Hemicellulose containing pentoses and hexoses (as oligomer and/or monomer) obtained by hydrothermal treatment of *Pinus pinaster* was used for LVA production by homogenous catalysis with sulphuric acid, yielding 66% of LVA of the stoichiometric value (Rivas et al. 2013). As an alternative to mineral acids, heterogeneous catalysts have also been evaluated for LVA production (Sajid et al. 2021). Similar to HMF conversion, the selectivity and yield of LVA are strongly dependent on acid strength. Temperatures in the range of 80–200 °C for 0.5–24 h have been evaluated for glucose conversion to LVA, obtaining yields varying 20–79% using catalysts such as HCl, $FeCl_3$ or Amberlite IR-120 (Sajid et al. 2021). For LVA production from xylose, temperatures in the range of 120–200 °C for 0.5–6 h were employed using solvents such as water-acetone, water or water-methyl ethyl ketone catalysed with Cu-NbP or H_2SO_4 (Sajid et al. 2021).

Despite the high value of LVA and the possibility of its production from renewable resources such as lignocellulosic biomass, the research focused on the development of more stable catalysts using non-metals with synthetic polymers is still necessary. In this sense, the pretreatment that allows a suitable fractionation of lignocellulosic biomass is mandatory for its utilization.

5.5 Conclusion

The complexity and recalcitrance of LCB, composed of a blend of cellulose fibres coated by hemicelluloses and lignin at different proportions depending on the species, do not allow a straightforward valorization to produce biofuels and/or green platform chemicals not dependent on fossil resources. Hence, pretreatments are needed to promote the separation of the main constituents of LCB in separated streams, providing a more efficient valorization. Traditional pretreatments, including the use of different chemicals such as acids, alkalis, oxidizing agents and organic solvents, or even those pretreatments avoiding the use of reagents, such as steam explosion, autohydrolysis or biological treatments, have shown certain limitations, hampering full-fledged commercial adaptation of such traditional processes. In the last years, alternative green and sustainable pretreatment technologies have been developed, aiming to overcome the bottlenecks of traditional technologies. Microwave- and ultrasonication-assisted technologies have shown high effectivity on a variety of lignocellulosic biomass. On the other hand, green solvents, e.g. supercritical fluid, ionic liquid and deep eutectic solvent (DES)-based pretreatment techniques, have already shown great potential in the pretreatment of different LCB.

The transformation of biomass feedstock into 5-HMF, FDCA and LA is of particular interest. These compounds, included in the DOE Platform Chemical List, show strong potential as platform chemicals may serve as a primary building block of the biorefinery and can provide direct substitutes for existing petrochemicals. Although there have been remarkable advances in the last years, these processes are still emerging for fulfilling industrial needs. Some remaining challenges still have to be overcome in bio-based products from biorefinery carbohydrates.

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Part II

Biomaterials

6

Current Approaches for Polyurethane Production from Lignin

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Abbreviations

BA	Blowing agent
BPU	Branch-chained polyurethanes
CASE	Coatings, adhesives, sealants, and elastomers
CAT	Catalyst
CMR	Carcinogenic, mutagenic, and reprotoxic
CNSL	Cashew nutshell liquid
CPU	Crosslinked polyurethanes
DABCO	1,4-Diazobicyclo[2.2.2]-octane
DBTDL	Dibutyltin dilaurate
FAME	Fatty acid methyl esters
F-PUF	Flexible polyurethane foams
G	Guaiacyl
GHG	Greenhouse gases
H	*p*-Hydroxyphenyl
HPU	Hyperbranched polyurethanes
HTL	Hydrothermal liquefaction
KL	Kraft lignin
LCA	Life cycle analysis

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LPU	Linear polyurethanes
LS	Lignosulphonates
MDI	Methylene diphenyl diisocyanate
NIPU	Non-isocyanate polyurethane
PCM	Phase change materials
PDI	Pentamethylene diisocyanate
PEG	Polyethylene glycol
PHU	Poly(hydroxyurethane)
PI	Polyisocyanate
PO	Propylene oxide
PU	Polyurethane
PUD	Polyurethane dendrimers
PUF	Polyurethane foams
PUSM	Polyurethane smart materials
R-PUF	Rigid polyurethane foams
S	Syringyl
SF	Surfactant
STL	Solvothermal liquefaction
TBAB	Tetrabutylammonium bromide
TDI	Toluene diisocyanate
TEA	Techno-economic analysis
UV	Ultraviolet

6.1 Introduction

The use of fossil resources to produce energy, chemicals, fuels, and synthetic products deteriorates the environmental conditions and leads to the emission of greenhouse gases (GHG), which eventually results in intensifying global climate change (Qasim et al. 2021). In addition, the growth of population and energy and chemical demand is accelerating the depletion of these fossil or non-renewable resources. Therefore, the production of energy, fuels, and value-added chemicals or materials from renewable resources is a great challenge in the current society. One of the main renewable resources distributed all over the world is lignocellulosic biomass which is an abundant, inexpensive, and environmentally friendly feedstock with huge potential for the production of biofuels, chemicals, and materials (Kawaguchi et al. 2022; Zhou et al. 2022).

Lignocellulosic biomass can be defined as a composite matrix made up of cellulose, hemicellulose, and lignin (Saravanan et al. 2022) which are distributed as a complex network within the plant cell walls (Khemthong et al. 2021). The percentage composition of these three different components could vary significantly based on the source of the biomass feedstock (Mankar et al. 2021). Cellulose is the main component of lignocellulosic biomass comprising around 30–50% of the total weight (Cheng and Whang 2022) and is a linear polymer of D-glucoses linked by β-glycosidic linkages (Dadwal et al. 2021). Cellulose is a polysaccharide which is derived from the glucose dehydration, and it provides the structural support to plant cell wall (Rangabhashiyam and Balasubramanian 2019). Hemicelluloses are also polysaccharides from the plant cell walls composed of xyloglucans, xylans, mannans and glucomannans, and β-(1,3 and 1,4)-glucans (Kim et al. 2019). They account for 20–35% of the lignocellulosic biomass (Kassaye et al. 2016) and act as a binding agent between the cellulose and lignin fractions adding rigidity to the overall biomass matrix (Kumari and Singh 2018).

Finally, lignin is the second most abundant natural polymer and the main source of aromatic structures on earth (Deng et al. 2021). It comprises 15–40 wt%. of the total lignocellulosic biomass, and it protects cellulose and hemicelluloses from microbial degradation providing also strength and hydrophobicity to the plant cell walls (Yoo et al. 2020). The structure of native lignin is still relatively unknown since it cannot be isolated without altering its native structure (Gillet et al. 2017). There are many different methods for lignin extraction with their own characteristics and particularities which provide very diverse lignin types. Pulp and paper mills are the most important lignin producers in the world with a production of 97% of total lignin, of which 88% are lignosulphonates (LS) and 9% is Kraft lignin (KL) (Bajwa et al. 2019). These two types of lignins have sulfur content between 1.5 and 5 wt% in their structure and are usually employed for low added value applications, such as heat and electricity generation (Jędrzejczak et al. 2021). Other lignin extraction processes from which lignin can be isolated are several sulfur-free alternative methods, such as alkaline processes, organosolv processes, steam explosion, dilute acid hydrolysis, or more recently developed ionic liquids or deep eutectic solvent extraction processes (Bhutto et al. 2017; Das et al. 2019; Chen et al. 2020d; Usmani et al. 2020; Sidiras et al. 2022; Yu et al. 2022). These types of lignins have in general higher purity and more adequate properties than LS or KL to be further valorized in high added value applications.

Despite all the different kinds of lignins that can be isolated depending on the extraction method and type of lignocellulosic biomass, it is well accepted that lignin has a rigid polymer crosslinked 3D irregular structure (Börcsök and Pásztory 2021). It is constituted through an enzyme-mediated dehydrogenative polymerization of *p*-coumaryl, coniferyl, and sinapyl aromatic alcohols in which the respective polymer units are synthesized, forming *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) phenolic units (Fig. 6.1) (Kai et al. 2016; Zhang et al. 2022). These phenolic units appear in different proportion depending on the plant species; thus, lignin from softwood contains around 90–95% of coniferyl alcohol, whereas lignin from hardwood typically is made up of around 25–50% and 50–75% of coniferyl and sinapyl alcohols, respectively, and lignin from grass is composed of all three monomer alcohols (Chio et al. 2019; Huang et al. 2020).

The H, G, and S phenolic units are linked together ether bonds, such as β-O-4, α-O-4 and 4-O-5, and carbon-carbon bonds, such as 5-5, β-5, β-1, and β-β, of which the contents in different biomass are not the same (Leng et al. 2022). However, the most frequent linkage in natural lignocellulosic biomass lignin is the β-O-4 bond,

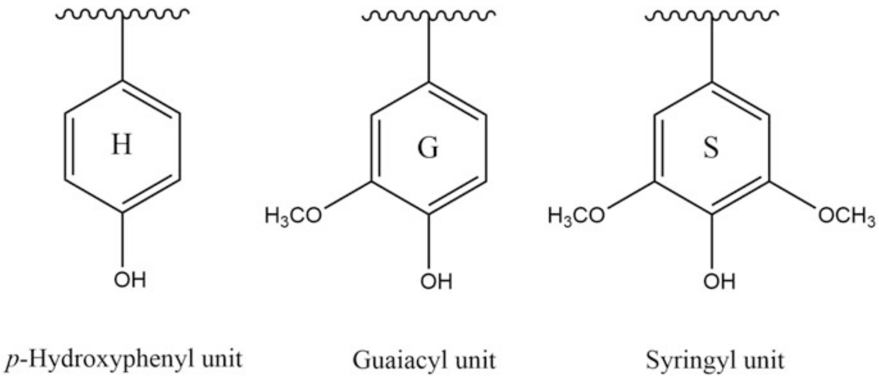

Fig. 6.1 Lignin phenolic units

Table 6.1 Percentage (wt %) of the main linkages in lignin (Li et al. 2015a; Ninomiya et al. 2018)

Linkage	Percentage (wt%)
β-O-4	45–60
α-O-4	4–7
4-O-5	2–10
5-5	5–25
β-5	4–12
β-1	2–10
β-β	2–7

Table 6.2 Percentage (wt %) of functional groups in lignin (Gao and Fatehi 2019)

Functional group	Percentage (wt%)
Methoxy	8.7–19.3
Phenolic hydroxyl	2.2–4.5
Aliphatic hydroxyl	3.1–10.1
Carboxyl	2.9–7.1
Carbonyl	2.1–4.5

which varies from 43% to 65% (Wu et al. 2020). The average percentage of each linkage in all type of lignins is showed in Table 6.1.

Otherwise, lignin has many different functional groups including hydroxyl, carbonyl, methoxy, and carboxyl groups that have an effect on lignin's reactivity (Meng et al. 2019a). The proportion of these functional groups in lignin molecule depends not only in the type of biomass but also in the lignin extraction method employed. The percentage of the main functional groups present in lignin is showed in Table 6.2.

Lignin chemical structure and high functionality have contributed to the study of lignin as an ideal candidate for the development of new bio-based materials such as carbon fibers, engineering plastics, asphalt binder modifier, thermoplastic elastomers' polymeric foams and membranes, as well as a variety of fuels and chemicals (Meng et al. 2019b). In addition, as mentioned before, lignin has high

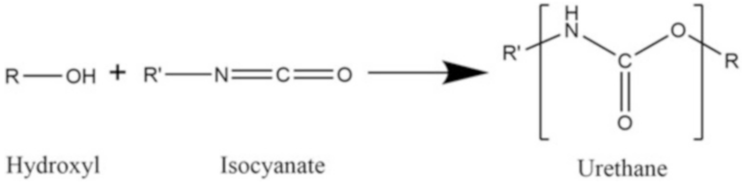

Fig. 6.2 Addition reaction between hydroxyl and isocyanate group to form urethane group

aromatic content with both aromatic and aliphatic hydroxyl groups which makes it a potential raw material for polyurethane production (Haridevan et al. 2021). However, the complex structure and the lack of repeatability of lignin as well as the still insufficiently developed technologies make difficult its practical application (Jędrzejczak et al. 2021).

Polyurethanes (PUs) are among the most flexible polymers due to their tunable mechanical properties and huge range of applications such as thermoplastics, foams, elastomers, adhesives, coatings, and sealants (Ponnusamy et al. 2019; Haridevan et al. 2021; Quinsaat et al. 2021). The worldwide production of PUs is around 20 million tons (Peyrton and Avérous 2021) and had a global market of $69.2 billion net worth in 2019, which projects a promising future with an expected growth of around 5.0–5.6% per year by 2025 (de Souza et al. 2021). PUs are formed by polyaddition reactions of hydroxyl containing components, mainly polyols and isocyanates. The addition reaction of a hydroxyl and isocyanate functional groups leads to the formation of a urethane group (Fig. 6.2). Therefore, PUs are usually synthesized from the condensation reaction between polyols, low molecular weight chain extenders, and a diisocyanate molecule to produce a repeating urethane bond (Mahmood et al. 2016).

Based on the function and nature of monomeric groups such as polyols and polyisocyanates involved in the PU synthesis, a diverse range of these polymers can be produced (Rajesh Banu et al. 2019). Therefore, when the functionality of the reactants is equal to two, thermoplastic PUs are obtained, whereas for higher functionalities, the obtained PUs are crosslinked. The PU can be grouped into several different classes based on the desired properties: rigid, flexible, thermoplastic, waterborne, binders, coating, adhesives, sealants, and elastomers (Akindoyo et al. 2016).

Generally, the polyols for PU production have been derived from fossil resources, but recently the use of renewable resources, such as lignin, is gaining importance (Reshmy et al. 2021). Lignin can be employed as a functional filler or as one of the reactants in PU formulation and can be modified or used without any modification (Ma et al. 2021). Due to the high content of hydroxyl groups, lignin shows great potential to partially or fully replace petroleum-based polyols in the PU synthesis (Upton and Kasko 2016). However, the irregular and complicated lignin structure does not facilitate the participation of the sterically hindered hydroxyl groups in the polymerization reaction of PU synthesis. Furthermore, it does not form homogeneous compositions of hard and soft segments that conventional PUs have

(Sternberg et al. 2021). Different strategies have been developed to use lignin in the PU synthesis, and its incorporation into various polyurethane products could provide performance advantages such as enhanced crosslinking density, improved biodegradability, increased ultraviolet (UV) stability, antioxidant properties, and enhanced mechanical strength and thermal stability (Alinejad et al. 2019).

Aforesaid, in general, lignin has been used as a partial or total replacement of the petro-based polyols in PU synthesis. However, the lignin without any modification can only replace 20–30% of the polyols (Mahmood et al. 2016), so several lignin modification techniques have been developed. Chemical modifications of lignin are often employed to enhance the reactivity of lignin molecule. Among these chemical modifications, hydroxymethylation (Chen et al. 2020b), oxypropylation (Westwood et al. 2016), and lignin liquefaction (Mohammadpour and Mir Mohamad Sadeghi 2020b) are the most common ones. Through hydroxymethylation, hydroxymethyl groups are introduced on the C5 position of G units by electrophilic substitution, thus increasing hydroxyl groups in lignin molecule (Chen et al. 2020b). Otherwise, in oxypropylation, the phenolic hydroxyl groups hindered inside the lignin molecule which are difficult to access are liberated from steric and/or electronic constraints, and at the same time, the solid lignin becomes a liquid polyol, due to the introduction of multiple ether moieties (Cateto et al. 2009). Finally, in liquefaction process, lignin is liquefied into liquid products through dehydration, dehydrogenation, deoxygenation, and decarboxylation reactions typically by polyhydric alcohols, such as polyethylene glycol (PEG) and glycerol in the presence of an acid catalyst (da Silva et al. 2019).

Lignin-based PUs can be used for multiple applications, but they are mainly employed for rigid and semi-rigid foam formulations, though the synthesis of PU adhesives has also been reported (Hu et al. 2014). Furthermore, besides using lignin to produce more environmentally friendly PUs, other strategies are also being investigated such as waterborne, radiation-curable, and non-isocyanate PU techniques (Tenorio-Alfonso et al. 2020).

Throughout this chapter, the employment of lignin for producing different types of PUs will be described. In the first place, the raw materials for the synthesis of PUs will be presented with special interest in polyols and specifically in obtaining polyols from lignin. Secondly, the different types of PUs that can be synthetized, such as foams or adhesives, will be defined. In third place, new and more sustainable PU fabrication methods will be shown including the new generation of PUs that do not require isocyanates in their synthesis. Finally, the main conclusions about lignin employments for different kinds of PU will be presented, and the future perspectives on this topic will be showed.

6.2 Polyols for Polyurethane Production

As mentioned above, the PU industry is of great relevance today. Therefore, considering that polyols are one of the fundamental components of these compounds, its market is equally relevant. In fact, in 2019, the polyol industry generated roughly $26.2 billion per year and is expected to grow to $34.4 billion by 2024 (Perez-Arce et al. 2021b). Polyols, which are commonly petroleum derived, are defined as chemicals which contain two or more hydroxyl groups or amine groups per molecule (Parcheta and Datta 2017). Polyols can be classified into two main categories according to their molecular weight: low molecular weight or monomeric polyols and high molecular weight or polymeric polyols, also called oligopolyols. The former, which may have two or more hydroxyl groups, are usually employed as chain extenders in the case of polyols with two hydroxyl groups (diol) or as crosslinkers in the case of having more than two hydroxyl groups (triols, tetraols, etc.) (Li et al. 2015b). These monomeric polyols can also be used to produce alkyd resins through polycondensation reaction of fatty oils or fatty acids, dibasic acids or acid anhydrides, and polyols with hydroxyl functionality greater than 2 (Orozco et al. 2021). The latter are polymers with molecular weight up to 10,000 Da with a maximum number of hydroxyl groups of eight (Ionescu 2019) and can be subclassified into two main categories, viz., polyether and polyester polyols, which are synthesized employing monomeric polyols. Thus, polyether polyols are usually formed through alkoxylation reactions between alkylene oxide monomers, such as ethylene or propylene oxide, with a low molecular weight polyol such as glycerol (Kong et al. 2012), while polyester polyols are synthesized mixing monomeric diols or triols with dibasic acids or anhydrides (Lukey 2001). These types of polymeric polyols are usually employed as “reinforced polyols” in PU foam formulation (Głowińska et al. 2018). Although the abovementioned chemicals are usually obtained from the petrochemical industry, the possibility of obtaining them from biomass is a reality that is being studied over the last decades. Vegetable oils (Fridrihsone et al. 2020), fatty acids (Junming et al. 2012; Paraskar and Kulkarni 2020), fatty acid methyl esters (FAME) (Mohd Norhisham et al. 2017; Tuan Ismail et al. 2018), crude glycerol (Cui et al. 2017), and lignocellulosic biomass-derived compounds (Li et al. 2015c) are some of the most studied raw materials for the production of bio-based polyols.

6.2.1 Polyols from Lignocellulosic Biomass

Lignocellulosic biomass is an abundant and renewable raw material which has the potential to develop biofuels and biochemicals for the chemical industry (Briones et al. 2012). It is mainly composed of cellulose, hemicellulose, and lignin, but also contains tannins, extractives, and inorganic compounds (de Hoyos-Martínez et al. 2019; Sillero et al. 2021a). Biopolyol synthesis from cellulose, tannins, and lignin has been reported as well as biopolyols from carbohydrate monomers that can be obtained from the degradation of cellulose and hemicellulose.

In the PU industry, cellulose has been mainly used as an additive to improve the final material properties and to a lesser extent for the manufacture of polyols (Szpiłyk et al. 2021). However, there are very few studies in the latter field. In a specific case, different amounts of biopolyol obtained through the liquefaction of cellulose with crude glycerol was employed to synthesize rigid PU foam (Kosmela et al. 2018). In another study, cellulose was reacted with glycidol and ethylene carbonate in water to produce a polyol used to elaborate PU foams (Szpiłyk et al. 2021). Tannins are also employed to produce polyols for the synthesis of PUs through liquefaction (Ge et al. 2003) or oxypropylation (Arbenz and Avérous 2015; Vevere et al. 2018). Cellulose and hemicellulose can be degraded through hydrolysis to obtain five and six carbon sugars, such as xylose, xylitol, fructose, glucose, or sorbitol among others, which can be used for polyol production (Furtwengler and Avérous 2018). However, the polyols from sugars are more employed as hydrogenated carbohydrate sugar substitutes in the food industry. The main reasons of their interest for this application are that they present multiple potential health benefits such as low caloric value, low glycemic (potentially helpful in diabetes and cardiovascular disease), low energy and low insulinemic (potentially helpful in obesity), low digestible (helpful in the colon), osmotic (colon-hydrating, laxative, and purifying), salivation induction, and non-cariogenic properties (Livesey 2003; Paulino et al. 2021). In addition, further degradation of these compounds can result in diols that are widely used in industry, such as ethylene glycol, which can be obtained through the catalytic conversion of cellulose (Pang et al. 2015).

Otherwise, as mentioned before, lignin, due to its low cost, its high availability, its phenolic character, and the presence of both aliphatic and phenolic hydroxyl groups, is considered as a great alternative to develop new bio-based added-value chemicals or key intermediates for the chemical industry, including bio-based polyols (Alinejad et al. 2019; Eraghi Kazzaz and Fatehi 2020). Unfortunately, many of the OH groups in the lignin molecule are sterically hindered leading to low reactivity of the lignin (Upton and Kasko 2016). To overcome this setback, different strategies have been developed, always with the aim of increasing the reactivity of the molecule. These processes can be classified into three main families: fragmentation or depolymerization of lignin, modification creating new chemical active sites, and functionalization of hydroxyl groups (Laurichesse and Avérous 2014). Among all the existing techniques encompassed in these three routes, liquefaction with polyhydric alcohols and oxyalkylation are the most widely studied strategies to synthesize polyols from lignin (Laurichesse and Avérous 2014; Gosz et al. 2018). Therefore, this section focuses on the production of biopolyols from lignin using these two techniques.

6.2.2 Liquefaction with Polyhydric Alcohols

Liquefaction is a thermochemical conversion technology where biomass, or concretely lignin, is degraded to small molecular fragments by the application of heat in the presence of a liquid phase and at mild temperatures (200–400 °C) (Kim et al. 2019). Depending of the solvent used, liquefaction technology can be classified into two main groups: hydrothermal liquefaction (HTL) and solvothermal liquefaction (STL) (Zhang et al. 2020a). In HTL, water is the main solvent used, while in STL, non-aqueous solvents such as phenol, tetralin γ-valerolactone, or polyhydric alcohols, such as PEG or glycerol, can be employed (Haverly et al. 2018; Vale et al. 2019).

The STL of lignin with polyhydric alcohols is the main process to obtain biopolyols for PU production. Normally, the solvents used in the process of liquefaction are PEG, glycerol, or 1,4-butanediol, and the catalysts are strong acids, mainly sulfuric acid or in some studies bases, such as sodium hydroxide (Gosz et al. 2018; Vale et al. 2019). The reason of employing sulfuric acid as the principal catalyst is the lower temperature requirement of the process (110–180 °C), while for base catalyst, the temperature needed to obtain similar polyol yields is around 250 °C (da Silva et al. 2019). Raw material-to-solvent ratio, solvent type, catalyst concentration, liquefaction temperature, and time have great influence on acid and hydroxyl numbers and yield of the polyols (Hassan and Shukry 2008).

The STL has been carried out in atmospheric pressure reactors heated by heating mantle at high temperatures (240 °C) and for long residence times (3 h) (Hu and Li 2014). However, these high temperatures and prolonged residence times could decrease the yield of the polyols (Hu et al. 2014). Therefore, as an alternative to the classical heating in the liquefaction processes, microwave irradiation technology has been developed (Amran et al. 2017). Using the microwave irradiation, the heating is faster and more homogeneous so the time needed for completing the liquefaction is reduced to only few minutes (Xue et al. 2015; da Silva et al. 2017, 2019; Gosz et al. 2018).

6.2.3 Oxyalkylation or Oxypropylation

The oxyalkylation pathway, also called oxypropylation, is an etherification process which uses alkylene oxides to produce polyols from lignin (Sardon et al. 2021). In the first stages of this technique, the reaction was a single step in which biomass functionalization and oxypropylation were carried out at the same time. Nowadays, the process consists of two well-defined stages, with functionalization taking place first, followed by oxypropylation (Aniceto et al. 2012). The most commonly used oxirane is the propylene oxide (PO) (Sadeghifar et al. 2012), and the most employed reaction is the anionic ring opening polymerization (AROP) employing KOH as catalyst (Perez-Arce et al. 2020) which is summarized in Fig. 6.3.

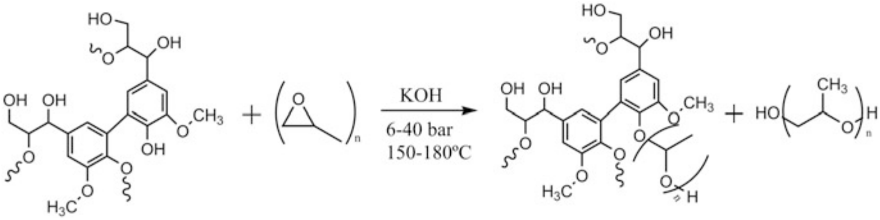

Fig. 6.3 Oxypropylation of lignin through anionic ring opening polymerization under usual reaction conditions

Through this process, the solid lignin is transformed into a polyol soluble in many organic solvents (Glasser et al. 1982). The reason for this is that the oxypropylation reaction is highly selective with the phenolic OH groups which are usually sterically impeded. Thus, these OH groups of lignin are converted to ether groups by reacting with the heterocyclic compounds giving rise to more accessible terminal OH groups (Cateto et al. 2009). Numerous studies have been carried out to transform different types of lignin into suitable polyols for PU manufacture by oxypropylation reaction since Glasser and co-workers did it for the first time in the 1980s (Laurichesse and Avérous 2014). These studies were focused on elucidating the effects of different parameters such as temperature, pressure, lignin/PO ratio, catalyst/PO ratio, or lignin type on the final properties of the polyols (Nadji et al. 2005; Cateto et al. 2009). The reaction can be carried out at temperatures ranging from 150 to 300 °C, being the most common for oxypropylation of lignin between 150 and 180 °C. Pressure ranges from 6 to 40 bar, and the lignin/PO ratio usually varies between 10/90 and 40/60 (w/v), while the catalyst ranges from 1% to 10% (wt%) (Laurichesse and Avérous 2014; Perez-Arce et al. 2020; Sardon et al. 2021).

Ahvazi et al. (2011) performed the oxypropylation of soda lignin from wheat straw using both, one-step and two-step oxypropylation. For the one-step reaction, different catalysts were used (H_2SO_4 and NaOH), while for the two-step reaction, maleic anhydride and propylene oxide were employed and reacted at room temperature for 7 days. They concluded that the polyols obtained through the one-step reaction under alkaline conditions showed the highest content of aliphatic OH (Ahvazi et al. 2011). Following a similar procedure to that described by Ahvazi et al. (2011), in a more recent study, Wu et al. (2021) concluded that an alkali lignin/PO ratio of 2:1 increased the molecular weight, the thermal stability, and the amount of secondary OH of the synthesized polyol. To provide an added value to the pyrolytic lignin, this type of lignin has been oxypropylated using different reaction conditions and varying both, the lignin/PO ratio and the KOH/lignin ratio. It was found that a lignin/PO/KOH ratio of 50/50/5 at 209 °C resulted in a polyol with an hydroxyl index of 703 mg KOH/mg, which is suitable for the synthesis of rigid PU foams (Saffar et al. 2020). Organosolv lignin from exhausted olive pomace was also subjected to a one-step oxypropylation process employing different lignin/PO ratio and KOH concentration. Then, PU foams were synthesized with the obtained polyols, and it was determined that the foam that was processed with a lignin/PO ratio of 15/75 and 5% of catalyst (%w/w) showed the most similar characteristic to commercial foams (Abid et al. 2020). However, the abovementioned reaction conditions could produce an excess of homopolymer, insoluble fractions, and bad odor of the polyol due to the formation of lignin monomers, making the product industrially less desirable (Cateto et al. 2009; Perez-Arce et al. 2020).

To avoid these drawbacks, Perez Arce and co-workers developed a new lignin oxypropylation route that consists in the cationic ring opening polymerization of oxiranes by dissolving lignin in THF (Perez-Arce et al. 2020, 2021b) (Fig. 6.4). The reaction was carried out at room temperature and under atmospheric pressure.

Through this new pathway, they reduced the formation of homopolymer up to 5%, and they were able to control the final properties of the polyols, which makes the

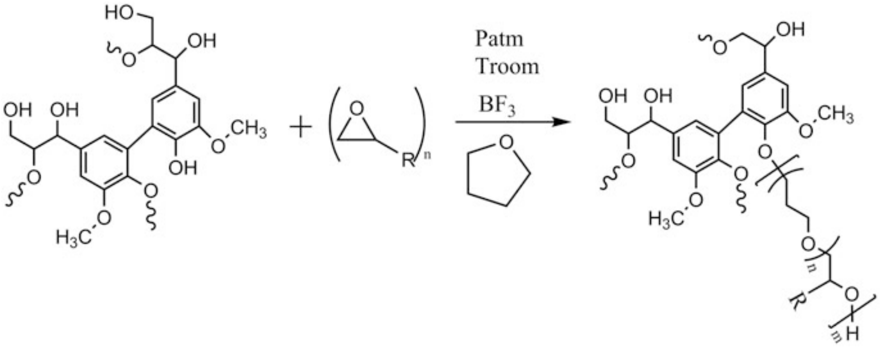

Fig. 6.4 Lignin oxypropylation by cationic ring opening polymerization

Table 6.3 Main PU types based on the different existing criteria

PU classification			
Structure	Origin	Thermal behavior	Product application
Linear	Synthetic	Thermoplastic	Foams
			Fibers
Branch-chained	Biosourced	Thermosetting	CASE (coatings, adhesives, sealants, and elastomers)
Crosslinked			Smart materials (ionomers)

method very attractive for the industry (Perez-Arce et al. 2020, 2021b). Lignin polyols synthesized through this new route were tested for the first time as phase change materials (PCM) for energy storage at low temperatures (Perez-Arce et al. 2021a).

6.3 Types of Polyurethane Products

The PU polymer family is known by displaying a high level of versatility and flexibility with a plethora of different derived products. For this reason, it is not possible to establish a single categorization for these compounds. On the contrary, several classifications can be found depending on the criteria considered. In this sense, in this work, four kinds of categorization are presented taking into consideration the structure, thermal behavior, origin, and product application of the PUs (Table 6.3). These classifications were based on previous works from the literature by Karak (2017) and Akindoyo et al. (2016).

6.3.1 Type of Classifications

6.3.1.1 Polyurethanes Based on Their Structure

Considering their structure representation and the distribution of the functional groups, PUs can be majorly divided into linear polyurethanes (LPU) and branch-chained polyurethanes (BPU). The former PUs are formed by a linear chain with no side urethane moieties attached to the polymer skeleton, whereas the second group is characterized by several urethane units linked to the backbone chain. The pattern and degree of branching can result in different geometries and therefore different types. Among them, hyperbranched polyurethanes (HPU) and polyurethane dendrimers (PUD) can be highlighted. Another group of PU can be found regarding its structure, namely, crosslinked polyurethanes (CPU). In this case, there are not only side chains of urethane groups bond to the backbone chain, but these groups react with other functionalities forming covalent bonds and complex, fixed, and strong structures. The first two types are generally associated with thermoplastic polymers, while the latter one is mostly related to thermosetting. The previously mentioned PU structures are depicted in Fig. 6.5.

6.3.1.2 Polyurethanes Based on Their Thermal Behavior

Commercial PU products can be classified either as thermoplastic or as thermosetting based on their thermal response. Nonetheless, it is possible in some particular cases to find some PU products, which constitute a mixture between the two previous types.

In general, thermoplastics and thermosetting display completely different properties and features as summarized in Table 6.4.

On the one side, PU thermoplastics are a kind of polymer with a high level of flexibility since they can be softened by heat several times (Li et al. 2017). Moreover, they are easily processable upon melting, and therefore, they can be transformed

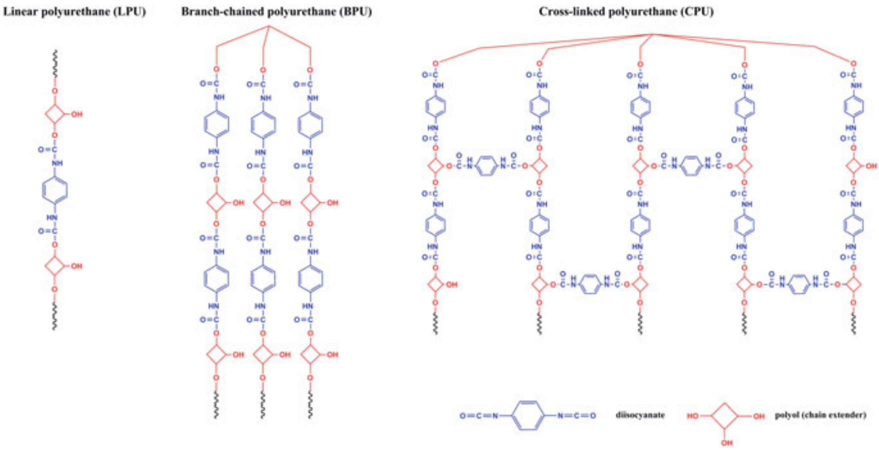

Fig. 6.5 Types of PUs considering their structure and disposition of functionalities

Table 6.4 Main features of PU thermoplastics and thermosetting

Categories	Thermoplastic PU	Thermosetting PU
Structure	Linear	Crosslinked
Processability	Excellent (they can be reshaped upon heating)	Poor (they fixed a permanent structure upon heating)
Applications	Diverse (properties can be tailored from rubber to plastic polymers)	Limited (need to accommodate polymerization on site)
Market	High performance, high added value, innovative products, commodity type	Large volume and commodity type
Industry	Aerospace, healthcare, engineering, and electronic	Construction, automotive, and furniture

through diverse methods, e.g., extrusion injection, compression molding, or solution coating. Chemically, they are defined as multiblock copolymers of linear structure, which are composed of soft and hard segments. These hard segments (ordered domains) are dispersed into the soft ones, and since they are not chemically bond, it can result in microphase separation (An et al. 2021). Notwithstanding, by controlling the composition of each of the segments, their properties can be tailored from soft rubbers to hard plastics (Yao et al. 2021). Their main weakness is the poor thermal stability and limited mechanical strength and aging characteristics (Khalifa et al. 2020).

On the other side, PU thermosetting are polymers with a high level of crosslinking, displaying good mechanical and physical properties (Ding et al. 2020). Unlike the former type, they cannot be reshaped, and once heated, they set a permanent structure owing to the chemical crosslinking reactions (Cao et al. 2017). In this sense, they display some processing limitations, and therefore, they are used predominantly in applications in which the polymerization can be done on site. They are employed specially in commodity and large-size applications, and accordingly, their market is considerably price-sensitive.

6.3.1.3 Polyurethanes Based on Their Origin

This categorization makes distinction between PUs regarding the source from which their raw materials are obtained. On the one hand, those whose components are fossil source-derived are generally named as synthetic PUs. On the other hand, those synthetized by using renewable raw materials or their sub-products, either completely or partially, are known as biosourced PUs. The former type is the most abundant and widespread in industry. Nevertheless, in the last years, there is an ongoing tendency toward the utilization of the latter type, owing to the environmental concerns and health hazards derived from the synthetic products. Moreover, through the development of biosourced PUs, the spotlight can be brought to several topics of great importance nowadays, such as sustainable development, green chemistry, or carbon credit. Consequently, along the different sections of this chapter, special focus is being stressed over these PUs of environmentally friendly nature.

6.3.1.4 Polyurethanes Based on Their Product Applications

In addition to the classifications previously presented, the one mostly found both, within industry and academia, is that oriented toward the PU applications. In this categorization, the stress is made over the PU product manufactured for a certain use and their particular features. Considering these points, four major types of PUs can be distinguished: foams, CASE (coatings, adhesives, sealants, and elastomers), fibers, and smart materials. Traditionally, in all these categories, the PUs have been of synthetic nature, i.e., depending on petroleum-derived raw materials. Nonetheless, in the recent years, the introduction of biosourced and renewable raw materials (as described in Sect. 6.3.2) has been implemented in all the range of different PU products and applications. In this respect, especial attention should be paid to lignocellulosic biomass and more specifically to one of its components that is lignin. In Sect. 6.2, it was already displayed that lignin can be the ideal substitute to synthetic polyols in the reaction of synthesis of PUs, owing to its polyhydroxylated structure and renewable and natural origin.

In the following subsections, the main PU products are presented. Moreover, the introduction of lignin for each intended application (aiming the manufacture of a biosourced product) is described highlighting the comparison to the traditional synthetic PU product. Additionally, the most recent works from the literature related to each PU application product are gathered in table format to point out their prominent advantages and disadvantages.

6.3.2 Polyurethane Foams (PUF)

Foams represent one of the most important products from the PU family. In fact, in 2019, PUF were reported as the largest segment considering the total consumption of PUs in Europe and the USA (Amran et al. 2021). Moreover, their market is said to account for the 65% of the global market of PUs (Peyrton and Avérous 2021). They are an excellent type of porous materials, which generally display low values of density. The conventional production of PUF consists in the complex combination of a polyol, a polyisocyanate, a blowing agent, a surfactant, and a catalyst. In some cases, it is possible the incorporation of other additives, such as fillers or flame retardants, to improve some properties of the foam (Table 6.5).

The polyol and the polyisocyanate are the most important components of the foam formulations. In fact, their contents play a significant role, since they can determine the structure and type of the polyurethane foam synthesized. Thus, their properties can be adjusted by controlling the amounts of these components (Akindoyo et al. 2016). The NCO/OH index is usually considered for this purpose, and it is employed to measure the ratio isocyanate/polyol through their functional groups. The increment of this parameter means an increase of the isocyanate functionalities in detriment of polyol ones. This promotes the formation of more covalent crosslinking, and it results generally in harder and more brittle PUF (Gogoi et al. 2014). On the contrary, the decrease of this variable (higher content of hydroxyl groups compared to cyano ones) leads to more flexible PUF.

Table 6.5 Major component of a PUF formulation

Components	Function	Examples
Polyol	– Primary reaction with polyisocyanate to form the foam	– Polyethylene glycol (PEG) – Glycerol
Polyisocyanate (PI)	– Primary reaction with polyol to form the foam – Secondary reaction with water (humidity) to promote the blowing of the foam	– Toluene diisocyanate (TDI) – Methylene diphenyl diisocyanate (MDI)
Surfactant (SF)	– To regulate and to balance the size and the dispersion of the air bubbles from the initial reactive foaming mixture	– Silicone compounds (silicone oil, TEGOSTAB®)
Catalyst (CAT)	– Promote the reaction of formation of PUs (improved selectivity of polyisocyanate toward polyols) – Shift the reaction equilibrium to the formation of urethanes	– Dibutyltin dilaurate (DBTDL) – 1,4-Diazobicyclo [2.2.2]-octane (DABCO)
Blowing agent (BA)	– Release of gas during foam reaction to start the expansion	– Water – *n*-Pentane, cyclopentane

In general, PUF can be divided into two main types, namely, flexible and rigid foams (Gama et al. 2015). Likewise, they can also be subcategorized into semi-rigid and semi-flexible foams (Furtwengler and Avérous 2018). On the one side, flexible polyurethane foams (F-PUF) are the major commercial product of PU, and they cover the main part of the foam market (Cifarelli et al. 2021). They are obtained when polyols of relatively low molecular weight are employed (until 6000 g/mol), and they display an average functionality higher than 2 and a NCO/OH <1. F-PUF are mainly utilized in furniture, carpet underlays, automotive insides, bed, and transportation cushioning and packaging (Yang et al. 2019). On the other side, rigid polyurethane foams (R-PUF) are produced from polyols of higher molecular weights and higher functionalities (greater than 3). Moreover, they present generally an index NCO/OH ≥ 1. They are mainly applied in the construction and transportation as insulators. In this respect, they are the leading thermal insulators utilized in the market, owing to their low thermal conductivity and density in contrast to other materials such as mineral wool, polymers like polystyrene, or lignocellulose products (Abu-Jdayil et al. 2019).

As mentioned at the beginning of the section for the PU family, there is also an ongoing tendency among the PUF toward the removal of toxic and fossil-dependent components. Thereby, by substituting these with renewable and more natural ones, it is possible to improve the environmental properties and reduce the health-derived risks of the PUF (Błażek and Datta 2019). With this purpose, two approaches are commonly used, namely, the replacement of isocyanates or synthesis of bioisocyanates and the substitution of synthetic polyols. The former way is consisting in either the use of alternatives to polyisocyanates, which can provide the same effect and properties to the foams, e.g., polyamines and polycyclic carbonates (Monie et al. 2020), or the synthesis of polyisocyanates from renewable feedstock such as sugars, oils, or amino acids (Konieczny and Loos 2019). Full disclosure of this approach is presented in the next section of this chapter. The latter one is based on the employment of polyols of renewable nature, such as those obtained from animal or vegetal oils and biomass. However, they can also be obtained from natural polyhydroxylated compounds, e.g., cellulose, lignin, and tannins, or be replaced by them. The main processes of synthesis of polyols from these different sources were already described in the previous section of the present chapter.

From all the previous feedstock, the use of lignin directly as polyol or formerly modified can be highlighted. On the one hand, the use of lignin is preferred for being a low-cost feedstock. In fact, it is obtained as a sub-product in the pulp and paper industry, and it is usually dispose as a residue and burnt (Shrotri et al. 2017). On the other hand, lignin is a widespread and abundant compound with a high level of availability in nature (Low et al. 2021). Consequently, nowadays, a great deal of attention has been devoted to lignin for PUF application in literature (Table 6.6).

Taking into consideration the previous table, some conclusions related to the employment of lignin for the synthesis of PUF can be extracted. Firstly, it can be observed that almost any type of lignin can be implemented in the synthesis of PUF. Nonetheless, KL was abundantly employed among the works from literature. This could be related to the fact that it can be easily precipitated from the black liquor, which is a residue from the pulp and paper industry, and this could influence positively to the price of the final product (Zhu and Theliander 2015). Additionally, OL was also attracting a great deal of attention owing to its high purity and to its environmentally friendly nature (greener process of extraction and sulfur-free lignin) (Luo and Abu-Omar 2017). Secondly, it can be pointed out that lignin is commonly subjected to chemical modification. This is due, among other reasons, to the fact that pristine lignin usually presents a high number of aromatic hydroxyl groups and isocyanate displays a moderately higher selectivity for aliphatic hydroxyl groups over phenolic ones (Karunarathna and Smith 2020). Consequently, lignin should be subjected to chemical/structural transformation, to increment the number of OH groups available for the reaction. From the methodologies used through literature, oxypropylation and liquefaction are preferred, since they are the major reactions for the production of polyols (as commented in Sect. 6.2). By means of these processes, it is possible to reduce the molecular weight of the lignin or/and increase its number of hydroxyl group (Jeong et al. 2021). Both are convenient features for the lignin to be used as polyol in the PUF synthesis. Thirdly, it was seen that the total substitution of the synthetic polyol by lignin is a challenging topic. Therefore, the utilization of certain percentage of additional polyols is commonly needed. In respect to the components selected for the foam formulations and their process of synthesis, they resulted to be similar to the generally used for the synthetic PUF as regard to the data provided in Table 6.6.

Lastly, regarding the properties of the PUF, two main outcomes were detected. On the one hand, it was seen that lignin introduction provided a significant impact to foams. For instance, Flôres et al. (2021) presented that the use of KL affected the

Table 6.6 Lignin-derived PUF works from the literature

Lignin type	Lignin modification	Additional polyol	Components	Synthesis conditions	Reference
KL	–	– PEO/PO triol[a] – PPG diol[b] – mPEG[c]	– TEGOSTAB B 8228 (SF) – DABCO BL11, 33LV (CAT) – Deionized water (BA) – Diisocyanate prepolymer (PI)	– 3000 rpm, 25 °C, 7 s (growing) – 25 °C, 168 h (curing)	Flôres et al. (2021)
KL	Hydroxypropylation (PO) + NaOH	Polyester polyol (STEPANOL PS2352)	– Silstab 2755 (SF) – Jeffcat Z20 (CAT) – Water (BA) – pMDI (PI)	– Vigorous stirring, 25 °C, until growing – 25 °C, 96 h (curing)	Liu et al. (2021)
OL[d]	Oxypropylation (PO) + KOH	Glycerol	– DABCO (CAT) – DMCHA[e] (CAT) – pMDI (PI)	– Vigorous stirring, 25 °C, until growing – 25 °C, 24 h (healing)	Abid et al. (2020)
OL	Oxypropylation (PO) + KOH	1,4-Butanediol	– Silicone oil (SF) – TEDA[f], stannous octoate (CAT) – Deionized water (BA) – pMDI (PI)	– Vigorous stirring, 25 °C, until growing – 25 °C, 48 h (curing)	Li et al. (2020)
KL	Liquefaction assisted by microwave (PEG + glycerol)	Polypropylene glycol triol	– DBTDL, DABCO 331V (CAT) – Water (BA) – MDI (PI)	– 2000 rpm, 25 °C, 6 s (growing) – 25 °C, 48 h (curing)	Mohammadpour and Mir Mohamad Sadeghi (2020a)
SEL[g]	Oxidation (NaOCl)	Polyether polyol	– AK 158 silicone-based (SF) – DBTDL (CAT)	– Stirred magnetically, 10 min – Additional 30 s stirring and left to foam	Wang et al. (2019a)

(continued)

Table 6.6 (continued)

Lignin type	Lignin modification	Additional polyol	Components	Synthesis conditions	Reference
			– Distilled water (BA) – MDI (PI)		
LS	Liquefaction (glycerol)	–	– DC5357 (SF) – Polycat 5, Polycat 8 (CAT) – Water (BA) – MDI (PI)	– 6000 rpm, 25 °C, 10–15 s (growing) – 25 °C, 24 h (curing)	Muller et al. (2018)
KL	Surface functionalization (pMDI)	Polyester polyol (R-23-015)	– Silicone oil (SF) – DABCO, 1,1,1,3,3-pentafluorobutane (CAT) – Water (BA)	– 2500 rpm, 25 °C, 10 s (growing) – 25 °C, 48 h (curing)	Zhang et al. (2018)
AL[h]	Liquefaction (PEG + glycol)	–	– Polymethylphenylsiloxane (SF) – DBTDL (CAT) – Water (BA) – pMDI (PI)	– Vigorous mixing, 25 °C, 30 s (growing) – 25 °C, 48 h (curing)	Oribayo et al. (2017)

[a] *PEO/PO triol* propylene-oxide-polyether triol
[b] *PPG diol* propylene-glycol-polyether diol
[c] *mPEG* methoxy polyethylene glycol
[d] *OL* organosolv lignin
[e] *DMCHA* dimethylcyclohexylamine
[f] *TEDA* triethylenediamine
[g] *SEL* steam explosion lignin
[h] *AL* alkaline lignin

processability and final properties of the foam. In particular, it led to higher level of shrinkage and to an increased resilience of the foams. Likewise, Li et al. (2020) showed that the properties of OL, such as lower molecular weight and higher content of aliphatic groups, effected a reduction and an increment in the density and compressive strength of the foams, respectively. On the other hand, it was confirmed that the implementation of lignin as an alternative to synthetic polyols for PUF did not jeopardize their performance. In fact, lignin-derived PUF were proved to be comparable or even better in some of the properties to the traditional synthetic PUF. In this sense, Abid et al. (2020) showed that PUF with a polyol partly derived from lignin (30%) presented similar characteristics in terms of compressive strength, density, and thermal conductivity to commercial PUF. These results were in agreement with the work of Zhang et al. (2018), who produced PUF derived from KL with a content of 30% in the polyol as well.

6.3.3 Polyurethane Coatings, Adhesives, Sealants, and Elastomers (CASE)

The acronym CASE represents a category of products used in industry, which covers coatings, adhesives, sealants, and elastomers. Due to the excellent range properties displayed by PUs, they are able to meet the wide demands of these applications (Rajput et al. 2014). In fact, PU CASE applications represent another important segment of PU family provided with an advantageous market.

As coatings, PUs are easily deposited over the substrate at ambient conditions, they do not need a process of post-curing, and they are typically aiming a protective and aesthetic effect (Dutta and Karak 2006). Among these coatings, several types can be found (based on the physical state of the polymer and solvent used), namely, solventborne, waterborne, and solid. The major applications of PU coatings are directed to wood, metal, plastic, leather, and textile applications (Alinejad et al. 2019).

PUs have been successfully used as adhesives for many years due to their strong binding properties and high tensile strength and shear (Silva et al. 2010). Nevertheless, it should be considered that their properties are highly impacted by the nature of its constituents, i.e., isocyanate and polyol. They can be classified into one-component systems (heat cured or moisture cured) and two-component systems depending on the phases present in their formulation (Dunky and Pizzi 2002). PU adhesives are typically used in wood-engineered products in applications such as flooring, roofing, wallboard, and door/window, owing to their convenient properties (Somarathna et al. 2018).

PU sealants represent one of the most popular and employed type in industry owing to the advantageous properties of these compounds, such as high level of toughness, simplicity in preparation, and resistance to abrasion (Li et al. 2021). Moreover, another relevant point is the fact that PUs can be tailored into materials, which can adapt to expansion and deformation caused by temperature due to their structure with soft and hard moieties (Shen et al. 2018). They are commonly applied in pavements (concrete and asphalt) to adapt and manage the movement of the slabs (Ahn and Lee 2016).

Finally as elastomers, PUs are usually constituted of long-chain macroglycols of moderate-high molecular weight and low molecular weight diols used as chain extenders, besides the diisocyanate (Karak et al. 2009). They provide a wide range of advantages, such as the high degree of variability of shapes in which they can be molded and their low weight and convenient stress recovery properties (Chattopadhyay and Webster 2009). They are employed in a variety of applications from flooring or interiors in the automotive industry to the shoe industry.

The desire toward more bio-based products has been also developed within these PU applications. In this respect, the incorporation of lignin as polyol substitute has also been implemented with the aim of generating these products with a performance comparable to that of the traditional synthetic ones. In Table 6.7, some of the most relevant works focused on PUs based on lignin for CASE applications are presented.

In regard to the lignin-PU coatings, the employment of different types of lignin was possible. Another important point is the fact that lignin is usually subjected to chemical modification with the aim of improving its reactivity (Zhang et al. 2019) and its selectivity toward the formation of PUs (Chen et al. 2020b). These tendencies were also observed in the lignin-based PUF presented before. The type of coatings found within the works from the literature was predominantly a solventborne system compared to the waterborne one. This is due to the fact that lignin displays a low solubility in water, whereas it can be easily dissolved in organic solvents (Melro et al. 2018). Different amines are used as catalyst of the reaction, and MDI and TDI are majorly selected as isocyanates. The main effects provided by the use of lignin in the coatings were the enhancement of the mechanical (Liu et al. 2013), antimicrobial (Klein et al. 2019a), and antiaging properties (Zhang et al. 2020b). For example, Xie et al. (2021) synthetized lignin-PU-coated papers with double tensile strength in dry state and 40 times-improved tensile strength under wet conditions. Additionally, Mozheiko et al. (1981) confirmed that the use of lignin-PU coating formulation provided an improved performance against weathering compared to that of a coating prepared with synthetic polyols.

Regarding the lignin-derived PU adhesives, the most commonly used type of lignin was KL, owing to availability in industry and convenient properties for the PU synthesis. It should be highlighted that within the literature, lignin for PU adhesives is employed both, in its pristine state and after modification. The former case is the simplest solution for the incorporation of lignin into the adhesive formulation. Nevertheless, in most of the cases, it needs from a previous solubilization of the lignin with organic solvents such as THF (Dos Santos et al. 2021). In the latter case, the modification is utilized as a procedure for the improvement of the reactivity of the lignin and its dispersion into the rest of the components. For instance, Chen et al. (2020c) confirmed the increase of the lignin reactivity after demethylation, provided by the conversion of methoxy moieties of the aromatic groups to phenolic hydroxyls. In respect to the components, it is once more observed that additional secondary polyols are added into the adhesive formulations. The reason for that is the reduction of the brittleness derived from the lignin incorporation (especially at high

Table 6.7 Lignin-derived PU for CASE application works from the literature

Lignin type	PU application	Lignin modification	Components and synthesis conditions	Reference
Commercial lignin	Solventborne PU coating (THF[a]) (paper)	–	– Lignin, HDI[b], TDI, PEG 400 – Mixture at high-speed stirring at 25 ° C – Drying overnight at 105 °C	Xie et al. (2021)
Commercial lignin	Waterborne PU coating (fabric)	–	– WPU[c] (40%), block isocyanate, dispersing agent, and lignin – Mixing at 25 °C and high-speed stirring – Curing 170 °C and 90 s	Zhang et al. (2020b)
OL	Solventborne PU coating (DMF[d])	Oxidation (ozone)	– Lignin, PEG 200, DBTDL, HDI – Stirring at 60 °C and 1 h – Curing at 40 °C, 12 h	Zhang et al. (2019)
KL	Solventborne PU coating (THF)	–	– Lignin, PEG425, MDI, TEA[e] – Mixture at 25 °C – Curing at 35 °C, 1 h	Klein et al. (2019b)
KL	Solventborne PU coating (THF)	Demethylation (Na_2SO_3)	– PEG400, MDI, TEA, lignin – Mixture under constant agitation of components – Curing at 35 °C and 3 h	Klein et al. (2019a)
KL	Waterborne PU coating	Lignin amination (DETA[f], formaldehyde)	– PPG[g], TDI, DPA[h], aminated lignin – Mixture of components with ice amine lignin water (emulsification) – Curing at 25 °C by solvent casting	Liu et al. (2013)
LS	Solventborne PU coating (cyclohexanone)	Oxypropylation (glycerol)	– Lignosulfonate, TEA, TEDA[i], oligoether, MDI – Mixture with	Mozheiko et al. (1981)

(continued)

Table 6.7 (continued)

Lignin type	PU application	Lignin modification	Components and synthesis conditions	Reference
			strong agitation at 25 °C – Drying 50 °C, 2 h	
KL	PU adhesive	Hydroxypropylation (propylene oxide)	– Lignin, castor oil, MDI – Mechanical mixture at 20 rpm for 2 min	Gouveia et al. (2020)
OL	PU adhesive	Hydroxymethylation (formaldehyde)	– Lignin, DBDTL, PEG200, TDI – Magnetically stirring of components – Polymerization of mixture at 25 °C and 2.5 h	Chen et al. (2020b)
KL	PU adhesive	–	– Lignin, PPG 2000, MDI – Mixture under N_2 in round-bottom flask – Polymerization at 85 °C and 2 h – Curing at 25 °C for 24 h	Gadhave et al. (2019)
OL	PU adhesive	Demethylation (TBHDPB[j])	– Lignin, PEG, DBDTL, TDI – Mixture mechanically stirred – Polymerization at 25 °C and 2 h	Chen et al. (2020a)
KL	PU adhesive	–	– Lignin, DBTDL, PEG4000, MDI – Mixture at 25 °C – Curing at 25 °C for 2 days	Wang et al. (2019b)
KL	PU adhesive	–	– Lignin, modified castor oil, MDI – Mixture for 20 rpm, 2 min – Curing 25 °C for 7 days	Tavares et al. (2016)
KL	PU adhesive	Fractionation (MeTHF[k])	– Lignin, TDI – Magnetic	

(continued)

Table 6.7 (continued)

Lignin type	PU application	Lignin modification	Components and synthesis conditions	Reference
			stirring at 25 °C for 30 min – Polymerization at 120 °C for 1 h	Griffini et al. (2015)
EHL[l]	PU elastomer	Liquefaction (NPG[m], EG)	– Lignin, DBTDL, TDI – Mixture by stirring at 25 °C – Drying at 80 °C for 12 h (vacuum)	Sun et al. (2021)
OL	PU elastomer	Hydroxylation (H_2O_2)	– Lignin, PTMEG[n], DBTDL, HDI – Polymerization at 60 °C for 4 h – Drying at 60 °C for 8 h and 80 °C for 6 h (vacuum)	He et al. (2021)
KL	PU elastomer	–	– Lignin, DBTDL, TDI – Mixture with stirring at 100 °C – Curing at 25 °C overnight	Lang et al. (2018)
AL	PU elastomer	Depolymerization (NaOH)	– Lignin, PPGTDI[o] – Magnetic stirring at 25 °C for 10 h – Curing at 120 °C for 2 h	Li et al. (2017)
KL	PU sealant	–	– Lignin, polyglycol, lead and calcium octoate, MDI – Mixture at 25 °C under inert atmosphere (N_2) for 3 min – Curing at 25 °C for 24 h	Feldman and Lacasse (1994)

[a] *THF* tetrahydrofuran
[b] *HDI* hexamethylene diisocyanate
[c] *WPU* waterborne polyurethane
[d] *DMF* dimethylformamide
[e] *TEA* triethyleneamine
[f] *DETA* diethylenetriamine
[g] *PPG* propylene-glycol-polyether

[h] *DPA* dimethylol propionic acid
[i] *TEDA* triethylenediamine
[j] *TBHDPB* hexadecyltributylphosphonium bromide
[k] *MeTHF* methyltetrahydrofuran
[l] *EHL* enzymatically hydrolyzed lignin
[m] *NPG* neopentyl glycol
[n] *PTMEG* polytetramethylene ether glycol
[o] *PPGTDI* poly(propylene glycol) tolylene 2,4-diisocyanate

percentages) and the increase of the ductility of the PU adhesives (Wang et al. 2019b). Finally, concerning the impact of the lignin in the PU adhesive formulations, it can be highlighted the great improvement of both thermal (Tavares et al. 2016; Chen et al. 2020b) and mechanical (Gouveia et al. 2020) properties. Moreover, a high degree of adhesion to different substrates is achieved by the incorporation of lignin into the PU adhesives, which can be even higher to that of standard PU adhesives (Gadhave et al. 2019).

The lignin-based PU elastomers showed again the importance of a previous modification of the lignin oriented toward either an increase of the reactivity or the reduction of the molecular weight. These aspects are important for the appropriate dispersion of the lignin within the rest of the polymeric components. In this respect, He et al. (2021) demonstrated the significant role of the hydroxylation of lignin to obtain polyols of higher reactivity and lower molecular weight. In general, the major strengths provided by the addition of lignin in PU elastomers are the enhancement of the mechanical performance and the thermal resistance of these materials. For example, Sun et al. (2021) presented that the introduction of lignin considerably improved the mechanical properties, owing to the formation of a partial order microphase structure. In other work, Li et al. (2017) proved that with increasing content of lignin, the values of T_g experimented an increment, due the incorporation of more hard segments into the PU elastomer.

Finally, in regard to the lignin-sourced PU sealants, the role of the lignin is majorly as a filler directed to enhance the mechanical properties of the material (Feldman and Lacasse 2012; Lacasse and Feldman 2012). Besides, the lignin significantly influences the process of curing of the material and therefore its thermal properties (Feldman et al. 1988). Another important point is the particle size of the lignin, as it can provide a different effect on the cohesion of the material and accordingly either promote or hinder the reinforcing effect (Feldman and Lacasse 1994).

6.3.4 Polyurethane Fibers (PUFI)

These PU products are synthetic polymeric materials, which are distinguished by displaying an exceptional degree of elasticity or stretchability (Otaigbe and Madbouly 2009). They represent another important segment of the PU polymer industry, with well-known and established products, e.g., Spandex®, also known as

Elastane®. The mentioned product is characterized by having a significant strength and lightness and by having the ability to stretch to almost 500% of its length (Hu et al. 2008). Considering their structure, PUs are known to be copolymers composed of alternate segments of polyether diol/polyester (soft) and PU-urea (hard). The mentioned units are usually subjected to microphase separation into hard and soft segments depending on glass transition temperature (Huang et al. 2019). This effect is the one accountable for the outstanding elastic properties. In respect to the production of these PU fibers, there are four different methods generally considered: dry, wet, reactive, and melt spinning. However, dry spinning continues to be one whose implementation is most widespread, owing to high level of production and fiber quality (Jing 2020).

Regarding the trend toward the production of bio-based PU, in this particular case, the field of application of PU fibers with the incorporation of lignin is rather limited. The reason for that is that not all polymers either natural or synthetic can be successfully transformed into appropriate fibers. In fact, they must meet certain criteria, among which displaying linear and flexible chains can be highlighted (Hamidreza 2016). In general, lignin is introduced in bio-based PU as substitute of the synthetic polyols. Notwithstanding lignin replaces polyols in PU structure (soft segment of the PU), in PU fibers, it generally plays the role of hard segment owing to its aromatic structure (Tavares et al. 2016). Accordingly, the production of PU fibers with sufficient and convenient elasticity and/or stretchability will be hindered, since the contribution of the lignin would be more oriented toward the improvement of the mechanical strength.

6.3.5 Polyurethane Smart Materials (PUSM)

These type of PUs are a singular family of materials, which are defined by having the ability of inherently performing special functions under certain stimulus (Thakur and Karak 2015). Within these PUs, different categories can be found depending on the special function that they can perform, e.g., shape memory, self-cleaning, or self-healing materials. A current tendency with these smart materials is based on the introduction of ions into the PU skeleton to achieve these special features. The incorporation of these ions significantly affects the phase structure of the polymer, and it changes completely its properties (Deka et al. 2015). As previously mentioned, PUs are characterized by alternately arranged soft and hard segments. Nevertheless, when it comes to the introduction of ions, the structure gets more complex, owing to the presence of anions and cations introduced by the reaction of compounds with ion forming functions, e.g., carboxylic or sulfonic (Król and Król 2020). Three main types can be distinguished, depending on the ions introduced into the PU backbone structure, namely, anionomers, cationomers, and zwitterionomers (Jaudouin et al. 2012).

Concerning the application of lignin in this type of PU products, currently, it is not showing a great degree of development. This is due to similar limitations to the ones described in the previous category of PU applications. However, it is a field with great potential, especially considering the fact that lignin fractions can be obtained with functionalities, such as carbonyl or sulfonic ions, upon a process of lignin modification.

Regardless of PU classification, they are usually produced from non-renewable resources. However, the polyols, as has been described in the previous section, can be replaced by natural derived compounds. In addition, the other main compound in PU synthesis, the isocyanates, which are very hazardous, can also be substituted by bio-based isocyanates, or even PUs without isocyanates can be produced.

6.4 Greener Alternatives for Polyurethane Synthesis

As mentioned above, PUs are a versatile family of polymers which are widely used in the modern society as foams (rigid or flexible), elastomers, composites, paints, coatings, and adhesives.

These compounds are formed by polyaddition reactions between isocyanates and polyols forming the hard and soft segments of PUs, respectively (Crescentini et al. 2019). Since both are usually obtained from petrochemical resources, the environmental impact of the PU industry is an unfinished business for the chemical industry if it wants to comply with the regulations that are becoming more and more restrictive. Nevertheless, as discussed in Sect. 6.2, the PU industry is incorporating polyols from renewable sources to mitigate these environmental effects. In fact, the main drawback of the PU industry lies in the key component of the reaction: the isocyanates. There are several reasons for this: on the one hand, the petrochemical origin of the isocyanates and on the other hand, the toxicity of isocyanates and of the reaction that is generally used to obtain them, the phosgenation reaction. The former contributes to the environmental degradation, while the latter is the cause of illness and even death due to the lethal and reactive phosgene gas which is employed (Ghasemlou et al. 2019).

MDI and TDI are the most employed isocyanates in the PU industry with demands of 61.3% and 34.1%, respectively (Kreye et al. 2013). Although both are less hazardous than the methyl isocyanate, responsible for the Bhopal disaster in 1984 (Andersson et al. 1988), MDI and TDI are classified as carcinogenic, mutagenic, and reprotoxic (CMR), representing an important health risk for workers of the PU industry (Stachak et al. 2021). The most commonly diseased are those related to the respiratory system and skin problems; in fact, elevated concentration of diisocyanates can affect the mucous membranes producing rhinitis (Świerczyńska-Machura et al. 2015), and diisocyanates are also responsible for occupational asthma (Mapp et al. 1994). Although the inhalation of these compounds is the primary responsible for the occupational asthma, skin contact may also cause this disease, since, despite preventive measures taken to avoid inhalation, asthma cases among workers are still occurring (Bello et al. 2007). Apart from asthma, other less common pathologies, such as hypersensitivity pneumonitis, rhinitis (Musk et al. 1988), and contact dermatitis (Frick et al. 2003), can be caused through exposure and contact with isocyanates. Thus, in recent years, new methods are emerging in the search for safer and more environmentally friendly alternative in the PU production, such as the synthesis of bio-based isocyanates (Mhd. Haniffa et al. 2021).

6.4.1 Bio-Based Isocyanates

In an attempt to increase the bio-based content of PUs, the synthesis of bio-based isocyanates employing different bio-based chemicals (amino acids, sugars, furans, vegetable oil, cashew nutshell liquid, and lignin) obtained from biomass such as wood, agricultural products, solid waste, and algae is currently being studied (An et al. 2021). For instance, L-lysine amino acid was used to synthesize both methyl and ethyl ester L-lysine diisocyanates (Nowick et al. 1992; Sanda et al. 1995), which are of great interest for the manufacture of PUs for medical applications (Guelcher et al. 2008; Mathew et al. 2015). A further amino acid used to synthesize isocyanates is the Fmoc-amino acid azide (Patil et al. 2003). Different diisocyanates have been synthesized from sugars and their derivatives. Pentamethylene diisocyanate (PDI), created by the Covestro company from glucose, was the first commercialized bio-based diisocyanate (Parcheta and Datta 2017). Isosorbide and dianhydrohexitol, both obtained from sorbitol, were also used to synthesize diisocyanates for PU production (Bachmann et al. 2001; Zenner et al. 2013). It was Garber in 1962 the first who synthesized furan-based diisocyanates employing 2,5-dimethylfuran and 2,5-dimethyltetrahydrofuran (Garber 1962). From methyl-2-furancarboxylate (methyl pyromucate) using the Curtius rearrangement, different diisocyanates could be obtained (Cawse et al. 1984; Nielek and Lesiak 1988). The synthesis of isocyanates from vegetable oil avoiding the phosgenation reaction is currently being studied. For instance, Hojabri et al. (2009, 2010) synthesized two different diisocyanates employing oleic acid via the Curtius rearrangement. Plant oil triglyceride (soybean oil) was used to produce polyisocyanates by two different routes. In the first one, a bromination reaction of the allylic positions followed by a reaction with AgNCO to convert the brominated species into isocyanate bonds was employed (Çayli and Küsefoğlu 2008). On the other hand, a one-step reaction was carried out in which the methyl oleate was reacted with AgNCO together with I_2 (Çayli and Küsefoğlu 2010). Methyl 10-undecenoate has also been studied as a precursor for the synthesis of diisocyanates in the manufacture of PUs (More et al. 2013).

In an effort to replace petro-based aromatic isocyanates such as MDI or TDI among others, the synthesis of bio-based isocyanates derived from aromatic compounds from biomass was also studied. Thus, raw materials like cashew nutshell liquid (CNSL) or lignin were employed for this purpose. CNSL is a viscous liquid which is mainly composed of anacardic acid, cardanol, cardol, and 2-methyl cardol and is obtained as a by-product during the processing of cashew nut (Paramashivappa et al. 2001). Cardanol, due to its aromatic ring, phenolic OH group, and unsaturated pentadecenyl chain, possesses a great reactivity that can be exploited as a precursor in the synthesis of monomers (Mele and Vasapollo 2008), such as diisocyanates among others (Attanasi et al. 2006). Among the lignin-derived aromatic compounds, vanillin, vanillic acid, and syringic acid are reported as precursors in the synthesis of bio-based aromatic isocyanates. Vanillic acid was employed to obtain through the Curtius rearrangement two diisocyanates, namely, bis(4-isocyanato-2-methoxyphenoxy)alkane (Kuhire et al. 2017) and 1,4-bis (4-isocyanatao-2-methoxyphenoxy)butane (De Haro et al. 2019). (*E*)-1,2-bis (4-cyanato-3-methoxyphenyl)ethene and 1,2-bis(4-cyanato-3-methoxyphenyl)ethane were synthesized employing vanillin bisphenols as precursors (Harvey et al. 2015), while bis(4-isocyanatao-2,6-dimethoxypehnoxy)alkane diisocyanate was obtained through the Curtius rearrangement of syringic acid (Kuhire et al. 2017).

For a better understanding, the abovementioned compounds as well as the reaction that was employed are summarized in Table 6.8.

Nevertheless, although this approach reduces the use of petroleum-derived compounds, in many cases, it is still necessary the use of phosgene, while in the Curtius reactions, harmful azide group intermediates, such as acyl azide or diacyl azide, are involved (Ghasemlou et al. 2019).

For this reason, on the road to a more environmentally friendly PU production, non-isocyanate polyurethanes (NIPU) have emerged as the most attractive alternative, as this route avoids the use of the hazardous isocyanates and allows the use of a large number of precursors derived from renewable resources (Ghasemlou et al. 2019). In addition, companies involved in PU production will be able to comply with the REACH regulation adopted by the European Chemicals Agency, which was established to improve the protection of human health and the environment against the risks associated with chemical substances and mixtures (Gomez-Lopez et al. 2021).

6.4.2 Non-isocyanate Polyurethanes (NIPU)

Since the first NIPU developed by Groszos and Drechsel (1957) through the aminolysis of cyclic carbonate, several routes for NIPU production were described (Fig. 6.6), of which polycondensation, rearrangement, ring opening polymerization, and polyaddition are the most important ones (Stachak et al. 2021). Nevertheless, not all these routes could satisfy the requirements of REACH regulation; as a matter of fact, polycondensation pathway for NIPU production involves phosgene or its derivatives to synthesize the polycarbamate needed to react with a polyol through a transurethanization reaction. In addition, elevated temperatures are necessary to carry out the reaction in which by-products such as HCl or alcohols are generated. All these factors make the polycondensation route industrially unattractive (Ghasemlou et al. 2019).

The synthesis of NIPUs through rearrangement also presents drawbacks, viz., the use of hazardous acyl azides, carboxamides, and hydroxamic azides and the use of halogens such as bromine or chlorine (Unverferth et al. 2013). Moreover, the fact that isocyanate is produced as intermediate during the reaction reduces the industrial interest of this approach (Stachak et al. 2021). The third method abovementioned, the ring opening polymerization, also involves toxic products such as phosgene or

Table 6.8 Bioisocyanates from bio-based compounds

Precursor	Reaction	Compound	Reference
L-Lysine	Phosgenation	L-Leucine methyl ester isocyanate	Sanda et al. (1995)
L-Lysine	Phosgenation	L-Leucine ethyl ester isocyanate	Nowick et al. (1992)
Fmoc-amino acid	Curtius rearrangement	–	Patil et al. (2003)
Glucose	Phosgenation	PDI	Parcheta and Datta (2017)
Dianhydrohexitol	Phosgenation	1,4:3,6-Dianhydro-2,5-dideoxy-2,5-diisocyanato (D-sorbitol; L-iditol; D-mannitol) 1,4:3,6-Dianhydro-2,5-dideoxy-2,5-dithioisocyanato-L-iditol	Bachmann et al. (2001)
Isosorbide	Curtius rearrangement	Isosorbide-based diisocyanates	Zenner et al. (2013)
2,5-Dimethylfuran 2,5-Dimethyltetrahydrofuran	Phosgenation	5-Isocyanatomethyl-2-furfuryl isocyanate 2,2′-oxy dimethylene bis (5-isocyanatomethyl furan) 5-Isocyanatomethyl-2-tetrahydorfurfuryl isocyanate 2,2′-oxy dimethylene bis (5-isocyanatomethyl tetrahydrofuran)	Garber (1962)
Methyl-2-furancarboxylate	Phosgenation	Methylenebis (2,5-furandiylmethylene) diisocyanate and ethylidenebis (2,5-furandiylmethylene) diisocyanate Isopropylidenebis (2,5-furandiylmethylene) diisocyanate; 5,5′-methylenebis (2,5-furandiyl) diisocyanate-and ethylidenebis (2,5-furandiyl) diisocyanate	Cawse et al. (1984)
Methyl-2-furancarboxylate	Curtius rearrangement	2,5-Diisocyanatofuran	Nielek and Lesiak (1988)
Oleic acid	Curtius rearrangement	1,7-Heptamethyelene diisocyanate	Hojabri et al. (2009)
Oleic acid	Curtius rearrangement	1,16-Diisocyanatohexadec-8-ene	Hojabri et al. (2010)

(continued)

Table 6.8 (continued)

Precursor	Reaction	Compound	Reference
Plant oil triglycerides	Substitution of allylic bromides with AgNCO	Soybean oil isocyanate	Çayli and Küsefoğlu (2008)
Plant oil triglycerides	One step synthesis	Soybean oil iodo isocyanate	Çayli and Küsefoğlu (2010)
Methyl 10-ondecenoeate	Diacyl hydrazide intermediate	1,8-Diisocyanatooctane 1-Isocyanato-10-[(isocyanatomethyl)thio] decane	More et al. (2013)
Cardanol	Obtained as intermediate during the Curtius rearrangement	–	Attanasi et al. (2006)
Vanillic acid Syringic acid	Curtius rearrangement	Bis(4-isocyanato-2-methoxyphenoxy)alkane Bis(4-isocyanatao-2,6-dimethoxypehnoxy)alkane diisocyanate	Kuhire et al. (2017)
Vanillic acid	Curtius rearrangement	1,4-Bis(4-isocyanatao-2-methoxyphenoxy)butane	De Haro et al. (2019)
Vanillin	Electrochemical route and McMurry coupling reaction	(*E*)-1,2-bis(4-cyanato-3-methoxyphenyl)ethene 1,2-Bis(4-cyanato-3-methoxyphenyl)ethane	Harvey et al. (2015)

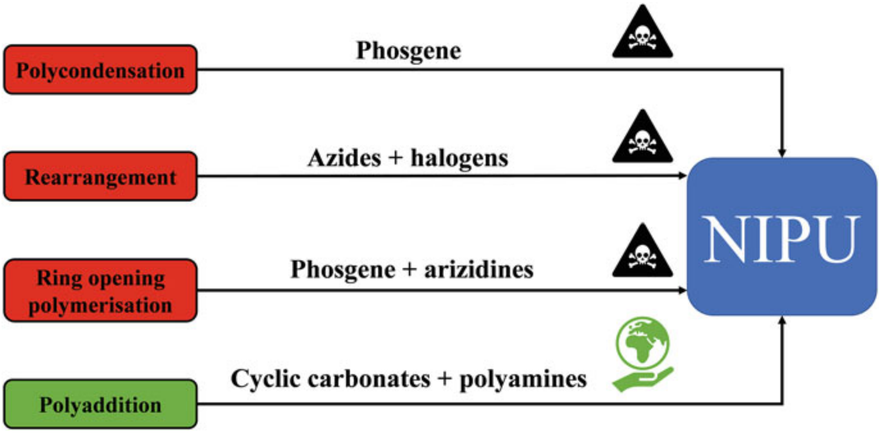

Fig. 6.6 Pathways for the synthesis of NIPUs

aziridines (Chen et al. 2017), and elevated temperature is also necessary to increase the effectiveness of the reaction (Cornille et al. 2017).

However, among all the options presented, it is the latter, the polyaddition pathway, which has attracted the greatest interest in recent years (Gomez-Lopez et al. 2021). This is due to the following factors: the amines used can be bio-based, the poly(cyclic carbonate)s are non-toxic, they can also be bio-based, and they are not sensitive to moisture, making their storage less dangerous (Llevot and Meier 2019). Furthermore, since the reaction between cyclic carbonates and amines does not generate volatile compounds, it is possible to use it for coating applications (Ghasemlou et al. 2019).

6.4.3 Synthesis of NIPUs Through Polyaddition Between Cyclic Carbonates and Amines

The reaction between cyclic carbonate and amine takes place in three steps (Fig. 6.7). First, the amine attacks the carboxyl group of the cyclic carbonate. This is followed by deprotonation of the tetrahedral intermediate and elimination of the hydrogen ions, and finally, the carbon-oxygen bond is broken, resulting in the NIPU (Garipov et al. 2003). In this reaction, cyclic carbonate could be considered as the main constituent. As mentioned in the previous point, both cyclic carbonates and amines can be synthesized employing bio-based routes, by transforming a variety of bio-based compounds into the desired carbonates and amines through different synthetic routes (Ghasemlou et al. 2019).

6.4.3.1 Synthesis of Cyclic Carbonates from Bio-Based Resources

The transesterification of diols with alkylene carbonates, catalytic carbonization of epoxides with CO_2, and catalytic reaction of CO_2 with oxiranes and dialcohols, among others, are the three classical routes for the production of cyclic carbonates (Bähr et al. 2012; Martín et al. 2015). Notably, the last two routes, those using CO_2 as feedstock, have attracted a great deal of interest, as they use one of the main contributors to the global warming to produce useful chemicals with a low carbon footprint, being the epoxide pathway the most attractive for industry (Llevot and

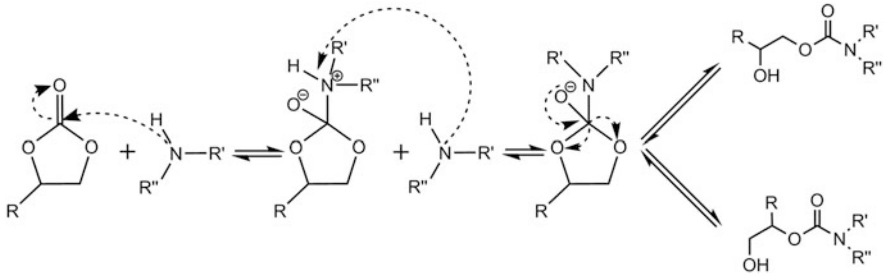

Fig. 6.7 Formation of NIPU through the reaction between cyclic carbonate with an amine

Meier 2019). However, although these pathways are the most employed to produce cyclic carbonates, due to the necessity of greener routes, several renewable raw materials have been employed to synthesize cyclic carbonates. These include compounds from vegetable oil, polyols, terpene derivatives, and aromatic derivatives, such as cardanol, and compounds from lignin (Ghasemlou et al. 2019).

Lignin and its derived compounds could be extremely interesting precursors for the synthesis of bio-based cyclic carbonates, mainly due to their aromatic nature and the reactivity of their multiple hydroxyl groups. In this sense, a creosol-based bis (cyclic carbonate) was prepared as follows. Creosol was treated with lignosulfonic acid to synthesize the bisphenol which was then reacted with epichlorohydrin obtaining a bisepoxide monomer. After that, the bisepoxide was subjected to a cycloaddition reaction with CO_2 employing tetrabutylammonium bromide (TBAB) and benzyltriethylammonium chloride ($BnET_3NCL$) phase transfer catalysts (Chen et al. 2015). From syringaldehyde, which can be obtained from lignocellulosic biomass, a bis-epoxy syringaresinol was produced in order to use it as a precursor for the synthesis of a syringaresinol bis(cyclic carbonate). The bis-epoxy syringaresinol was finally reacted employing lithium bromide in DMF at 80 °C under 20 bar of CO_2 for 24 h to obtain the cyclic carbonate (Janvier et al. 2017). Vanillin can be obtained through chemical synthesis employing guaiacol from the petrochemical industry or lignin or extracted from the beans of vanilla orchid (Fernández-Rodríguez et al. 2019). This flavoring compound can be used as precursor for bio-based building blocks, including bis(cyclic carbonate)s. Fache et al. (2014) synthesized three cyclic carbonate compounds from three epoxides obtained from compounds derived from vanillin, namely, methoxyhydroquinone, vanillic acid, and vanillyl alcohol. Ferulic acid is another lignin-derived compound which was employed to produce a bis(cyclic carbonate). Ferulic acid was first converted into a bis-epoxide by glycidylation via a chemo-enzymatic reaction and then transformed into a bis(cyclic carbonate) through a reaction under CO_2 atmosphere (Ménard et al. 2017).

However, since these compounds are difficult to separate from the lignin molecule, commercial model reagents were used in the above-described cases. In addition, in recent years, the use of different types of lignin for the synthesis of cyclic carbonates is being studied. In this way, OL from beech wood was converted into a cyclic carbonate through a two-step reaction. First, the organosolv lignin was oxyalkylated with glycerol carbonate and then transesterified with dimethyl carbonate in DMSO (Kühnel et al. 2018). In another study, soda lignin and KL were first epoxidized employing epichlorohydrin at 70 °C for 3 h and under constant stirring, and then through a 20-h coupling reaction with CO_2 at 80 °C, they were converted into cyclic carbonates (Salanti et al. 2016). Softwood KL, under the trade name of "BioChoice lignin," was oxyalkylated with glycerol carbonate and then reacted with dimethyl carbonate resulting in a cyclocarbonated lignin (Sternberg and Pilla 2020). LS was also studied as a precursor for the synthesis of cyclic carbonates to produce NIPUs. Mimini et al. (2020) employed beech LS for this purpose. In their study, LS reacted with glycerol carbonate to etherify it and then transesterified with dimethyl carbonate to obtain the final cyclic carbonate.

6.4.3.2 Synthesis of Polyamines from Bio-Based Resources

Similar to the synthesis of bio-based cyclic carbonates, several bio-based resources are available to synthesize polyamines. Among them, amino acids, vegetable oil derivatives, sugar derivatives, and cardanol and lignin derivatives are the most commonly used (Ghasemlou et al. 2019). Unfortunately, in the case of lignin, due to the complex reactions involved in the depolymerization process, there are limited options to produce amines directly from lignin. Therefore, current efforts are focused on the use of lignin-derived compounds. However, only vanillin and syringaldehyde have attracted some interest (Froidevaux et al. 2016). In fact, the reaction between an aldehyde and an amine, known as Schiff base, to lead a secondary aldimine is a well-known reaction (Fache et al. 2015). Fache et al. (2014) obtained three different diamines, using three previously allylated vanillin precursors through a thiol-ene coupling reaction.

6.4.3.3 Lignin-Based Poly(Hydroxyurethane)S (PHUs) Via Polyaddition Pathway

As mentioned above, lignin is the second most abundant renewable polymer after cellulose and the most abundant renewable phenolic polymer on earth. Therefore, due to its availability, renewability, and low cost, lignin and its derivatives could replace many petroleum-based precursors in a wide range of areas of the chemical industry. Among others, lignin and certain of its derivatives have been employed for the synthesis of NIPU. The polyaddition route employing lignin as precursor was used to synthesize different thermoplastic and thermosets. Of these, thermosets are the most reported compounds. In this way, Sternberg and Pilla (2020) processed a foam by reacting a lignin-based cyclic carbonate with a diamine. The resulting foam had a high bio-based content, shape memory, and good thermal and mechanical properties. Resins which are another type of thermosets were also reported employing different lignins. Thus, soda lignin from herbaceous species was used to prepare a thermoset resin. The process consisted in the reaction of the previously synthesized cyclic carbonated lignin with 1,12-diaminododecane in the presence of poly(ethylene glycol) bis(cyclic carbonate) (Salanti et al. 2017). Enzymatic hydrolysis lignin from corncob was used to produce a thermoplastic composite. Due to its excellent mechanical and thermal properties, high reprocessability and recyclability, shape memory, and self-healing properties, this new material could potentially be used in a wide range of applications (Zhao et al. 2021). LS is also a viable raw material to produce PHU, even though the application areas may differ from those of KL or OL. This is due to the special properties of LS, e.g., HSO_3 content, water solubility, and relatively high hydrophilicity (Mimini et al. 2020). In addition, lignin derivatives, such as ferulic acid, syringaresinol, and creosol, were also employed in PHU production. Ménard et al. (2017) were able to synthesize different PHU employing ferulic acid as a precursor of cyclic carbonates, which reacted with different amines resulting in various thermoplastic and thermoset materials. Similarly, but utilizing syringaresinol as the precursor of the cyclic carbonates and using different amines, a new set of thermoplastic and thermoset compounds were synthesized (Janvier et al. 2017). In another study, creosol-based bis(cyclic carbonate) was employed to produce NIPU with a great content of amorphous region (Chen et al. 2015).

6.5 Life Cycle Assessment and Techno-Economic Analysis of Lignin Polyurethanes

As mentioned above, as legislation becomes more restrictive and the environmental awareness of society increases, science is engaged in the search for new raw materials to make existing products, such as PUs, more sustainable and environmentally friendly. However, scientists must be able to ensure a safe, responsible, and sustainable commercialization of these new products. Therefore, it is necessary to determine whether the transition to these new raw materials presents a lower environmental impact than the one they are intended to replace (Bajwa et al. 2019). For this purpose, the life cycle assessment (LCA) becomes an essential tool for a comprehensive environmental evaluation of a product. However, there are some drawbacks that make the interpretation of an LCA a complicated and delicate task. For instance, different LCA tools can be employed to perform these studies, which require the correct choice of the allocation methods as well as the impact categories to be studied (Sillero et al. 2021b). On the other hand, LCA studies are often not based on the knowledge of product development experts, but rather on the knowledge and data to which experts have access (Lettner et al. 2018). In addition, in the early stage of new technologies and product development, as in the case of new lignin-derived materials, the limited data and knowledge and the continuous product modification make it difficult to perform a full LCA, so a more simplified approach is often used (Hetherington et al. 2014).

Regarding lignin, despite the huge number of studies conducted over the last years on its conversion into high value-added products, LCA studies in this area have been comparatively scarce. Moreover, most of these studies focused on the use of lignin to produce chemical compounds, such as phenolics, and fuels (Bajwa et al. 2019). However, some studies have demonstrated that the use of lignin in the synthesis of some polymers, such as PUFs, is environmentally preferable to some petroleum-derived compounds (Kulas et al. 2021). Manzardo et al. (2019) performed a full cradle-to-grave study for PUFs employing KL-derived biopolyols and concluded that they are not always a better choice than their fossil counterparts. In fact, they showed lower non-renewable energy use and lower GHG emissions, while indicators such as ozone depletion potential and marine eutrophication were higher. On the other hand, through sensitivity analysis, they demonstrated that the density and conductivity of foams were determining parameters which had a great influence on global impacts, confirming that the use of a renewable raw material is not sustainable in itself if comparable properties to fossil-based foams are not obtained. Kulas et al. (2021) used high molecular weight fractions obtained from the lignin fractionation through an ALPHA process to synthesize polyurethane foams and concluded that greenhouse gas emissions were lower or similar to those observed from fossil resources. Recently, Arias et al. (2022) investigated through LCA the environmental profile of different NIPU adhesives using four different raw materials, namely, tannins, soybean, KL, and OL. They concluded that the use of OL for the synthesis of NIPU adhesives showed the best environmental behavior than those obtained with the other raw materials and even better than those of fully industrially optimized synthetic adhesives.

The techno-economic analysis (TEA) represents another useful instrument to guarantee a secure, responsible, and sustainable commercialization. TEA provides an estimation for the major parameters of an industrial plant devoted to certain processes such as the performance, emissions, and costs (Frey and Zhu 2012**).** In fact, it is a very important tool to assess the feasibility of scaling up any process, which has already proven to be successful in the laboratory scale. It has already been disclosed that one of the main approaches for the production of polyurethane from lignin is its use as a polyol substituent. In general, this is accomplished by means of a process of liquefaction which yields lignin-based polyols that can be used into the PU formulation directly. Owing to the success of this approach and the interest on the production of more environmentally friendly polyurethanes, in the recent years, some works have been devoted to the assessment of techno-economic aspects of this process (Benali et al. 2016). The majority of the works display a scenario in which the production of biopolyols for the PU production is not the only process. Instead, they propose a model of biorefinery with integrated processes, where lignocellulosic biomass, and more specifically lignin, is valorized for the production of the different high value-added applications (Wenger et al. 2020). In this sense, Kulas et al. (2021) depicted a process of conversion of waste lignin with ethanol toward three main applications, namely, carbon fibers, polyurethane foam, and activated carbon production. They proved that integration of several lignin-converted products into the same biorefinery could reduce the market risks associated with the uncertainty of the lignin-derived product prices. Concerning the production of PU from lignin, in their study, they estimated a significantly high year profit ($85.7MM), owing to the high quantity and low per unit profit of this lignin application. Moreover, they predicted a year production of 4.4 MM tons, which would be able to satisfy almost the 17% of the market. Another study by Ou et al. (2021) presented a model, where the production of lignin-derived polyols for PU is combined with production of xylitol through the hemicellulose valorization. In fact, they confirmed that in the scenario, in which polyols and xylitol were produced, the overall operating costs were significantly reduced as both by-products brought considerable credit to the biorefinery and high added value. In addition to that, they found that, despite the capital investment required for the polyol production, the high values achieved outweighed the capital costs. This was due to the low heating demand of the polyol production process compared to the one of xylitol.

In regard to these data, it can be seen that from the economic and technical point of view, the scaling up of the conversion of lignin for the PU production displays a great potential as a feasible process. However, there are also some limitations inherent to the process and raw materials employed, as pointed out from the sensitivity analyses performed by these authors. The constraints are generally related to the yield of lignin isolated or that of the conversion of the lignin to polyols and to the level of substitution of lignin-derived polyols into the PU formulation (Kulas et al. 2021). Another important factor is the uncertainty of the operating costs, since the prices of lignin-derived products, such as the polyols and the final polyurethanes, are considerably subjected to high variations. This is due to the fact that generally the prices of these products are linked to petroleum market fluctuations and market supply and demand (Dessbesell et al. 2017).

Nevertheless, there are very few studies on both LCA and TEA in this area, and more extensive research is needed to determine whether the use of lignin for the synthesis of polyurethanes is environmentally and socially beneficial.

6.6 Conclusions

Nowadays, the PU industry is of great importance with a global market of $69.2 billion net worth in 2019 and an estimated growth of about 5.0–5.6% per year by 2025. Generally, PUs are synthesized by polyaddition reactions of hydroxyl containing components, mainly polyols and isocyanates. In most of the cases, these compounds are petroleum derived, and in the case of isocyanates, they are also very hazardous. Therefore, new ways for the production of PUs are being investigated which are both environmentally sustainable and less hazardous.

In this sense, the use of renewable resources, such as lignin, is gaining importance. On the one hand, the use of lignin or lignocellulosic biomass to substitute petroleum-derived polyols has been investigated, and many research works have obtained promising results. Different routes have been proposed, but lignin (or biomass) liquefaction and oxyalkylation are the main techniques to produce polyols from lignin. On the other hand, bio-based isocyanates or the production of PUs without isocyanates is another research field. Amino acids, sugars, furans, vegetable oil, and lignin have been used to produce bio-based isocyanates. However, usually in the reaction to produce these isocyanates, the use of phosgene is still necessary, or harmful azide group intermediates, such as acyl azide or diacyl azide, are involved. Thus, avoiding the use of isocyanate to produce the so-called NIPUs has emerged as the most attractive alternative. Nevertheless, some the methods that do not use isocyanates still produce harmful intermediates so the polyaddition pathway, which uses non-toxic cyclic carbonates and amines, is the most promising route to synthetize NIPUs.

In conclusion, many efforts have been made to find alternative ways to produce PUs. These new routes intend to use renewable compounds such as lignin and use processes in which dangerous compounds are not needed or produced. With all this, future work will be aimed at optimizing the use of lignin as a substitute for polyols and the production of NIPUs that have the same characteristics and performance as the PUs which are currently produced employing petroleum-derived compounds. In addition, more extensive research is needed to determine whether the synthesis of these greener PUs is environmentally and socially beneficial and economically competitive.

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Biobased Graphene for Synthesis of Nanophotocatalysts in the Treatment of Wastewater: A Review and Future Perspective

7

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Abbreviations

Ag^+	Silver
AgCl	Silver chloride
AO	Acridine orange
Au	Gold
Bi_2O_3	Dibismuth trioxide
C_3N_4	Carbon nitride
Ca^{2+}	Calcium
CB	Conduction band
CdS	Cadmium sulfide
Ce^{3+}	Cerium
CeO_2	Cerium dioxide
CO_2	Carbon dioxide
Co^{2+}	Cobalt
Cr^{3+}	Chromium
Cu	Copper
Cu^{2+}	Copper
CuO	Copper oxide

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DCDA	Dicyandiamide
DSSC	Dye-sensitized solar cell
EtOH	Ethanol
Fe^{2+}	Iron
Fe_3O_4	Iron oxide
$FeCl_3$	Ferric chloride
G	Graphene
GCS	Graphitic carbon sheet
GO	Graphene oxide
h^+	Holes
H_2O	Water
H_2O_2	Hydrogen peroxide
$H_2PO_4^-$	Dihydrogen phosphate
KOH	Potassium hydroxide
MB	Methylene blue
MG	Malachite green
Mn^{2+}	Manganese
MnO_2	Manganese dioxide
Mo_2C	Molybdenum carbide
MV	Methyl violet
NCPCs	Nanocomposite photocatalysts
NH_4	Ammonium
Ni^{2+}	Nickel
NPs	Nanoparticles
OH	Hydroxyl radicals
Pt	Platinum
RGO	Reduce graphene oxide
RhB	Rhodamine B
SnO_2	Tin dioxide
TiO_2	Titanium oxide
TSS	Total suspended solid
VB	Valence band
Zn^{2+}	Zinc
ZnO	Zinc oxide
ZrO_2	Zirconium dioxide

7.1 Background

In the last few years, process implementation for the reusability and reclamation of wastewater by the substantial removal of pollutant such as pathogen, organic dyes, etc. gathers potential attention due to scarcity of water which arose as a consequence of climate change and limited water resources. Water, being an extremely vital

Table 7.1 Types of water pollutants and its sources and health impacts (Yaqoob et al. 2020)

Water pollutants	Sources	Effects
Pathogens	Sewage discharge, industrial wastewater	Waterborne diseases
Suspended solids and sediments	Land cultivation, mining operations, demolition, and construction	Damaging fish spawning, affecting aquatic ecosystem
Agricultural pollutants	Fertilizers, pesticides	Directly affect the lakes and rivers
Organic pollutants	Detergents, fungicides, insecticides, herbicides	Aquatic life problems, cacogenic
Inorganic pollutants	Metal compounds, trace elements, heavy metals, and mineral acids	Public health concerns, aquatic flora and fauna
Nutrient pollutants	Plant debris, sewage, and fertilizer	Affect eutrophication process and deoxygenation of water
Radioactive pollutants	Mining, ores processing, discharge from nuclear power plant	Affect bones and skin, can cause cancer

Table 7.2 Conventional wastewater treatment techniques and their shortcomings (Khan et al. 2019)

Treatment methods	Limitations
Distillation	Requirement of high energy and water. Difficult to remove pollutant with boiling point less than 100 °C. Difficult to remove most contaminants
Coagulation (flocculation)	Less efficacy, complex method, and pH dependent and generation of high sludge volume
Ultraviolet treatment	Not a cost-effective method; can be ineffective due to total suspended solid (TSS) and turbidity; sometime organism can repair due to photoreactivation or dark repair
Biological treatment	Microorganisms required optimum favorable environmental condition and difficult to control. By-products may be damage cells of microorganism. Slow and costly process
Chemical transformation	Requirement of excess reagents; low-quality mixture product may be formed. Inactive in adverse conditions
Ultrafiltration/ nanofiltration/ microfiltration	High operating and maintenance cost, fast membrane fouling, and requirement of high energy

natural resource, needs proper conservation (Ali et al. 2019). As water is required for sustenance of flora and fauna, treatment of wastewater with efficient low-cost techniques is the need of today's world, in order to use it for drinking and other purposes. In wastewater, the organic pollutants are categorized on the basis of their biodegradation ability (Burkhard and Lukasewycz 2008). Wastewater must be purified for the removal of effluents so that its quality is enhanced and health complications are mitigated. Table 7.1 enlists various types of water pollutants with major sources and their adverse effects (Yaqoob et al. 2020).

There are different techniques available for the treatment of wastewater. It is reported in Table 7.2, the conventional treatment techniques and their restrictions in application at commercial scale.

Amid these methods, photocatalytic degradation and adsorption are considered as simple, most effective, low-cost, and practical methods (Mohamed et al. 2018; Byrne et al. 2018). In current decades, adsorption and photocatalysis have gathered wide attention for the wastewater treatment (Han et al. 2018; Rauf and Ashraf 2009). Photocatalytic degradation method is a promising advanced oxidation process to eliminate the organic pollutants which are present in wastewater (Lin et al. 2011). In this technique, the decomposition of the organic pollutants is carried out by the species like holes (h^+) and hydroxyl radicals ($^{\bullet}OH^-$) which are highly reactive. They are produced during the interaction of photocatalyst with the oxidizing agent in the presence of electromagnetic radiation (usually ultraviolet or visible) (Ahmed et al. 2010; Moon et al. 2013). In the past many decades, several researchers have used semiconductor materials as photocatalyst for organic pollutant removal (Luan et al. 2015). However, pure photocatalyst's limited photostability, fast electron-hole pair recombination, and low adsorption ability generally affect their photocatalytic performance (Chen et al. 2013). Additionally, the separation of photocatalyst from the reaction mixture is complicated, which makes it unsuitable for use in large-scale industries (Khemthong et al. 2013; Veréb et al. 2013). Recently, nanotechnology has been employed in almost all areas of human activities, counting treatment of wastewater (Ali et al. 2019). Advance development in nanotechnology and nanoengineering promises a great scope of improvement in the quality of water through the application of bioactive nanoparticles (Papageorgiou et al. 2012), nano-sorbents, nanoparticle-enhanced filtration, and nano-catalysts (Ren et al. 2011). At the nanoscale range (1–100 nm), materials reveal considerably different chemical and physical properties from their bulk counterparts. Moreover, the surface reactivity dramatically increases due to its higher surface area-to-volume ratio. Consequently, products based on nanotechnology decrease the quantity of toxic substances to sub-ppb levels which allows in achieving water quality standards. These comprise nanoparticles of carbon nanotubes, metals, graphite, metal oxides, plant-based nanocomposites, fullerenes, etc. (Burkhard and Lukasewycz 2008; Rao et al. 2007; Seymour et al. 2012; Santhosh et al. 2016).

The nanophotocatalyst is utilized in the treatment of wastewater, and it is classified as graphene-semiconductor, plasma-mediated, and metal-organic framework materials. Among the various processes for wastewater treatment, semiconductor photocatalyst is an advantageous method because of mild operating condition, simple operation, using solar light for degradation, etc. Photosynthesis is an essential photocatalytic reaction which occurs naturally. Fujishima and Honda achieved a breakthrough in controlled laboratory environment for the photocatalytic reactions (Fujishima and Honda 1972). Amid semiconductors, titanium oxide (TiO_2) and zinc oxide (ZnO) gather attention due to their high stability, low cost, low toxicity, etc. TiO_2 and ZnO both have approximately the same bandgap, but the latter one has higher absorption efficiency over large fraction of solar spectrum (Adhikari et al. 2016). Graphene has excellent properties such as chemical stability, electrical conductivity, high surface area, and high electron mobility which make its good choice to accelerate the activity of photocatalyst (Iftekhar Uddin et al. 2015; Liu et al. 2013a). In the literature review, mostly a two-step process is used for the synthesis of graphene-ZnO/graphene-TiO_2 nanocomposite in which graphene and ZnO or TiO_2 nanoparticles are prepared separately and then disperse nanoparticles in graphene. In the single-step process, graphene oxide reduces to graphene and Zn or Ti salt oxide to ZnO or TiO_2. It is reported in literature about the graphene-based $NCPC_S$ for the degradation of dye wastewaters and pharmaceutical/agricultural pesticide-contaminated wastewater. Fu et al. found that adsorption of dyes increases with graphene loading in ZnO-graphene catalyst during the photocatalytic process (Fu et al. 2013). Zhou et al. have also reported that photocatalytic degradation of organic pollutant was found to improve with ZnO-rGO hybrid catalyst (Zhou et al. 2012). Graphene-TiO_2 prepared shows high efficiency in the degradation of methylene blue (MB) under visible light (Liu et al. 2013a). Even photocatalysis is an efficient method for the degradation of polycyclic aromatic hydrocarbons present in oil sludge (Da Rocha et al. 2010). Degradation of λ-cyhalothrin pesticide was also studied under visible light using ZnO-Bi_2O_3 as photocatalyst. It was observed that 85.7% degradation efficiency of pesticide was achieved in comparison to pristine ZnO in 2 h of photocatalytic activity (Premalatha and Miranda 2019). Despite the nanophotocatalyst preparation using graphene, to our best knowledge, no literature has reported on the in situ synthesis of graphene-ZnO/graphene-TiO_2 nanocomposite and its application as photocatalyst on wastewater treatment. Biomass waste such as alginate can act as a precursor for graphene and template for ZnO or TiO_2 nanoparticles.

The present review describes about the bio-derived graphene synthesis and graphene-based nanophotocatalyst and its application in wastewater treatment. Based on the literature review, a recommendation has been made for the in situ synthesis of ZnO-/TiO_2-nanocomposite photocatalysts (NCPCs) embedded on graphene (G)-based matrix using alginate (a natural biopolymer) as a precursor, which can be utilized for the industrial and agricultural wastewaters as UV or visible UV and visible light as a source of irradiation. Based on the literature review and past research activities, a recommendation has been made to utilize the renewable source of graphene precursor and templating agent for NCPCs.

7.2 Graphene

A single layer of carbon of graphite structure is defined as graphene. Novoselov et al. were the first to synthesize graphene by mechanical exfoliation from graphite, of which high mechanical strength, large surface area, high electron mobility, high electrical conductivity, and high elasticity are some of the notable properties of graphene (Novoselov et al. 2004). Technically, a non-metal graphene is often denoted as quasi-metal because of its properties similar to that of the semiconducting metals. It has some unique properties with which graphene stood out from other available non-metallic materials. Graphene has a hexagonal array structure of carbon atoms (SP_2 hybridized) facilitating its extraordinary electronic, optical, magnetic, thermal, and mechanical properties (Cheaptubes.com n.d.). It is very important to synthesize graphene of high quality to explore its application in different sectors. The nanocomposite of graphene with other semiconductors such as metal oxide and metal sulfides increases its surface area making it an excellent absorbent material for the elimination of organic effluents from the wastewater. It also reduces the recombination of electron-hole pair and possesses high mobility of electron which improves the photocatalytic activity of the semiconductor (Giovannetti et al. 2017).

7.2.1 Synthesis Method of Graphene

Several approaches have been developed for the synthesis of graphene. These approaches are mainly divided into two groups as top-down method and bottom-up method. Top-down techniques follow the progressive size reduction strategy of graphite. Top-down method includes mechanical exfoliation, chemical/electrochemical exfoliation, chemical/electrochemical fabrication, and laser ablations. Bottom-up approaches follow progressive self-assembling strategy of nanostructural atom and molecules of starting material. These methods include pyrolysis, CVD, plasma deposition, and arc discharge method (Lee et al. 2019). Illustration of method for the synthesis of graphene is presented in Fig. 7.1.

7.2.2 Conventional Precursor for Graphene Synthesis

Graphite and graphite oxides are the conventional precursors for the synthesis of graphene. Novoselov et al. used the mechanical exfoliation method for the production of single or few layers of graphene by using highly oriented pyrolytic graphite (Novoselov et al. 2004). Graphene produced by this process was pristine graphene. Researchers have reported about the production of monolayer graphene without defect by exfoliation of graphite in *N*-methyl-2-pyrrolidone solvent (Hernandez et al. 2008; Blake et al. 2008). Stankovich et al. have demonstrated the preparation of graphene-like sheets from graphite oxide. In this process, graphite oxide was prepared by oxidation of natural graphite (purified). The hydrophilic nature of graphite oxide was easily exfoliated in water and formed graphene oxide by using the ultrasonication method. Exfoliated graphite oxide was reduced with hydrazine hydride to form graphene-like sheets (Stankovich et al. 2007).

7.2.3 Bio-Based Precursor for Graphene Synthesis

In the recent year, application of graphene significantly increases which increases the urge to use the biomaterials as precursor for graphene synthesis. It also attracts the researcher attention due to its low cost and abundance in the environment. Biomass, for example, sugarcane bagasse, rice husk, dead camphor leaves, disposable paper

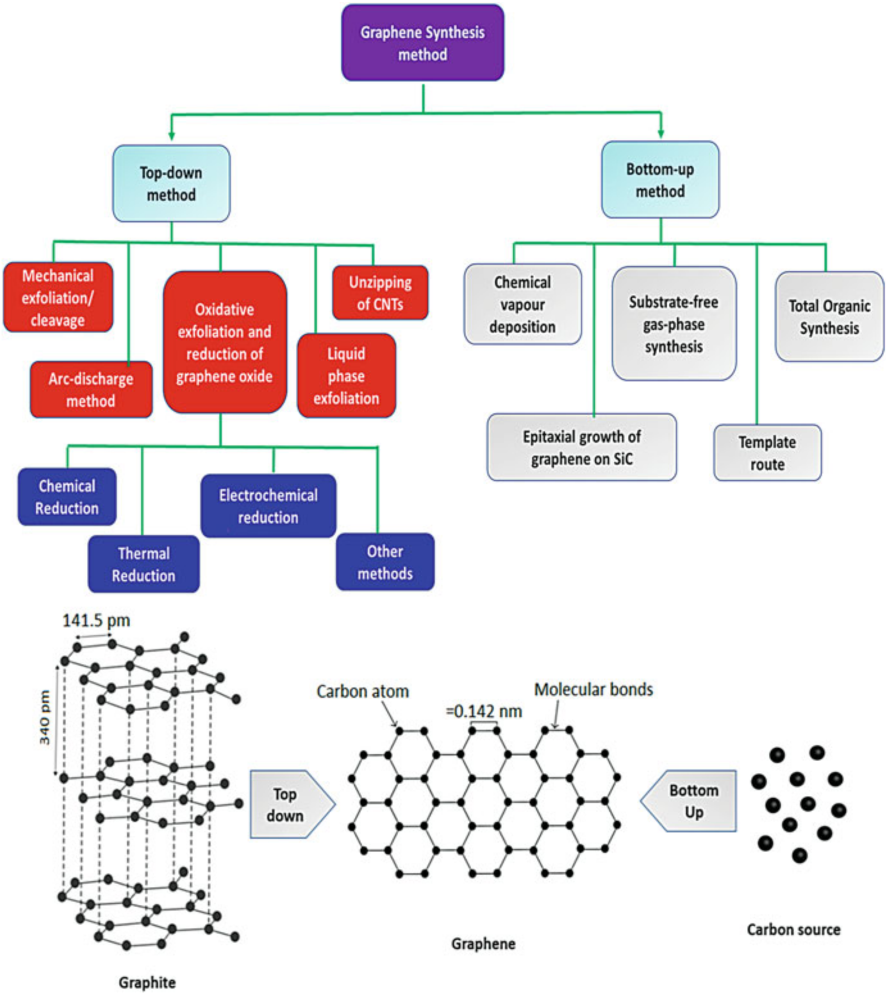

Fig. 7.1 Different methods for the synthesis of graphene

cups, waste papers, food remnants, and insects, can be used to synthesize graphene and its derivatives. Biomass being an easily sourced precursor, non-toxic, environmentally friendly, sustainable, and cost-effective plays a crucial role in manufacturing value-added products. Biomass is a waste material for the environment; use of it as a carbon source for graphene synthesis helps in the reduction of waste. Mass production of graphene can be achieved by using biomass precursor which makes production economical (Safian et al. 2020). In the synthesis of graphene, the selection of biomass depends on its properties and chemical composition, generally its texture and carbon content in terms of porosity (varying from meso to micro). Consequently, different varieties of biomass have particular preparation process appropriate for them. For example, high water content, grainy, and meso-/macroporosity of pear have been utilized to produce aerogels of graphene exploiting hydrothermal carbonization. Different sources of biomaterial precursor are rice husk, hemp fiber, glucose, chitosan, and alginate (Yan et al. 2020).

7.2.3.1 Rice Husk

Rice is the third largest cultivated crop in the world. Rice husk is the outer shell of rice kernels. Due to its abundant production, it attracted the keen attention of researcher as a starting material for the synthesis of silicon product and carbonaceous component. Singh et al. were the first who reported the preparation of graphene from rice husk activated with KOH at 1123 K. Formation of monolayer corrugated graphene with clean and stable edge was confirmed by following same method validate the formation of few-layered graphene with silica agglomeration (Singh et al. 2017). Sankar et al. have reported the preparation of ultrathin graphene nanosheet by carbonization followed by KOH activation of rice husk. Graphene nanosheet with high porosity with high surface area 1225 m^2/g was used as supercapacitor electrodes (Sankar et al. 2017). Liou et al. utilize rice husk ash for the synthesis of graphene oxide/SAB-15 mesoporous nanocomposite. It shows excellent adsorption capacity of methylene blue dye (Liou and Liou 2021).

7.2.3.2 Chitosan

Chitosan is a biopolymer containing amino and hydroxyl groups. It is the second most abundant natural polymer after cellulose. It is obtained from the hard outer skeleton of crustaceans. Primo et al. reported about the preparation of nitrogen-doped single- or few-layered graphene on arbitrary substrates using pyrolysis under argon atmosphere of chitosan at 800 °C. They have also reported about the synthesis of graphitized chitosan sphere using thermal treatment at 400–800 °C under inert condition, and it shows remarkable adsorption capacity of CO_2 (Primo et al. 2012a, b). Hao and co-worker represented the synthesis of N-doped graphene from chitosan using pyrolysis at 800 °C under inert condition as the same was activated with KOH and used as semiconductor having high specific capacitance and current density (Hao et al. 2015).

7.2.3.3 Glucose

Glucose is an abundantly available monosaccharide carbohydrate in the nature and a renewable resource of carbon. It gathers tremendous attention among researchers as a raw material for graphene due to its copious availability and renewable property. Zhang et al. reported the preparation of high-quality graphene by carbonization and calcination of graphene and $FeCl_3$. In this process, $FeCl_3$ plays a vital role because it acts as a catalyst and template for graphene. The author claims that the electric conductivity of the prepared graphene is higher than produced by CVD technique (Zhang et al. 2014a, b). Li and co-worker prepared monolayer 2D graphene using glucose and dicyandiamide (DCDA). In this process, DCDA acts as a sacrificial template and prepared graphene termed as patched graphene. Authors claim that prepared graphene was an atomically clean and highly crystalline graphene (Li et al. 2012). Wang and co-worker developed a sugar blowing method for the production of 3D graphene named as strutted graphene. The produced graphene-based supercapacitor shows high power density (Wang et al. 2013a, b). Hallaj and co-worker studied a new and facile procedure with chemiluminescence (CL) reaction with hypochlorite-prepared graphene quantum dots by pyrolysis of glucose and used it in the quantitative analysis of free chlorine present in water (Hallaj et al. 2015). Shehab et al. synthesized graphene quantum dots from glucose by carbonization and functionalized it with phenyl boronic salt. As-prepared graphene quantum dots were used in the detection of glucose molecules (Shehab et al. 2017).

7.2.3.4 Hemp Fiber

Hemp is a quickly growing annual herbaceous plant which can nourish without requiring any specific climate, fertilizer, or pesticide. Hemp fiber can be derived from hemp bast. Hemp is used as a source of textile, paper, building material, medicine, oil, fuel, and food industries (Zhang et al. 2017; Johnson 2019; Guan et al. 2019). Cultivation of hemp fiber has increased due to its high demand. Hemp stem is an agricultural waste which contains high quality of crystalline cellulose, hemicellulose, and lignin. Wang and co-worker utilized hemp bast fiber for the synthesis of graphene-like 2D interconnected carbon nanosheet using hydrothermal process and activated with KOH. Carbon nanosheet with 10–13 nm thickness has high specific surface area and good electrical conductivity (Wang et al. 2013a, b). Wang et al. reported the synthesis of well-shaped activated carbon sphere by hydrothermal technique and KOH activation (Wang et al. 2015a, b). Activated carbon sphere was synthesized by utilizing hemicellulose extracted from hemp stem. Highly porous activated carbon sphere shows excellent electrochemical performance.

7.2.3.5 Alginate

Alginate is a naturally occurring polysaccharide typically extracted from the cell wall of sea weeds specially brown algae. It is a linear block copolymer of β-D-mannonate and α-L-guluronate. It is abundant in nature and biocompatible which implies its widespread application. It has the ability to form gel with divalent cation (Supriya et al. 2019, 2021). Lavorato and co-worker utilize alginate as a precursor for graphene and template for ceria nanoparticles. Few-layered graphene matrix has been prepared by using pyrolysis method. As-prepared ceria/graphene nanoparticles have been utilized as a photocatalyst for water oxidation (Lavorato et al. 2014a, b). Cui et al. reported the synthesis of Mo_2C nanoparticle-decorated graphitic carbon sheet (Mo_2C/GCS) by using one-step solid-state reaction at 900 °C. In this process, alginate was used as a precursor for graphitic carbon sheet. Authors claim that the adopted synthesis process is facial, simple, and fast. Mo_2C/GCS was used as an electrocatalyst in hydrogen generation reaction with high efficiency and excellent corrosion stability in acid medium (Cui et al. 2014). Primo et al. reported the preparation of graphitic carbon sphere at 400–800 °C by thermal treatment under inert condition (Primo et al. 2012a, b). The preparation of multilayered graphene quantum dots by utilizing alginate as precursor, by pyrolysis at 900 °C under argon atmosphere followed by laser ablation at 532 nm in acetonitrile, water, or other solvents. They proposed in this study the exfoliation of small carbon debris from graphitic alginate beads in the solution resulting in the formation of graphene quantum dots (Atienzar et al. 2013). As-prepared graphene quantum dots reveal photoluminescence (Hu et al. 2013).

7.3 Graphene-Based Nanophotocatalysts

Graphene acts either as a substrate for the immobilization of other components or as a functional component in graphene-based nanophotocatalyst. Superior properties of graphene enhance the catalytic activities of nanophotocatalyst by extension of light absorption range, enhancing absorptivity and surface area, and improving charge transportation and separation. It also enhances electron transfer rate and decreases hole/electron recombination. Williams et al. reported the preparation of graphene-TiO_2 nanocomposite by using UV-induced photocatalytic reduction technique. In this technique, TiO_2 plays the role of transfer electrons to graphene oxide which undergo reduction (Williams et al. 2008). Sun et al. prepared TiO_2-graphene nanocomposite by heterogeneous coagulation between commercial TiO_2 nanoparticles (P25) and Nafion-functionalized graphene. As-prepared TiO_2-graphene nanocomposite has been used to fabricate dye-sensitized solar cell (DSSC). Incorporation of graphene improves the performance of DSSC by increasing dye's absorption rate and significant high lifetime (Sun et al. 2010). Li et al. prepared graphene-cadmium sulfide (CdS) nanocomposite, and it serves as a highly efficient photocatalyst in hydrogen production. In this report, graphene not only serves as a support of CdS clusters but also improves its specific surface area and crystallinity (Li et al. 2011a, b). Ren and co-worker used hydrothermal process for the synthesis of graphene-CdS nanocomposite and used it as an efficient photocatalyst for selective organic transformation. Authors claimed that reduced graphene enhances the separation of electron-hole pair and it serves as an electron transporter and collector (Ren et al. 2014). Zhang et al. reported the preparation of reduced graphene oxide-tin dioxide nanocomposite (RGO-SnO_2) and reduced graphene-titanium dioxide (RGO-TiO_2) nanocomposite using direct redox reaction. In this reaction, graphene oxide was reduced to RGO, and reactive cation Ti^+ and Sn^+ were oxidized to TiO_2 and SnO_2, respectively. RGO-SnO_2 and RGO-TiO_2 nanoparticles were well dispersed on the surface of RGO sheets. These nanocomposites were used as an efficient photocatalyst in the degradation of rhodamine B (RhB) using visible light irradiation (Zhang et al. 2011). Che et al. reported the photodegradation of nitrophenols and pharmaceutical wastewater under visible light by using RGO/AgIn5S8 nanocomposite, which was prepared by using solvothermal method (Che et al. 2018). Zou and co-worker have developed a simple promising and general nanocrystal seed-directed hydrothermal route for the growth of nanorod array of various semiconductor metal oxides (MO) comprising ZnO, TiO_2, CuO, MnO_2, and ZrO_2 (Zou et al. 2011). Li et al. stated the synthesis of ZnO@graphene composite by incorporation of graphene with TiO_2 using chemical

Fig. 7.2 Process for the preparation of CeO_x/G nanocomposite: (a) precipitation of the alginate hydrogel containing Ce^{3+} with $(NH_4)_2Ce(NO_3)_6$; (b) drying by H_2O to EtOH exchange followed by supercritical CO_2 drying; and (c) pyrolysis under argon flow

deposition approach. As-prepared ZnO@graphene show excellent photocatalytic degradation of RhB under UV or visible light irradiation and filtrate dyes from water as filtration membrane (Li et al. 2011b). Sandwich-like heterostructure has been formed by deposition of metal oxide on both sides of graphene sheet. Authors claim that three-layered TiO_2/graphene/TiO_2 shows fourth times faster photocatalytic degradation rate of MB than that of TiO_2 nanorod (Zhang et al. 2014a, b). Zhang et al. demonstrated a simple and general method for the preparation of graphene-CdS nanocomposite by incorporating a small amount of metal ion as mediator (such as Cr^{3+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, and Ni^{2+}) into the interface of graphene and CdS. They reported that this approach significantly improves the photocatalytic performance of graphene-CdS nanocomposite in the presence of visible light (Zhang et al. 2010). Lavorato et al. have shown the preparation of ceria photocatalyst ceria nanoparticles embedded on graphene, as presented in Fig. 7.2. CeO_2/graphene composite is utilized as a photocatalyst for oxidizing water with the help of Ag^+ playing the role of sacrificial electron acceptor (Lavorato et al. 2014a, b). Zhang et al. utilized hydrothermal approach for the preparation of TiO_2-graphene nanocomposite and used as a photocatalyst for gas-phase degradation of benzene. Authors observed that increase in weight ratio in TiO_2-graphene decrease the photocatalytic activity of both gas-phase degradation and liquid-phase degradation of benzene and dyes, respectively (Zhang et al. 2010). Lui et al. described the synthesis of graphene-wrapped hierarchical TiO_2 nanostructure using two-step solvo-/hydrothermal approaches. Photocatalytic activity was demonstrated by MB photodegradation under UV irradiation. Sol-gel synthesis method for graphene-TiO_2 composite was employed for efficient photocatalytic degradation for MB. Graphene improves the performance of photocatalytic by increasing the conductivity, suppressing the recombination, and providing the absorption site for MB (Lui et al. 2013). Ton et al. demonstrated a novel method for synthesizing graphene-TiO_2 nanocomposite on the basis of chemical exfoliation method. Prepared graphene-TiO_2 nanocomposite exhibited excellent photocatalysis in methylene blue degradation under visible irradiation (Ton et al. 2018).

A group of researchers reported the pyrolysis of bio-polysaccharide such as chitosan and alginate under inert atmosphere to obtain defective single-, few-, or multilayered N-doped graphene or graphene as summarized in Table 7.3 (Primo et al. 2015; Cui et al. 2014; Mateo et al. 2016, 2019; Garcia et al. 2017; Lavorato et al. 2014a, b; Latorre-Sánchez et al. 2013; Esteve-Adell et al. 2018; An and Yu 2011). When these polysaccharide films was coated with Au and Cu salt facet oriented metal nanoplatelets coated graphene has obtained. These facet-oriented nanoplatelets on few-layered graphene exhibit higher photocatalytic activity for

Table 7.3 Summary of graphene-based nanophotocatalysts synthesized from biomass waste and its applications

S. No.	Catalyst	Precursor for graphene	Method and condition	Applications	Reference
1	$\overline{Cu_2O}$/fl-G (Cu_2O, 2.0.0 oriented Cu_2O nanoplates; fl, few layer; G, graphene)	Cellulose	Pyrolysis at 900 °C under inert atmosphere	Overall water splitting	Mateo et al. (2017)
2	$\overline{Au}$/ml-G (Au, 1.1.1 oriented Au nanoplates; ml, multilayer; G, doped graphene)	Cellulose	Pyrolysis at 900 °C under inert atmosphere	Overall water splitting	Mateo et al. (2016)
3	Nitrogen-doped multilayered graphene	Cellulose	Pyrolysis at 900 °C under inert atmosphere	Photoelectrode catalyst for hydrogen evolution	Garcia et al. (2017)
4	Nitrogen-doped multilayered graphene	Chitosan	Pyrolysis of chitosan followed by ultrasound exfoliation	Photocatalyst for hydrogen generation from methanol-water mixture	Lavorato et al. (2014a, b)
5	Phosphorus-doped graphene	Alginate	Pyrolysis at 900 °C under inert atmosphere	Photocatalyst for hydrogen generation from methanol-water mixture	Latorre-Sánchez et al. (2013)
6	(N)graphene/h-BN	Chitosan	Pyrolysis at 900 °C under inert atmosphere	Capacitor	Mateo et al. (2019)
7	$RhCrO_x$/STO:Al/N-G	Chitosan	Pyrolysis of chitosan followed by impregnation	Overall water splitting	Mateo et al. (2019)
8	CeO_x/Graphene	Alginate	Pyrolysis at 900 °C under inert atmosphere	Water oxidation	Lavorato et al. (2014a, b)

overall water splitting. N-doped graphene was obtained by pyrolysis of chitosan or pyrolysis of chitosan followed by ultrasound exfoliation (Mateo et al. 2016; Garcia et al. 2017). This N-doped graphene acts as a photocatalyst for hydrogen generation. Researchers claim that N-doped graphene photoelectrode works as a photocatalyst as well as a semitransparent electrode. Phosphorus-doped graphene was prepared by pyrolysis of H_2PO_4-modified alginate, and it acts as a photocatalyst for the generation of hydrogen from methanol-water mixture (Lavorato et al. 2014a, b; Latorre-Sánchez et al. 2013). Following similar approach, defective nitrogen-doped graphene on the hexagonal boron nitride layer ((N) graphene/h-BN) has been prepared. RhCrOx/STO:Al/N-G photocatalyst has been prepared by the impregnation of Al-doped $SrTiO_3$ containing $RhCrO_x$ nanoparticles on N-doped defective graphene synthesized from pyrolysis of chitosan $RhCrO_x$/STO:Al/N-G (Esteve-Adell et al. 2018). Summary of graphene-based nanophotocatalysts synthesized from different sources is listed out in Table 7.3.

7.4 Plausible Mechanism of Photocatalysis by Graphene-Semiconductor Nanocomposite

There are mainly two probable mechanisms to describe the progress in photocatalytic activity of a semiconductor incorporated on graphene as presented in Fig. 7.3. In the first proposed mechanism under irradiation of light, photon absorbed by the semiconductor is in the range of energy gap between conduction band (CB) and valence band (VB), due to which excited electron is transferred from VB to CB leaving the holes in VB. Now electron in conduction band is transferred to graphene. Graphene scavenges photogenerated electron and facilitated the electron-hole separation.

As per the second proposed mechanism, photocatalytic activity is initiated by graphene because the bandgap of the semiconductor is large to absorb the photon. In this process, graphene acts as a photosensitizer. Excited graphene has formed by absorption of radiation. Photoexcited electron is transferred into the conduction band of the semiconductor from the excited graphene (Zhang et al. 2012; Radhika et al. 2019). This electron successively reacts with oxygen for the formation of superoxide

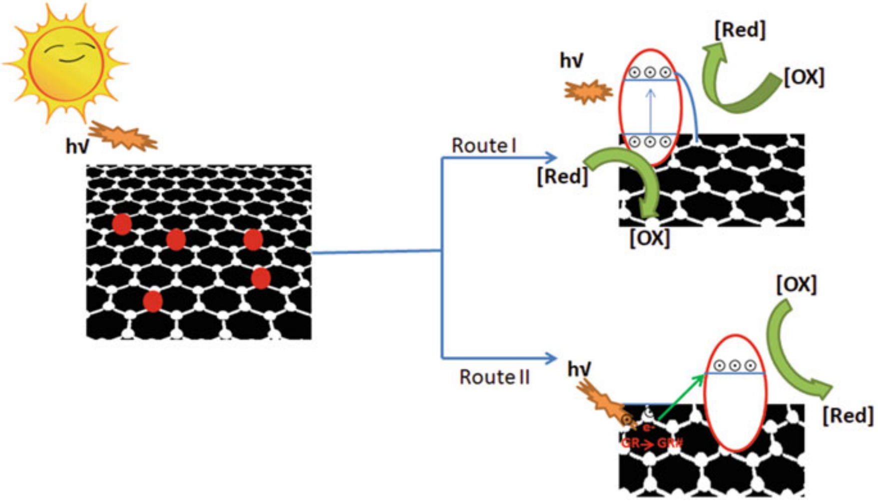

Fig. 7.3 Illustration of photocatalysis of graphene-based semiconductor nanocomposite, where [Ox] are oxidized particles and [Red] are reduced particles

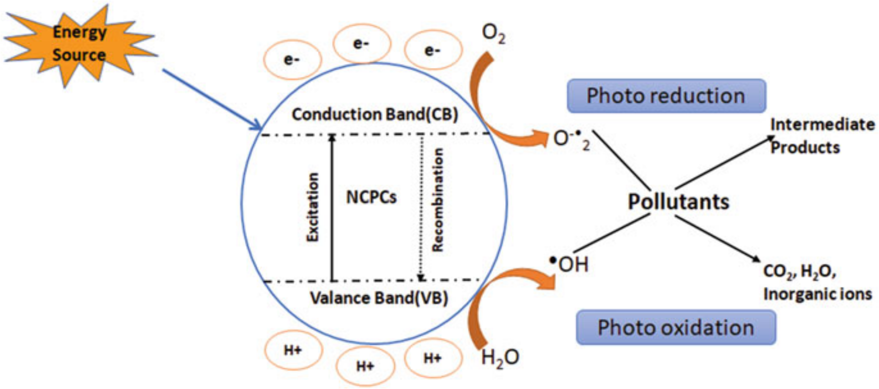

Fig. 7.4 Mechanism of degradation of pollutants using graphene-based nanophotocatalyst

radicals. These radicals help in selective oxidation reaction. The presence of graphene in nanocomposite improves its photocatalytic activity because it has a large surface area and high electron mobility and conductivity and graphene reduces the recombination between holes and electron which enhances the interaction possibility with the substrate (Giovannetti et al. 2017; Hoffmann et al. 1995). The availability of the graphene increases the photoactivity of the nanocomposite in the visible region of the spectrum.

Mechanism of the photocatalytic oxidation includes various intermediate steps. The initial step is the generation of electron-hole pair which happens by exposing the catalyst surface to the electromagnetic radiation having intensity equal to or greater than that of the catalyst bandgap (Srikanth et al. 2017). During this process, energy gained by the electrons is sufficient to cross the bandgap and reach CB from VB as shown in Fig. 7.4 (Linsebigler et al. 1995). Due to this, an electronic vacancy is generated in the valence band (holes). The holes of valence band and the electrons of conduction band act as strong oxidizing and reducing agents, respectively. At the surface, the holes oxidize an electron donor after migrating to the surface; thus, the semiconductor is able to donate electrons for reducing an electron acceptor. The semiconductor is capable of altering its action depending upon the nature of particles surrounding it. Example includes if the photocatalytic reaction occurs with the adsorption of molecular oxygen on the surface of catalyst, superoxide radical is formed and, if the photocatalytic reaction happens between water molecules, *OH radical is formed. *OH and superoxide radicals are predominantly responsible for degrading effluents (Zhao et al. 2015). Extensive applications of semiconductor photocatalysis appear in wastewater treatment. During photocatalysis process, primarily, the semiconductors are supposed to transfer their energy from the incident radiation to the charge carrier (Ahmed and Haider 2018). ZnO and TiO_2 semiconductors have a wide bandgap and are displaying strong adsorption property under ultraviolet radiation. This makes them appropriate for efficient photodegradation of organic effluents and toxic metal ions (Ziolli and Jardim 2002). Additionally, these semiconductors can be used for seawater treatment specifically for polluted seawater due to oil spills in the ocean, to separate water-soluble fractions of crude oil (Da Rocha et al. 2010; Zhu et al. 2015).

7.5 Photocatalyst in Wastewater Treatment

In the wastewater treatment, generally used photocatalyst is reported in Table 7.4. Numerous studies conducted in the recent decades reported about the photocatalytic behavior of various materials such as CdS (Yue et al. 2017; Das et al. 2017), nanorods of ZnO (Rodríguez et al. 2010; Rajendran et al. 2016), and AgCl nanotube, upon visible light irradiation (Shu et al. 2014). TiO_2 is the extensively researched nanomaterial and is bestowed with excellent photocatalytic activity, anti-reflection, as well as self-cleaning ability.

For enabling magnetic separation for TiO_2, using Fe_3O_4 core was found very practical (Yang et al. 2014). Fe_3O_4 is itself a photocatalyst which exhibits superparamagnetic activities at particle sizes lower than 20 nm, because of the finite size effect (Mascolo et al. 2013; Upadhyay et al. 2016; Han et al. 2017). This photocatalytic activity characteristic was found to be very useful in the wastewater treatment and water purification across the world by researchers (Bagbi et al. 2017). Similarly, in recent times, ZnO and g-C_3N_4 were used as promising materials for photocatalytic applications (Feng et al. 2017; Sampaio et al. 2017; Tang et al. 2015). These semiconductors decompose the contaminants and microorganisms present in the wastewater by using heterogeneous photocatalysis (Ziolli and Jardim 2002). Till date, several researches have paid attention to semiconductors coupled with graphene materials having considerable benefit for the separation of electron-hole pairs and allowing the reduction and oxidation reactions simultaneously at two different locations. Combining other semiconductors with CdS-graphene composites has gained much recognition because of its charge separation, increased life span of charge carrier, and enhanced charge transfer efficiency (Huo et al. 2016).

Table 7.4 Commonly used nanoparticles for wastewater treatment

Nanoparticle	Properties of nanoparticle	Technology
Carbon-based nanotubes	High specific surface area, large no. of adsorption sites, effective reaction or interaction with pollutants, changeable surface chemistry, reuse is feasible	Contaminant preconcentration/ detection, adsorption of recalcitrant pollutants
Nano-Ag	A broad range of antimicrobial ability, non-hazardous	Anti-biofouling membranes
Nano-magnetite	Can alter surface chemistry, superparamagnetic	Forward osmosis
Nano-TiO_2	Photocatalytic behavior with UV and visible light, non-hazardous to animals, and cost-effective	Photocatalytic reactors, solar disinfection systems
Derivatives of fullerene	Working in solar spectrum, larger selectivity	Photocatalytic reactors, disinfection systems

7.5.1 Graphene-Based Nanophotocatalysts for Wastewater Treatment

7.5.1.1 Removal of Dyes

Synthetic dyes majorly serve as extensively used coloring agents in different sectors such as paint, textile, and cosmetic manufacturing industries. Figure 7.5 also shows the application of graphene based nanophotocatalysts in other sectors of industries such as, antibiotics, pesticides, and oils apart from dye industries. Considering environmental effects, the process of organic dyes in dyes and textile industries poses a tremendous challenge. According to the form of electric charge introduced in the wastewater, dye pollutants can be categorized into ionic and non-ionic (neutral) dyes. The cationic dyes include methylene blue (MB), safranin O, malachite green (MG), brilliant green, methyl violet (MV), and RhB (Tiwari et al. 2013; Khan 2015). Anionic dyes include methyl orange (MO), calcein (CA), and increased Bengal salt (RB) (Wang et al. 2012a, b; Kheirabadi et al. 2019), and acridine orange (AO) is the neutral dye (Tju et al. 2016). The possible mechanism of the photocatalytic degradation of MB dye using graphene-based nanoparticles is given as follows:

$$\begin{aligned}&(\text{Graphene} - \text{based–NPs}) + h\nu\ (\text{photons}) \rightarrow \text{Graphene}\\&\quad - \text{based–NPs}\ ({\text{h}_{\text{VB}}}^{+} + {\text{e}_{\text{CB}}}^{-})\end{aligned}$$

where VB is the valence band and CB, conduction band. Upon irradiation, the electrons get excited from the valence band to the conduction band of graphene-based nanophotocatalyst. Holes (h^+) are left in the valence shell.

$$\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^\bullet$$

The $^\bullet$OH radical oxidizes the organic dyes at room temperature.

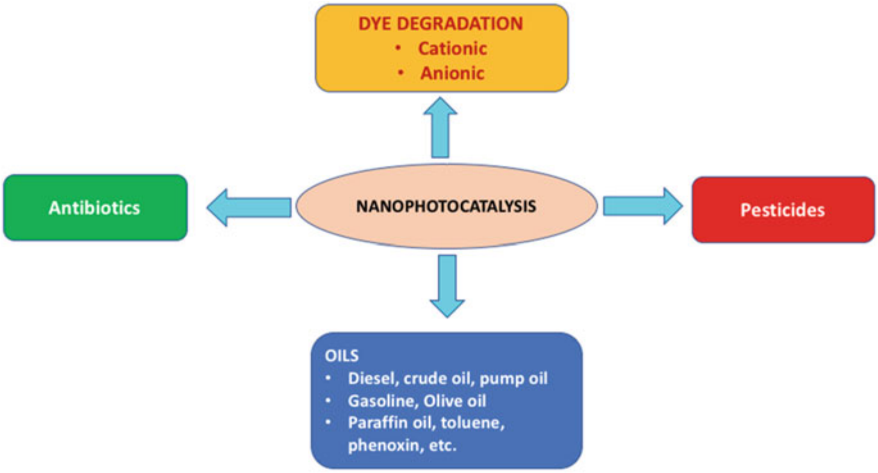

Fig. 7.5 Application of graphene-based nanophotocatalyst in the treatment of organic pollutants

$$2h_{VB}{}^{+} + 2H_2O \rightarrow 2H^{+} + H_2O_2 \text{ (hydrogen peroxide)}$$

$$H_2O_2 \rightarrow 2OH^{\bullet}$$

$$2e_{CB}{}^{-} + O_2 \rightarrow {}^{\bullet}O_2{}^{-} \text{ (Superoxide radical)}$$

$${}^{\bullet}O_2{}^{-} + 2H^{+} \rightarrow H_2O_2 + O_2$$

$$H_2O_2 \rightarrow 2OH^{\bullet}$$

The electrons and holes reacted with active compounds and formed radicals of superoxide and hydroxyl. These will be reacting with the dye (here methylene blue) which gets trapped on the surface of graphene nanophotocatalyst and degrade it further to harmless molecules/products.

$$MB^{*} + (\text{Graphene} - \text{based} - \text{NPs}) \rightarrow MB^{\bullet +}\ e_{CB}{}^{-}\ (\text{Graphene} - \text{based–NPs})$$

$$MB^{\bullet +} + OH^{-} \rightarrow MB + OH^{\bullet}$$

$$MB^{\bullet +} + OH^{\bullet} \rightarrow \text{Products } (CO_2 + H_2O + \ldots)$$

$$MB^{\bullet +} + {}^{\bullet}O_2{}^{-} \rightarrow \text{Products } (CO_2 + H_2O + \ldots)$$

It is reported in Table 7.5 the dyes' degradation from wastewater using different kinds of photocatalyst.

7.5.1.2 Removal of Antibiotics

Antibiotics can be efficiently degraded into less harmful smaller fragments using visible or ultraviolet (UV) radiation with the help of active agents (OH radical, $^{-}O_2$ radical) produced by photocatalysts (Li et al. 2019). Thus, the degradation using such photocatalytic material is the most effective and extensively used process for mitigating antibiotic levels in industrial wastewaters. Graphene having favorable properties as discussed in earlier sections has been deeply analyzed for this purpose. Also, graphene in combination with other different functional materials (e.g., magnetite nanoparticles, zeolite, porous graphitic C_3N_4), polymer, and optical fibers has also been employed for the effective elimination of various antibiotics. In Table 7.6, different photocatalysts have been reported for the treatment of antibiotic wastewater by different researchers.

7.5.1.3 Removal of Pesticides

The presence of pesticides in the surface as well as in groundwater has significantly increased recently due to the higher-scale applications in agriculture, especially for crop safety (Pathania et al. 2019). The water bodies get polluted because of the direct use of insecticides, fungicides, bactericides, and herbicides. Organophosphates encapsulate a great choice of pesticides; glyphosate is the well-known of these. Malathion, parathion, and dimethoate are some of the examples of glyphosate family. Some of these possess potential to cause disruption of endocrine. This

Table 7.5 Removal of dyes from wastewater using graphene-based photocatalysis

Composition	Light source	Pollutant	Irradiation time (min)	Photodegradation efficiency (%)	Reference
Fe_3O_4-CuO-ZnO-nanographene	40 W UV	Methylene blue (30 mg/L)	120	93	Tju et al. (2016)
Fe_3O_4-ZnO-rGO	Visible	Methylene violet (408 mg/L)	120	83.5	Thangavel et al. (2016)
ZnO-graphene	UV (365 nm)	Deoxynivalenol (15 mg/L)	30	99	Bai et al. (2017)
CdS-ZnO-graphene	300 W visible	4-Nitroaniline (10 mg/L)	16	98	Han et al. (2015)
Au-ZnO-rGO	UV and visible	Rhodamine B	180	94	She et al. (2017)
TiO_2-GO	20 W UV	Methyl orange (10 mg/L)	9	90	Jiang et al. (2011)
Molecular imprinted TiO_2-graphene	Visible	Bisphenol A (4 mg/L)	180	67.6	Lai et al. (2016)
Co_3O_4-TiO_2-GO	300 W simulated sunlight	Congo red (10 mg/L)	90	91	Jo et al. (2017)
TiO_2-Fe_3O_4-rGO	150 W visible	Tetracycline HCl (20 mg/L)	330	92.6	Wang et al. (2017)
WO_3-rGO	200 W visible	Sulfamethoxazole (10 mg/L)	180	>98	Yusuf et al. (2017)
Polyacrylonitrile-carbon nanotubes	100 W UV	Indigo carmine (10 mg/L)	60	100	Li et al. (2011a, b)
CdS-gC_3N_4-rGO	350 W visible	Atrazine (10%)	300	70.8	Liu et al. (2016)
3DG-Fe nanoparticles	UV	Orange IV	60	94.5	Wang et al. (2015a, b)
Bi_2WO_6/3DGA	Visible	RhB Sulfanilamide	<60	98.75	Dong et al. (2019)
N-doped/GH	Visible	Acridine orange	300	70	Jiang et al. (2017)

Table 7.6 Graphene-based photocatalyst for antibiotic wastewater treatment

Photocatalyst	Antibiotic	Degradation time (min)	Removal efficiency (%)	Light source	Reference
TiO_2-NS/Pt/GO	Chlorotetracycline	90	45	Visible light	Liang et al. (2017)
Fe_3O_4@TiO_2-GO	Enrofloxacin	240	96	Visible light	Yu et al. (2017)
$ZnTiO_3$-graphene-8	Norfloxacin	60	93	Visible light	Wu et al. (2016)
ZnO/RGO	Metronidazole	160	49.3	Visible light	Dong et al. (2014)
RGO-$BiVO_4$	Ciprofloxacin	60	68.2	Visible light	Yan et al. (2013)
Cu/$Bi_2Ti_2O_7$/RGO	Tetracycline	90	92	Visible light	Shanavas et al. (2019)
Ag/Ag_3PO_4-graphene	Sulfamethoxazole	30	99.9	Simulated solar light	Zhou et al. (2016)

class of pesticides is associated with impact of the cholinesterase enzymes' functioning (Naushad 2018). There is another group called carbamate pesticides which disrupt an enzyme which regulates the neurotransmitter, thereby causing malfunctioning of the nervous system. Carbamate pesticides, like aldicarb, carbofuran, and ziram, form a different class associated with endocrine and reproductive disorders. There are fat-soluble organochlorine compounds that persist in both the body and the environment. The accumulation of organochlorine compounds (e.g., DDT, chlordane, and toxaphene) is a consequence of their chemical structure, polarity, and solubility. A synthetic form of pyrethrin which is a naturally occurring pesticide exists and is known as pyrethroid. These include active agents, pyrethrins (I–VI), among which pyrethrins I and II are the most active. These pesticides degrade quickly in the presence of light (Naushad 2018). It is reported in Table 7.7 about the degradation of pesticides in agricultural wastewater using graphene-based material.

Photocatalysis begins with the incidence of the solar irradiation of certain wavelength onto the semiconductor. When the incident radiation's energy is equivalent to the band energy of nanophotocatalyst, the electrons get energized and transit to the conduction band (CB) from the valence band (VB), leaving holes (h^+) in the valence shell. The electrons (e) and holes (h^+) then proceed for the subsequent oxidation and reduction reactions with the compounds deposited onto the semiconductor surface. This results in ionization of the pollutant and formation of decomposed products. The hydroxyl radicals (OH*) produced during the photocatalysis degrade the pesticides into innocuous materials.

Table 7.7 Graphene-based nanomaterials for the degradation of pesticides in agricultural wastewater

Graphene-based material	Pesticide	Reference
Reduced graphene oxide	Chlorpyrifos, endosulfan, and malathion	Maliyekkal et al. (2013)
Graphene-based magnetic nanocomposite	5 different carbamates	Wu et al. (2011)
$CoFe_2O_4$ + TiO_2/reduced graphene oxide photocatalyst	Chlorpyrifos	Gupta et al. (2015)
Magnetite + SiO_2 + TiO_2-reduced graphene	2,4-Dichlorophenoxyacetic acid	Tang et al. (2013)
Graphene magnetic nanoparticles	Neonicotinoid insecticides	Wang et al. (2012a, b)
Cellulose/graphene composite	Six triazine pesticides	Zhang et al. (2015)
Graphene-coated silica	Organophosphorus pesticides	Liu et al. (2013b)

Table 7.8 Characterization of graphene prepared from different precursors

	Graphene characteristics			
Precursor	I_D/I_G	I_{2D}/I_G	Layers	Reference
Rice husk	0.55	0.67	Multilayer	Singh et al. (2017)
Graphite	<0.5	–	Single layer or few layer (<6)	Liu et al. (2013c)
Graphite	~0.24	–	Multilayer	Deng et al. (2016)
Rice husk	0.87	1.56	Multilayer	Seitzhanova et al. (2019)
Chitosan	0.74	–	Four layers	Hao et al. (2015)

7.6 Comparison of Conventional Precursors and Biomass-Based Precursors

Characterization of graphene prepared from different precursors has been shown in Table 7.8. Impurities, quality, and morphology of graphite (precursor) affect the intrinsic properties and quality of graphene (Singh et al. 2017). Graphene synthesized from graphite oxide precursor contains enough defects which degrade the superlative electronic mobility of graphene (Yan et al. 2020). Biomass precursors contain a large amount of oxygen during the synthesis of graphene; it is difficult to eliminate oxygen completely. The quality of graphene produced from biomass is not as high as graphene derived from graphite due to the formation of multilayered defected graphene. But the presence of defect in the graphene helps in the modulation of the bandgap which makes it suitable for an electronic application (Whitener Jr and Sheehan 2014). Covalent bond functionalization on graphene oxide is easier than that on graphene due to the presence of oxygen containing group (Yu et al. 2020). Graphene quantum dots' (GQDs') synthesis from pristine graphene required an additional doping agent, but GQDs prepared from biomass did not require it because of its inherent elemental composition performed as a doping agent (Tade et al. 2020).

7.7 Advantages and Disadvantages of Nanophotocatalyst

Nanophotocatalysts are less expensive and readily accessible and possess excellent chemical stability along with potential photoactive properties within nano size (1–100 nm range) (Khan et al. 2019). Among the popular photocatalysts, TiO_2 has good photostability, while zinc oxide, metal sulfides, copper-based materials, etc. are comparatively less stable on account of photocorrosion (Weng et al. 2019). The key benefit of nanoparticles is associated with the quantum-size effect improvement of the energy bandgap and reduction in the particle's size (Rajabi et al. 2016). Nanophotocatalysis has played a very essential role in the mineralization of hazardous organic molecules at 25 °C and has been proved to be quite effective for detoxifying water (Tahir et al. 2019). Nanophotocatalysts also have some drawbacks like toxicity and catalyst recovery from the reaction mixture. Graphene-based nanomaterials have also been tested for their interactions with different cells, microbe particles, and animals by several researchers. This results in short- and long-term in vivo studies (Ema et al. 2017; Guo and Mei 2014; Lalwani et al. 2016; Sanchez et al. 2012). Graphene derivatives are bestowed with high bio-chemical activity which is responsible for the generation of reactive oxygen into the living systems. It can trigger oxidative stress, inflammation, disruption of plasma membrane, autophagy necrosis, chromosomal disorders, and apoptosis and affects the DNA. Graphene-negative effects in animals also include pulmonary edema, acute lung injury, weight loss, immune cell infiltration, and liver and spleen disorders. The exposure of graphene-based substances to crops and vegetables like cabbage, tomato, and red spinach plants inhibits their growth and depletes vital nutrients. The powerful bonds present in the single graphene nanosheets are responsible for higher tendency possessed by the 2D graphene-based materials in the powder form to agglomerate and their capability to restack, thus reforming a graphite composition (Bano et al. 2020a, b; Li et al. 2013). Thus, intrinsic properties of graphene cannot be exploited as the theoretically probable data. Furthermore, expensive and robust processes such as drying, centrifugation, cavitation, or ultrasonication are needed for the separation of powdered catalyst. The catalyst losses which occur during this process may enter in the animal or human body, seriously affecting their health (Fan et al. 2015; Zhu et al. 2011).

7.8 Conclusions and Future Perspectives

In summary, this chapter focused on the synthesis of graphene from biomass waste as a precursor. Meanwhile, production of graphene-based nanophotocatalyst and its application in wastewater treatment are also well summarized. Considering the importance of graphene in the industrial field, the source of graphene precursor and its synthesis methods are two important factors for the cost of graphene which limit its industrial application. Selection of biomass waste as graphene precursors abates the cost of graphene and also helps in biomass valorization. In situ synthesis process of graphene-based nanophotocatalyst reduces the synthesis time. From literature, photocatalytic activity of photocatalyst can be further enhanced by introducing a small amount of graphene. Defect in graphene depends on pH and temperature during its synthesis. Among the various challenges, utilization of biomasses as a precursor for graphene is the major one. As per literature review and most of the articles in the synthesis of graphene-based nanophotocatalyst, graphene has been prepared from the reduction of graphene oxide which is obtained from hammer process. There are few reports on the synthesis of graphene-based nanocomposite from biomass, in which a few reported about the in situ synthesis of graphene-based nanomaterials, wherein biomass acts as a precursor for graphene as well as a support for nanomaterials. More attention is still required in the in situ synthesis of N,P-doped graphene and metal/metal oxide nanoparticle-impregnated graphene derived from biomass. This method has a scope in the future being economical, eco-friendly, and time-saving features. As per the summary reported in Table 7.3, it can be concluded that renewable-based synthesis of nanophotocatalyst is still untouched and has a wide scope in the treatment of various kinds of wastewater.

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Utilization of Rice and Sugarcane Ashes in Wastewater Treatment: A Case Study for Pesticide Removal from Aqueous Solution

8

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Abbreviations

BFA	Bagasse fly ash
BG	Brilliant green
BMA	Biomass ash
EL	Elovich
HPLC	High-performance liquid chromatography
IPD	Intraparticle diffusion
LDH	Layered double hydroxide
PFO	Pseudo-first-order
PSO	Pseudo-second order
RHA	Rice husk ash
RHS	Rice husk silica

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8.1 Introduction

8.1.1 Need of Wastewater Treatment

Water sources are continuously becoming insufficient in the world owing to the increasing consumption and decreasing availability of freshwater. The necessity of water is enhancing rapidly because of the following reasons:

- Growing population of the world and migration of living beings.
- Rapid development in the industrial sector causing more utilization of water.
- Weather change in crowded regions.

The quality of water is at risk due to the presence of infectious agents (Rizzo et al. 2013) and environmental changes caused directly or indirectly by human activities (Schwarzenbach et al. 2006). Additionally, the wastewater discharged from industrial and municipal treatment plants are one of the important factors leading to aquatic pollution (Reemtsma et al. 2006). In few developing countries, the wastewater generated in different industries is directly thrown into rivers without treatment or after primary treatment only (Dhote et al. 2012). In a nation like China, about 55% of the total sewage produced was being released into the environment untreated. The untreated wastewater thrown in the environment without treatment result in various environmental issues (Topare et al. 2011) such as:

- The untreated wastewater contains a large quantity of organic matter which requires higher oxygen for breakdown leading to higher biological oxygen demand. This reduces the amount of dissolved oxygen required for aquatic lives.
- The untreated wastewater contains pathogens and chemicals which create problems for human health.
- The wastewater also contains few nutrients which are necessary for the growth of aquatic plants and algae causing lake and stream eutrophication.
- Organic matter breakdown/decomposition by microorganisms results in the formation of aromatic gases in the region.

Given the aforementioned consequences, wastewater treatment is required prior to discharge into natural water bodies.

8.1.2 Biomass and Various Biomass Ashes

The extensive utilization of fossil fuels for energy production creates the global warming problems. As a result, interest in bioenergy as a replacement for fossil fuels has skyrocketed in recent years. The research on utilization of biomass for energy generation has been carried out worldwide (Vassilev et al. 2013). The biomass growth was previously estimated to be 112–220 billion tonnes per year globally. The biomass contributes 8–15% of world total energy supply in the form of heat, electricity, and fuel (Vassilev et al. 2013). The prominent biomasses which are used for energy generation are forest and agricultural residues, municipal solid wastes, and sewage. According to previous research, approximately 33–55% of the world's current energy consumption could be met by biomass. Ninety-five to ninety-seven percent of total bioenergy is produced through the direct combustion of biomass. Thus, approximately 476 million tonnes of biomass ash (BMA) may be produced annually across the globe (Vassilev et al. 2013).

BMAs can be generated by combustion in laboratory and industry. The BMAs produced in laboratory comprise low- and high-temperature ash, whereas ashes generated in industries include bottom ash and fly ash. The ashes produced from various biomasses are wood and woody biomass (wood of birch, pine, oak, hornbeam, poplar, acacia), energy crops (Virginia mallow, common reed, switchgrass), agricultural biomass (triticale straw, barley straw, wheat straw, oat straw, buckwheat straw, hay), forest residue (acacia bark, oak bark, beech bark, hornbeam bark), and agro-industry waste (rice hush, bagasse, cherry pits, sunflower husk, hazelnut shell, walnut shell, apple pomace) (Zaja et al. 2018). The content of BMAs depends mainly on the type of biomass and its storage time and condition of combustion (Zaja et al. 2018; Danielowska and Jabłońska 2022). The chemical and mineral contents of BMAs are significantly different from coal ash. Michalik and Wilczynska-Michalik reported large variation in the chemical composition of BMAs (Michalik and Michalik 2012). Many BMAs are high in K and Mg phosphates, while others are high in carbonates (e.g., calcite, fairchildite, kutnohorite), sulfates (arcanite), and lime, as well as quartz, cristobalite, and Fe oxides (Michalik and Michalik 2012).

8.1.3 Rice Husk Ash and Bagasse Fly Ash

Sugarcane bagasse and rice husk are the most important wastes generated globally by the sugar industry and rice mills, respectively. In the industries, biomass waste is used in conjunction with coal as an energy source for the production of energy. Though the combustion of such wastes may reduce the amount of waste, it introduces a new problem: the formation of ash. The combustion process of rice husk forms the ash known as RHA, whereas sugarcane bagasse after combustion left behind the BFA.

During paddy processing, approximately 78% of the weight was formed as rice, broken rice, and bran, while 22% of the weight was generated as rice husk. Rice husk on burning in boiler produces 25% RHA (Khan et al. 2012). The world's total paddy rice production was estimated at 713 million tonnes in 2021 (Childs and LeBeau 2022). Based on the above data and considering the milling of total paddy for the year 2021, the rice husk generated would be approximately 157 million tonnes which on fueling the boiler forms around 39 million tonnes of RHA.

One tonne of sugarcane produces approximately 26% of bagasse (Deokar et al. 2016a). After burning in the boiler, bagasse results in the formation of 0.62% BFA (Deokar et al. 2016a). The world's sugarcane production for the year 2020 was approximately 1870 million tonnes (Childs and LeBeau 2022). Assuming the crushing of complete sugarcane production, the generation of bagasse would be around 486 million tonnes. According to the above data, the burning of bagasse in the industry generated three million tonnes of BFA. Thus, a huge quantity of RHA and BFA is generated globally every year. These ashes produce a big problem of disposal if the ashes are not used for certain purposes.

8.1.4 Utilization of RHA and BFA

The BMA are produced worldwide in large quantity because of the utilization of different biomasses on large scale in domestic and industrial applications. To avoid the disposal issue, the biomass ashes should be used in some other application. In recent years, there has been a growing interest in investigating the use of RHA and BFA for various applications. Previously, RHA was investigated as an adsorbent for the removal of various pollutants from water and wastewater. Using RHA, various pollutants such as dyes, phenols, organic compounds, pesticides, inorganic anions, and heavy metals are effectively removed (Fernandes et al. 2016).

The high-purity silica was obtained from RHA to develop zeolite/catalyst which was used for transesterification of soybean oil by Dutta et al. (2017). In the study, the author reported about 90% yield of product using the catalyst synthesized from RHA silica. Despite the fact that silica is the most abundant element in RHA, trace amounts of magnesium, calcium, potassium, and sodium, as well as carbon, are also present. Thus, RHA contains a number of other components in addition to silica and carbon; this facilitates RHA as a basic material for different applications. The crystalline nature and high percentage of silica together with surface area provide pozzolanic properties to RHA. The addition of RHA in concrete making process makes the process economical and changes the properties of concrete because of the pozzolanic properties of RHA. This gives RHA an advantage in the production of high-strength concrete and refractory bricks (Hwang and Huynh 2015), which are used as feedstock in the silicon chip processing industry (Watari et al. 2006). RHA is also used as a refractory powder, for rubber vulcanization, as a clarifying agent in beer, and as a filler in polymer production (Kumar et al. 2016). RHA's insulating property allows it to be used as an excellent tundish powder to prevent the rapid cooling of steel and ensure uniform solidification during the casting process (Kumar et al. 2012).

The chemical composition of RHA and BFA is qualitatively similar, but both ashes are differing quantitatively. The percentage of carbon in BFA is significantly higher than in RHA which results in higher surface area of BFA than RHA. Similar to RHA, BFA is also utilized as an adsorbent for different heavy metals, dyes, organic chemicals, and pesticides (Patel 2020). The preparation of activated carbon from BFA is one of the important applications of BFA. It is found that the surface area of activated carbon made from BFA is 1200 m^2/g (Purnomo et al. 2011). BFA is found to be source of high-purity silica which was used to obtain beta-zeolite. This zeolite was used as a catalyst for the dehydration of methanol to dimethyl ether (Ahmaruzzaman 2010). The activated BFA is used as an electrode material for capacitive deionization to improve the electrosorption of salt (Lado et al. 2017). The charcoal from BFA was converted into briquettes which were used as alternative fuel (Teixeira et al. 2010). In construction industries, BFA is included with base materials to form the pastes, mortars, and reinforced ternary concrete (Patel 2020; Purnomo et al. 2011). These products from BFA were found to possess greater resistance to corrosion caused by chloride ion (Patel 2020; Purnomo et al. 2011).

8.2 Adsorption

Adsorption is the process of one or more ions or compounds sticking to the surface of a solid. The main parts of adsorption are the adsorbent and the adsorbate. Adsorbent is usually a solid (mostly a powder) that adsorption happens on, and adsorbate is the substance that gets absorbed. There are two types of adsorption: physical adsorption (also known as van der Waal's adsorption) and chemical adsorption (chemisorption).

Physical adsorption occurs due to van der Waal's force of interaction, and heat of this type of adsorption is generally in the range of 20–40 kJ/mol (Deokar et al. 2016c). Physical adsorption can be of two types: monolayer adsorption and multilayer adsorption. It is quick and reversible. In chemisorption, molecules that are being adsorbate on an adsorbent surface interact chemically. Typically, the heat of chemisorption ranges between 40 and 400 kJ/mol. Due to the strong force of interaction between the molecules of the adsorbent and adsorbate, which occurs during the relatively slow process, it is an irreversible process (Deokar et al. 2016b).

In adsorption process, commonly, the migration of adsorbate molecules takes place in three chronological steps: (1) migration of adsorbate molecules to the adsorbent's boundary, (2) intraparticle diffusion into pores, and (3) adsorption and desorption of solute (equilibrium step) (Rashid et al. 2021). The rates of the aforementioned steps are determined by the adsorbate, adsorbent, and matrix properties. The maximum adsorption capacity of adsorbent is determined using adsorption isotherms. Adsorption isotherm is a plot of equilibrium adsorbate solid phase concentration versus liquid phase concentration. The Langmuir isotherm, Freundlich isotherm, Temkin isotherm, and Brunauer-Emmett-Teller isotherm are the most widely used and significant isotherms. Typically, pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models are used to examine the adsorption rate (Rathi and Kumar 2021). Based on the applicability of kinetic models to adsorption process, the type of adsorption together with the rate controlling step in adsorption can be determined.

8.3 Biomass Ashes as an Adsorbent

RHA and BFA have fluctuating proportions of SiO_2, Fe_2O_3, K_2O, Na_2O, CaO, MgO, carbon, and silica depending on the cultivated area, fertilizer used, climatic conditions, soil properties, and geographical conditions (Foo and Hameed 2009).

The research on the application of RHA and BFA has primarily investigated its use as adsorbent in removing the contamination from water and wastewater. When it comes to the adsorption of different pollutants from water and wastewaters, the functional groups on the surface of RHA and BFA are crucial. The disappearance of bands and shifting of peaks are reported after adsorption of metals such as Cd(II), Ni (II), and Zn(II) onto RHA (Shamsollahia and Partovinia 2019). The same metals are used as adsorbate to analyze the comparative adsorption behavior of RHA and BFA (Srivastava et al. 2007). Many have studied the removal of gold (Nakbanpote et al. 2000), Cr(VI) (Bhattacharya et al. 2008), and Hg(II) (Tiwari et al. 1995) using RHA. Ahmaruzzaman and Gupta (2011) reported the utilization of RHA for the removal of dyes such as congo red, methylene blue, indigo carmine, and brilliant green and organic compounds such as phenols, pyridine, α-picoline, and humic acid. The silica and activated carbon were simultaneously obtained from RHA by Yan Liu et al. (2012). This activated carbon was used as a methylene blue adsorbent, and its capacity was determined to be 210 mg/g (Yan Liu et al. 2012). RHA was used to get high-purity amorphous silica, which was then used to make a cheap mesoporous adsorbent (RHS-MCM-41). The cationic dye brilliant green was taken out of water with the help of the RHS-MCM-41 (Dutta et al. 2014). In 2012, RHA was used as an adsorbent to clean biodiesel made from used frying oil. This showed that a 4% concentration of RHA was the best way to remove impurities from biodiesel (Manique et al. 2012) (Table 8.1).

Totlani et al. (2012) prepared carbon embedded silica from RHA, and its performance has been compared with RHA in the removal of Ni(II). The modified RHA and catalyst developed from RHA have been used in adsorption to remove pollutants (Dutta et al. 2017; Srivastava et al. 2006a). In comparison with RHA, BFA has higher carbon, lower silica content, and higher surface area (Deokar et al. 2016a). Removal of copper and zinc from aqueous solution/wastewater was carried out using bagasse fly ash by Gupta et al. (2000). Binary adsorption of Cd(II) and Zn(II) metal ions on BFA was investigated by Srivastava et al. (2006a), who reported higher removal efficiency for Zn(II) than Cd(II). The adsorption capacity of BFA for removing lead and chromium from wastewater in continuous adsorption process was evaluated previously (Gupta et al. 2003). The study reported 95–96% removal by BFA-packed bed at a flow rate of 0.5 mL/min. Like RHA, the uptake performance of BFA was also studied for the removal of dyes (congo red, malachite green, orange-G, brilliant green) and organic compounds (phenols) (Ahmaruzzaman 2010). After treatment with hydrogen peroxide, Gupta et al. (2000) used washed, dried, and sieved BFA for the removal of basic dyes, rhodamine B, and methylene blue. The authors estimated the cost of finished adsorbent as 12 US $/ton, which was quite cheap. In recent past, both RHA and BFA have been used for the removal of pesticides such as 2,4-dichlorophenoxy acetic acid, 4-chloro-2-methylphenoxyacetic acid, diuron, and paraquat from aqueous solution (Deokar et al. 2016b, c, 2020, 2021; Kamble et al. 2020). Batch as well as packed bed adsorption of these pesticides is performed for different experimental parameters. Deokar et al. (2016b, c) have determined the adsorption capacity of RHA and BFA in terms of mg/m^2 surface area of RHA and BFA. The adsorption capacity of RHA and BFA in

Table 8.1 Utilization of RHA and BFA as adsorbents for various pollutants

Adsorbates	RHA adsorption capacity (mg/g)	Reference	Adsorbates	BFA adsorption capacity (mg/g)	Reference
Zn(II)	26.10 17.84	Ahmaruzzaman and Gupta (2011)	Cu(II)	2.26	Gupta and Ali (2000)
Ni(II)	25.33 13.89	Ahmaruzzaman and Gupta (2011)	Zn(II)	2.34	Gupta and Ali (2000)
Cd(II)	25.27 11.79	Ahmaruzzaman and Gupta (2011)	Cd(II)	1.24	Gupta et al. (2003)
Phenol	0.886	Ahmaruzzaman and Gupta (2011)	Ni(II)	1.12	Gupta et al. (2003)
Oxytetracycline	5.2	Andrade et al. (2020)	Pb	2.50	Gupta and Ali (2004)
2,4-Dichlorophenol	0.16	Akhtar et al. (2006)	Cr	4.35	Gupta and Ali (2004)
Pd(II)	207.57 91.74	Wang and Lin (2008), Naiya et al. (2009)	2-Picoline	60.976	Lataye et al. (2008)
2-Chlorophenol	209.55×10^{-6}	Mbui et al. (2002)	Phenol	23.832	Srivastava et al. (2006b)
Resorcinol	888.59×10^{-5}	Mbui et al. (2002)	Barium lithol red	7.30–14.34	Noonpui et al. (2010)
α-Picoline	15.46	Lataye et al. (2009)	Malachite green	170.33	Mall et al. (2005)
Brilliant green	26.20	Mane et al. (2007a)	Methyl violet	26.24	Mall et al. (2006)
Indigo carmine	65.91	Lakshmi et al. (2009)	Orange-G	18.79	Mall et al. (2006)
Methylene blue	48.583	McKay et al. (1999)	Brilliant green	116.27	Mane et al. (2007b)
Congo red	171	Chou et al. (2001)	Lindane	2.51×10^{-3}	Gupta et al. (2002)
Fluoride	9–10	Ganvir and Das (2011)	Malathion	2.08×10^{-3}	Gupta et al. (2002)

mg/m^2 is compared with the previously used adsorbents such as activated carbon, Norit 0.8, Aquacarb 207C, Aquacarb 208A, Aquacarb 207EA, Mg-Al-CO_3-LDH, and activated spent bleaching earth for the above aforesaid pesticides (Deokar et al. 2016a, b, 2020, 2021; Kamble et al. 2020). The pesticide adsorption capacity of RHA and BFA is found to be greater than some of the adsorbents and comparable with other adsorbents. This proves that RHA and BFA are economically efficient adsorbents for pesticides because RHA and BFA are available chiefly in ample quantity. In addition to this, the research is still being done on application of fresh and modified RHA and BFA as adsorbent for pollutant removal.

8.4 A Case Study

RHA and BFA have been utilized as adsorbents for the removal of chlorinated herbicides from aqueous solution, including 2,4-dichlorophenoxyacetic acid (Deokar et al. 2016b), diuron (Deokar et al. 2016c), and 4-chloro-2-methylphenoxyacetic acid (Deokar et al. 2016d). The efficacy of RHA and BFA for the removal of another chlorinated herbicide such as 2,4,5-trichlorophenoxyacetic acid is not determined till date. Therefore, in this case study, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) is selected as adsorbate for RHA and BFA. Adsorption of 2,4,5-T from aqueous solution was performed at constant temperature 300 K and pH 6.5 to determine the adsorption capacity of RHA and BFA. The batch experiments were performed according to method reported in earlier study (Deokar et al. 2021). The effect of initial concentration on the removal of 2,4,5-T was studied by varying the concentration in the range between 50 and 200 mg/L at constant dose (1 g/20 mL for RHA, 0.5 g/20 mL for BFA), temperature 303 K, and time (720 min). The aforesaid experiments were also performed at 318 and 333 K. The kinetics of 2,4,5-T adsorption using RHA and BFA was studied for time 15–720 min at fixed concentration (100 mg/L), adsorbent dose (1 g/20 mL for RHA, 0.5 g/20 mL for BFA), and temperature 303 K; in addition to this, thermodynamic study was also performed. The concentration of 2,4,5-T was analyzed by a reverse-phase HPLC system consisting of Waters 515 HPLC pump fitted with SunFire C18 column (4.6 × 250 mm, 18.5 μm) and UV-Vis detector (Water UV-Vis Det 2489). With a flow rate of 1.4 mL/min, the isocratic mobile phase of 60% acetonitrile, 40% water, and 0.1% phosphoric acid was utilized.

Figure 8.1 shows the outcomes for the influence of initial concentration on 2,4,5-T removal. Nearly, complete removal of 2,4,5-T is achieved for 1 g RHA and 0.5 g BFA for 50 mg/L concentration of 2,4,5-T. The removal is reduced with increasing concentration of 2,4,5-T, and it is decreased approximately to 85% for 200 mg/L concentration. This is due to the limited number of available adsorption sites for higher concentrations. But the equilibrium capacities for both adsorbents are increased due to greater driving forces at higher concentrations. The efficiency of RHA and BFA is judged by applying Langmuir isotherm model for the above experimental data (Fig. 8.1). The application of Langmuir, Freundlich, and Temkin isotherm models is mainly reported in previously published studies (Deokar et al.

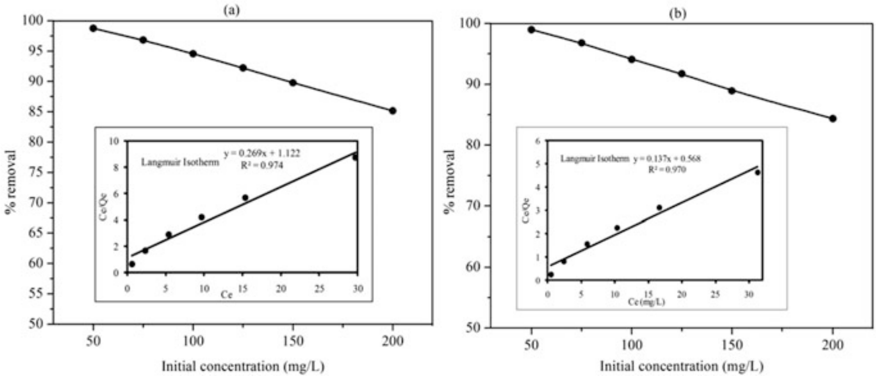
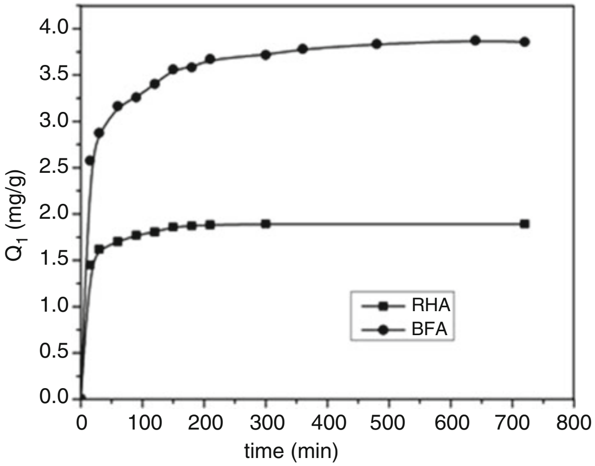


Fig. 8.1 Effect of initial concentration on the removal of 2,4,5-T using (**a**) RHA and (**b**) BFA

Fig. 8.2 Effect of contact time on the adsorption of 2,4,5-T using RHA and BFA



2020). Here, the mostly used model, i.e., Langmuir isotherm, is given to determine the adsorption capacity of RHA and BFA. Inset plots in Fig. 8.1 indicate the applicability of the Langmuir isotherm for the adsorption of 2,4,5-T on RHA and BFA. RHA and BFA have 3.72 mg/g and 7.30 mg/g Langmuir adsorption capacities, respectively. The Langmuir constant determined from intercept of lines is 0.239 L/mg for RHA and 0.241 L/mg for BFA. The dimensionless factor [$R_L = 1/(1 + K_L C_0)$] investigated from the Langmuir constant (K_L) is 0.04 for both adsorbents for $C_0 = 100$ mg/L. The value of dimensionless factor between 0 and 1 suggests the favorability of 2,4,5-T adsorption of RHA and BFA.

Batch experiments were performed for variable time from 15 to 720 min for the adsorption of 2,4,5-T onto RHA and BFA. Results obtained are shown in Fig. 8.2 for 100 mg/L concentration, 6.5 pH, and 303 K temperature. It was observed that approximately 80% and 72% removal (not shown in Figure) of 2,4,5-T were achieved within the first 30 min of adsorption experiments for RHA and BFA,

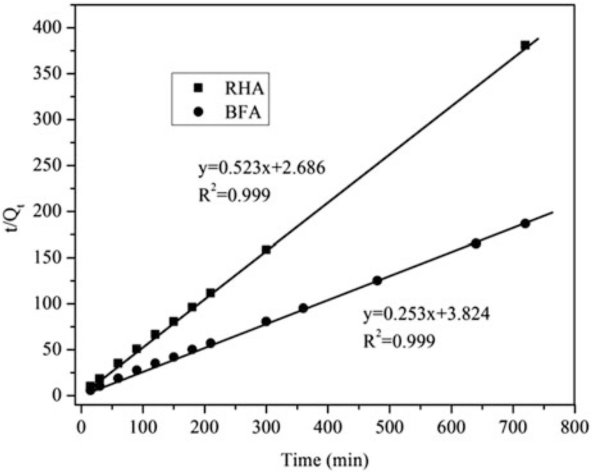


Fig. 8.3 Pseudo-second-order kinetic model for the adsorption of 2,4,5-T using RHA and BFA

respectively. Thus, the initial adsorption of 2,4,5-T is very fast for both adsorbents. The amount (Q_t, mg/g) of 2,4,5-T adsorbed on BFA is comparatively higher than on RHA as shown in Fig. 8.2. This is because BFA has a larger surface area (51 m^2/g) than RHA (33 m^2/g) (Deokar et al. 2016a). As the time progresses, the amount adsorbed (Q_t) increases for both adsorbents; but the increment in value of Q_t is significantly higher for BFA than for RHA. The adsorption rate gradually slows down on both adsorbents, and equilibrium is achieved. The equilibrium time for the adsorption of 2,4,5-T is around 200 min for RHA and 350 min for BFA as can be seen in Fig. 8.2. Thus, the equilibrium is achieved far early for RHA compared to BFA. This is due to the deeper pore on BFA surface and shallower pore on RHA surface which is previously reported for the adsorption of diuron herbicide on BFA and RHA surface (Deokar et al. 2016c). Therefore, pore diffusion in BFA is comparatively greater than in RHA. Compared to RHA, BFA has an equilibrium capacity that is nearly twice as high (Fig. 8.2).

Understanding the rate-controlling step and the underlying mechanism of adsorption requires a thorough understanding of adsorption kinetics. Most adsorption research employs one of four models: the pseudo-first-order (PFO), pseudo-second-order (PSO), intraparticle diffusion (IPD), or Elovich (EL). In present study, the coefficient of determination ($R^2 = 0.999$) is found nearly one for PSO model; therefore, PSO model is given in Fig. 8.3. As expected, the PSO model suggests an equilibrium capacity of 1.91 mg/g for RHA and 3.95 mg/g for BFA. The experimental values of equilibrium capacities are 1.89 mg/g for RHA and 3.87 mg/g for BFA. Adsorption of 2,4,5-T on RHA and BFA can be best explained by the PSO kinetic model. The applicability of PSO model infers the chemisorption of 2,4,5-T and heterogeneous nature of RHA and BFA (Mandal et al. 2019). The kinetic constants of PSO are calculated to be 0.102 (g/mg/min) for RHA and 0.017 (g/mg/min) for BFA.

8.5 Conclusion

In order to clean water that has been tainted with metals, dyes, and organic pollutants, biomass ashes, especially RHA and BFA, are used extensively. Though the adsorption capacity of RHA and BFA for some of the above adsorbates is slightly lesser than the other adsorbents such as activated carbon, the bulk availability of these ashes makes the adsorption economical. From the literature published on pesticide removal, it is clear that a wide range of adsorbents is utilized for the adsorption of different types of pesticides and most of the studies are carried out in batch mode. However, among the seven different classes of adsorbents, utilization of biomass ashes for pesticide removal is not much explored according the author's knowledge. Literature on use of RHA and BFA as adsorbents reveals that there is still scope for the utilization of RHA and BFA for the adsorption of pesticides.

The surface area of untreated RHA and BFA is comparatively lesser than the adsorbents such as activated carbon, activated carbon fiber, carbon nanotubes, and Mg-$AlCO_3$-layered double hydroxide. But the pesticide adsorption capacity of RHA and BFA in terms of mg/m^2 is greater than some of the adsorbents and is comparable with the other adsorbents.

A case study for the removal of 2,4,5-T pesticide using RHA and BFA indicates that the 100% removal of 2,4,5-T pesticide is possible with RHA and BFA. The adsorption capacity of BFA for 2,4,5-T pesticide is greater than that of RHA. But the equilibrium time is higher for 2,4,5-T adsorption using BFA. This is due to greater surface area and greater depth of pores of BFA than that of RHA. The Langmuir isotherm model is best to explain the adsorption of 2,4,5-T on both ashes. The PSO kinetic model explains the heterogeneous nature of both ashes.

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Trends and Scope of Utilization of Biochar in Wastewater Treatment

9

Perminder Jit Kaur, Vinita Khandegar, and Shruti Singh

9.1 Introduction

The presence of contaminants, heavy metals, dyes, and toxic pollutants from industrial and domestic sources in water is a threat to the global ecosystem (Khandegar et al. 2021). Ingestion of heavy metals like Cu, As, Pb, Hg, Au, and Pd by aquatic animals, plants, and humans has severe environmental consequences. The discharge of effluent-containing dyes from textile and fiber processing industries leads to water pollution, and it becomes unfit for human consumption. The problem of water pollution also causes wastage of water and has prompted global researchers to look for eco-friendly, low-cost, effective technology to treat the water for reuse. Some of the most commonly used water treatment processes are membrane separation, composting, landfarming, coagulation, chemical precipitation, advanced oxidation method, ozonation, and adsorption (Chauhan et al. 2020; Kaur et al. 2020a, b; Suri et al. 2020, 2021).

Low cost and ease of availability make adsorption an attractive process for wastewater treatment. Adsorption is a surface phenomenon with the accumulation of atoms, ions, or molecules on a surface from the bulk of fluids or dissolved solids. Molecules that get adsorbed are called adsorbate, and the material used for this purpose is called adsorbent. Two main types of adsorption processes are physisorption and chemisorption. In the first type of adsorption, the attractive force between adsorbate and adsorbent is primarily governed by van der Waals

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forces. The process has low adsorption enthalpy and is reversible. In chemisorption, a chemical reaction occurs between the adsorbate and adsorbent, breaking old bonds and forming new ones. This process is irreversible since the bonds formed in chemisorption are highly ionic or covalent.

Adsorption has an extensive application in industries. It is one of the essential separation processes in which specific components are removed from the fluids and transferred to the surface of the solid adsorbent (Odoemelam et al. 2015). Adsorption is also used to remove hazardous ingredients found in effluents from industries and water treatment plants. It also finds application in drying gases and liquids before loading them into industrial units. Adsorbents are used in gas masks to purify the air from harmful particles getting into our respiratory tracts. Another important application of this process is the removal of foul odor, by using silica gel (Dąbrowski 2001). The biomass sources include waste materials like agricultural or forestry residue and industrial biowaste (Chauhan et al. 2020).

Biochar can be further modified to produce activated charcoal (AC), which has superior properties. The use of AC as an adsorbent is not a new concept. They have been used for many adsorption processes for decades (Dąbrowski 2001). AC is a hydrophobic adsorbent. With the enhanced surface area, AS is successfully used to eliminate pollutants from the air, purify water, remove dyes, and even decolorize cane sugar in sugar industries. The primary advantage of using AC is its high porosity and large specific surface area of 500–2000 m^2/g (Mohammad-Khah and Ansari 2009).

The present chapter focuses on types of biomass used to produce biochar with enhanced surface area. An overview of biochar production processes and characteristics of biochar is provided here. The research on activated charcoal was fabricated from various biomasses to promote the usage of biowaste. The present chapter discusses multiple techniques and optimum conditions to form high-quality activated carbon from biomass, which can be used for industrial purposes, such as removing dyes, heavy metals, and organic and inorganic waste. Further, it can be used for cosmetic and pharmaceutical purposes. The chapter analyzes the scope of biochar for water treatment and provides future directions for research work.

9.2 Types of Biomass Suitable for Biochar Production

Biomass is a biological material obtained from living or recently living organisms. Some of the most common available biomass feedstocks are grains and starch crops which include sugarcane, corn, wheat, sugar beets, industrial sweet potatoes, etc.; agricultural residues like corn stover, wheat straw, rice straw, orchard prunings, etc.; food waste obtained from the food processing industries; forestry materials like logging residues, forest thinnings, etc.; animal by-products like tallow, fish oil, manure, etc.; energy crops like switchgrass, miscanthus, hybrid poplar, willow, algae, etc.; and urban and suburban wastes which include municipal solid wastes (MSW), lawn wastes, wastewater treatment sludge, urban wood wastes, disaster debris, trap grease, yellow grease, waste cooking oil, etc.

All these materials are lignin, cellulose, and hemicellulose with minor constituents like resin, gums, and tannins (Kaur et al. 2016a, b).

The relative proportion of these constituents varies among various species and within the same species grown under different geographical conditions (Kaur 2018). The conversion of biomass to energy depends on relative moisture content and other constituents present in the raw material. The sludges and herbaceous biomass materials with high moisture content undergo biologically meditated fermentation processes using enzymes as the catalyst to produce ethanol-based fuels. Though biological processes have several advantages like low energy consumption, ease of handling, and ability to handle significant feedstock simultaneously, the sensitivity and long treatment times make them challenging to handle. Thus, dry biomass materials like wood chips with lower moisture content can be chosen for thermal treatment processes. Lignin is a further complex polymer that needs a temperature higher than 350 °C to decompose and becomes a less desirable component for biochar production. Thus, biomass species richer in cellulose and lower in lignin content are generally preferred for biochar production.

9.3 Processes for Biochar Production

Char and biochar are similar materials, based on the raw material used for production. The decomposition of any organic materials leads to producing a black, porous compound known as char. When the biomass undergoes thermal decomposition, the material obtained is biochar. Being a waste biomass-based material, biochar is sustainable and helps to add value to a waste product. The general steps for producing biochar include pretreatment, thermal decomposition, char separation, and biochar activation (Fig. 9.1).

9.3.1 Pretreatment

The first step for biochar production includes biomass pretreatment to make it suitable for thermal treatment. Physical pretreatment of biomass can be done using

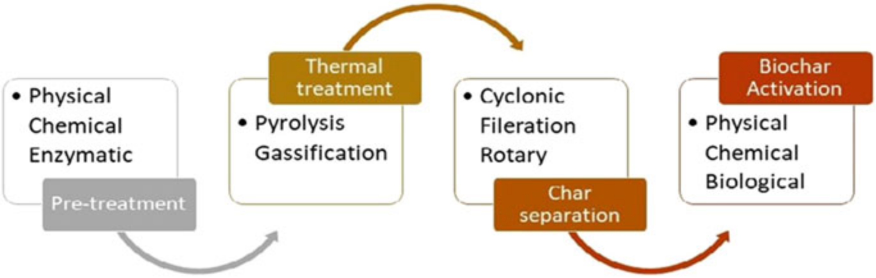

Fig. 9.1 General steps for the production of biochar

chunking, chipping, grinding, and crushing to reduce the particle size, reduce feed variability, and increase the surface area and energy density of feedstock. Various types of chemicals like acid, alkali, and oxidants can change the chemical composition of biomass and help in thermal conversion processes. Treatment with metal-based solutions like $FeCl_3$, $AlCl_3$, and $MgCl_2$ can lead to the generation of engineered biochar with metal hydroxides deposited on its outer surface. Biochar-based nano-composites can be produced by treatment of biomass material with nanoparticles like carbon nano-tubes, graphene oxide, etc. Biomass can also undergo biological treatment to produce biologically active biochar with very high surface area.

Moisture in the raw material leads to high energy consumption and makes biomass susceptible to fungal and microbial decay during storage. Water reduces the shelf-life of biomass species (Kaur et al. 2016a, b). Drying at 105 °C is further required to reduce and stabilize the moisture content. As shown in Table 9.1, there is a significant variation in lignin, cellulose, hemicellulose, fixed carbon, and moisture range of various biomass species. The choice of pretreatment method depends on the chemical composition of raw material, the type of biochar required, and the specific applications it needs to be used.

9.3.2 Thermal Treatment Processes

The heating of various biomass species under controlled conditions in specially designed equipment leads to biomass conversion to biochar. Pyrolyzers are the reactors used to heat materials without air in temperatures between 200 and 900 °C. While the temperature is less than 400 °C, solid products, i.e., biochar, can be obtained as the main product (Kaur et al. 2021). As shown in Fig. 9.2, a lower range of temperatures (200–400 °C) is required to produce solid biochar as the primary product. Biomass is a complex mixture of compounds richer in carbon, hydrogen, and oxygen, breaking down into smaller molecules during pyrolysis. While heating biomass material between 200 and 250 °C, water evaporation takes place. Rapid loss of biomass with the decomposition of cellulose, hemicellulose, devolatilization, and production of condensable and non-condensable gases occurs between temperatures 200 and 350 °C. In the intermediate range of temperature (400–600 °C), liquid bio-oil is obtained and collected. The heating of biomass to a temperature of more than 600 °C is required to produce gaseous products like syngas.

Biochar can be produced by slow pyrolysis of biomass (temperature less than 400 °C). The separation of biochar is required as soon as it is formed during the process, as char acts as a catalyst for developing polyaromatic hydrocarbons (PAH). Cyclone separators, in-bed vapor filtration, and rotary particle separator can be used to separate char.

Table 9.1 Chemical composition of various types of biomass

Type of biomass	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Moisture (%)	Fixed carbon (%)	Reference
Sunflower residue	20.94	–	35.18	–	–	Çepelioğullar and Pütün (2013)
Triticum aestivum (wheat straw)	16.3	39.1	24.1	13.2	20.3	Nanda et al. (2013)
Cotton stalk	20.51	40.17	27.98	6.92	14.75	Khan et al. (2020)
Sugarcane bagasse	4.01	38.01	33.27	8.79		Hua and Li (2016)
Walnut waste	36.89	32.19	26.20	6.98	15.99	Özsin and Pütün (2018)
Peach stone	39.26	29.50	25.10	6.88	19.84	Özsin and Pütün (2018), Demirbas (2005)
Hazelnut seed coat	53	29.6	15.7			
Phleum pratense (timothy grass)	18.1	34.2	30.1	9.3	12.6	Nanda et al. (2013)
D. strictus bamboo	25	53.6 (lignocellulose)	–	6.8	–	Kaur et al. (2016a, b)
Eucalyptus globulus	26.7	–	23.8	–	–	Pinto et al. (2018)
Beechwood	21.9	45.8	31.8	7.4	24.6	Demirbas (2005)

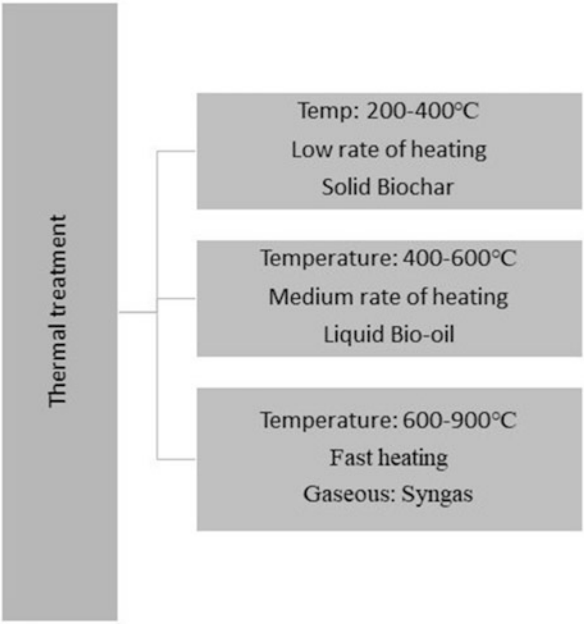

Fig. 9.2 Thermal treatment processes for the conversion of biomass to biochar

9.3.3 Posttreatment of Biochar

Once biochar is formed, selective posttreatment of biochar is required to make it appropriate for specific applications. Both physical and chemical posttreatments can produce biochar of necessary surface area, pore volume, and active functional groups. Inducing iron oxides in biochar can further help increase the surface area and pore volume. Another significant advantage of using activated charcoal as an adsorbent is that it can be regenerated by washing with organic solvents, mineral acids, caustic soda, or steam. Hence, the adsorbent can be reused (Mohammad-Khah and Ansari 2009).

Several materials with high carbon content are converted to AC by either gas/physical or chemical activation and carbonization. In the gas activation method, raw material is pyrolyzed to high temperatures to eliminate volatile matter after sun- or oven-drying. The next step is to oxidize, usually with carbon dioxide, or supply steam at yet higher temperatures for selective oxidation. As incomplete combustion takes place, the by-products leave the surface of carbon, creating voids and increasing the surface area of the adsorbent. The charcoal formed by this process is usually granular, which can be broken down to convert into powder form (Mohammad-Khah and Ansari 2009). Binding agents can be used further to form pellets of AC. Subjecting the biochar to a ball mill can also produce biochar nano-scale particle size of high surface area.

Chemical treatment is a simple method that alters the surface chemistry to enhance the surface area, porosity, negative zeta potential, and oxygen-containing functional groups of biochar particles. Various chemicals like HCl, HNO_3, KOH, NaOH, $KMnO_4$, and H_2O_2 have been used by researchers to alter the characteristics of chemical modified biochar. In the chemical activation process, chemicals like potassium hydroxide, zinc chloride, phosphoric acid, or other alkaline metal hydroxides are used to activate charcoal and carbonization at higher temperatures. The raw material is impregnated in proper ratios of the activating agent to achieve effective results. After activated charcoal is formed, the sample is washed to neutralize or remove excess chemicals.

9.4 Specific Characteristics of Biochar

AC has a structure of hexagonal graphite plates. Each carbon atom forms a covalent bond with three neighboring carbon atoms. The addition of some heteroatoms, like oxygen, hydrogen, sulfur, nitrogen, etc., in the carbon matrix can help improve the adsorption capacity of biochar. These heteroatoms act selectively toward specific adsorbates. AC has a large number of pores which are divided into three categories: micropores, macropores, and mesopores. The adsorbent is used with micro- and macropores for gas adsorption, whereas, in liquid adsorption, more mesopores are used. All these pores contribute to a significant surface area of AC which in turn enhances the adsorption (Chowdhury et al. 2013).

The principal property of AC is its high specific surface area and variable pore size distribution. Brunauer-Emmett-Teller (BET) isotherms are used to find the particular surface area of AC which gives five types of profiles. Generally, as mentioned earlier, the specific surface area of AC ranges from 500 to 2000 m^2/g. The factors that affect the porosity of AC are (1) activating agent, (2) activation temperature and time, (3) gases used in carbonization and activation, (4) mixing procedure, and (5) heating rate. Fourier transform infrared (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscope (SEM) techniques are used for the characterization of AC to see the overview of specific surface area, porosity, composition, and other characteristics of adsorbent.

Factors affecting the properties of AC as reported by Banerjee et al. (2020) are as follows:

- Raw materials: Organic materials with high carbon content are used to synthesize high-quality activated charcoal. Generally, the biomass used as a precursor should have high carbon content, low ash content, high density, high volatile content, and cost-effectiveness.
- Pyrolysis temperature: High temperatures are preferred for carbonizing the biomass to decompose the sample. The temperature is one of the factors that decide the properties of the prepared AC.
- Activating agent: Use of activating agent in proper ratio improves adsorption at the surface of the carbon.
- Activation time: Activation time affects the carbonization and hence the final properties of AC. If the time increases, the surface area of the adsorbent increases

as well, whereas the percentage yield decreases. Therefore, the sample has to be kept for the optimum time.

- Activation temperature: With the increase in temperature, new pores form, and existing pores broaden, increasing carbon adsorption. But the further increase in temperature decreases the yield due to the release of a high volume of volatile matters.

9.5 Classification of Activated Carbon

Activated carbon can be classified into diverse types depending on the production method, appearance, function, and pore size. AC can be divided into granular and powdered from the shape, and granular activated carbon includes amorphous and shaped forms. Depending on the raw materials, activated carbon can be divided into wood-based, coal-based, nut shell-based, petroleum, and regenerated activated carbon. According to the different functions of the application, it can be divided into liquid adsorption, catalytic performance, and gas adsorption of activated carbon. It can be physically activated carbon, chemically activated carbon, and physically and chemically activated carbon based on production methods.

9.5.1 Granular Activated Carbon (GAC)

Granular activated carbon uses coal-based carbon as raw material, which has a black amorphous appearance, a developed pore structure, good adsorption performance, high mechanical strength, easily repeated regeneration, and low cost. GAC can be used for various applications like decolorization, gas purification, and wastewater treatment. The majority of activated carbon particles with an apparent size larger than 0.18 nm (about 80 mesh) can be fragmented, spherical, and hollow microspheres in shape.

9.5.2 Powdered Activated Carbon (PAC)

Powdered activated carbon has the advantages of fast filtration speed, good adsorption performance, strong decolorization and odor removal ability, economic durability, etc. The products are widely used in food, beverage, medicine, tap water, sugar, oil, and other industries. However, two significant factors are restricting the application of powdered activated carbon in water treatment:

1. It is a complicated process to separate, recover, and regenerate separately after use.
2. Compared with granular activated carbon, the cost is higher.

In addition to powdered activated carbon produced from wood chips, it includes powdered products from granular activated carbon.

9.5.3 Activated Carbon Rods (CTO)

Activated carbon rods are processed and compressed based on granular activated carbon to form carbon rods, which can strengthen the removal of residual odors in the water. The adsorption capacity is faster and more robust. CTO is used in water treatment equipment to remove residual chlorine, chemical pesticides, different colors, and odors and to filter fine impurities in water.

9.5.4 Activated Carbon Fiber (ACF)

Traditional activated carbon has been activated and processed as porous carbon in powder or granular form. In contrast, activated carbon is fibrous, with micropores on the thread. Its ability to adsorb organic gases is higher than granular activated carbon in the air, 5–6 times higher in an aqueous solution, with a 100–1000 times faster absorption rate. ACF is the third generation of new adsorption materials following the widely used powdered activated carbon and granular activated carbon (compressed activated carbon).

9.5.5 Activated Carbon According to the Different Activators

Different activators such as zinc chloride, phosphoric acid, potassium hydroxide, sodium hydroxide, potassium hydroxide, sodium hydroxide, carbon dioxide, air, and steam are used to prepare activated carbon. While steam activation method is economically viable, chemical activation produces AC of high porosity and greater surface area (Hamad and Idrus 2022).

9.6 Biochar-Based Green Adsorbent

Studies have been performed to optimize the reaction conditions to produce activated charcoal from various biomasses. Waste materials like coconut shells were investigated to develop an activated charcoal adsorbent. Researchers have studied the effects of temperature, time, and impregnation ratio of activating reagent and found the ideal conditions.

Coconut shell: Coconut shell was collected, dried in the sun, and reduced to 2–3.5 mm in size. The raw material was carbonized in a Herbold pyrolyzer at an optimum temperature of 600 °C. Pyrolyzed coconut shell was activated using 40% $ZnCl_2$ solution for 50 min. The AC was washed with 0.1 N HCl and water and dried at 120 °C (Mozammel et al. 2002). Banana peel, a waste material used to prepare activated charcoal, showed a high surface area. Mopoung (2008) described the effects of pyrolysis temperature and mass ratio of KOH.

Banana peel: Banana peel was collected, washed, and dried at 110 °C for 3 h. The sample was carbonized at 500–700 °C for 1 h. Further, charcoal was impregnated with KOH in the ratio of C:KOH ranging between 1:2 and 1:4. AC was washed with HCl. pH was neutralized, and excess KOH was removed using hot water. The sample was dried at 110 °C. Cobb et al. (2012) produced a simple, inexpensive, and effective activated charcoal from an agricultural waste by-product, i.e., coconut shell, using pyrolysis and chemical activation techniques. They tested three different chemically activated charcoal adsorption capacities and found the one activated with sodium chloride to be most effective and feasible. The raw material was carbonized at 500–800 °C and activated by soaking in 50% NaCl solution for 24 h.

Getachew et al. (2015) dealt with defluoridation of water by activation of carbon fabricated from banana peel and coffee husk. Firstly, collected banana peels were washed, dried, and crushed. After the size reduction, the sample was kept in the furnace at 400 °C for 1 h for carbonization. For chemical activation, 40 mL of concentrated sulfuric acid was added to the carbonized banana peel and stirred continuously. The mixture was kept at 100 °C for 5 h. Prepared AC was cooled, washed, and dried at 110 °C for 5 h and saved for further use. Secondly, the coffee husk was collected and washed with hot distilled water at 100 °C. The sample was treated with 50 mL of concentrated sulfuric acid and pyrolyzed at 150 °C for 12 h. AC was dried and reduced to 0.6 mm in size.

Budhiary and Sumantri (2021) desired to fabricate AC from plantain peel to reduce the liquid waste produced by tofu-making industries. The banana peel was cut into 1–2 cm pieces and dehydrated in the oven at 60 °C for 6 days. Delignification of raw material was done by soaking it in NaOH solution for 12 h. Peels were filtered and washed with distilled water. The sample was then carbonized at 700 ° C for 2 h. The prepared AC was used for further adsorption studies.

Sugar beet bagasse: Samadi et al. (2009) investigate sugar beet bagasse-based AC to adsorb carcinogenic chromium (IV) from an aqueous solution. Bagasse was collected, cut into 2 cm pieces, washed with deionized water, and dried. The sample was mixed with 5 M $ZnCl_2$ for 24 h at room temperature and then carbonized at 160–180 °C for 8 h. The produced charcoal was thermally activated in a furnace at 650–750 °C for 2 h, using carbon dioxide as the purge gas. The prepared AC was washed with HCl acid solution and kept for further use (Table 9.2).

Olive stones: Olive stone is a lignocellulosic material, with hemicellulose, cellulose, and lignin as the main components. Olive stones could be an adequate feedstock to obtain active carbons with good adsorptive properties and hardness, which could be of interest in future environmental protection programs. Yakout and Sharaf El-Deen (2016) studied the effects of activating agent concentration on the pore structure and surface interaction of AC derived from olive stone using phosphoric acid as the activating agent. Olive stones were used as a precursor

Table 9.2 Various types of biomass used for biochar preparation

Biomass	Method	Reagent for activation	Optimum parameters	Reference
Coconut shell	Pyrolysis + Chemical activation	$CaCl_2$ or $ZnCl_2$	• Carbonization at 500–800 °C • Soaking in 25% activating reagent for 24 h	Cobb et al. (2012)
Coconut shell	Carbonization + Chemical activation	$ZnCl_2$	• 2–3.5 mm coconut shell • Carbonization at 400–600 °C • 1.8 g/cm^3 corresponding to 1100 g of $ZnCl_2$ • Activation time: 2 h	Mozammel et al. (2002)
Banana peel	Pyrolysis + Chemical activation	KOH	• Carbonization at the temperature of 500–700 °C for 1 h • Impregnating ratio of C: KOH from 1:2 to 1:4	Mopoung (2008)
Banana peel	Delignification + Carbonization	NaOH	• Cut to 1–2 cm and then dried at 60 °C for 6 days • Soaked in 1 M NaOH for 12 h • Carbonization at 700 °C for 2 h	Budhiary and Sumantri (2021)
Neem leaves	Chemical activation + Carbonization	H_3PO_4	• Leaves crushed to 400 ASM mesh • Impregnation with H_3PO_4 in a 2:1 ratio • Heating at 260 °C for 30 min	Marichelvam and Azhagurajan (2018)
Banana peel	Carbonization + Chemical activation	H_2SO_4	• Carbonized at 400 °C for 1 h • 40 mL of conc. H_2SO_4 was added to 1000 mL of charcoal for activation	Getachew et al. (2015)
Coffee husk	Chemical activation + Carbonization	H_2SO_4	• 100 g of husk activated with 50 mL of conc. H_2SO_4 • Carbonized at 150 °C for 12 h	Getachew et al. (2015)
Bamboo dust	Carbonization + Chemical activation	HNO_3	• Carbonization at 200 °C for 2 h • Activated using 0.5 M HNO_3 for 2 h at 350 °C	Odoemelam et al. (2015)
Bamboo	Carbonization + Oxidation	Air	• Carbonization from 400 to 1000 °C for 1 h • Air oxidation at 270 °C for 2 h	Odoemelam et al. (2015)
Wood apple fruit	Carbonization + Chemical activation	$ZnCl_2$	• Carbonization at 300 °C for 1 h • Activated using 1 N $ZnCl_2$ in a 1:5 ratio for 12 h	Ashtaputrey and Ashtaputrey (2020)

and were ground to 1 and 2 mm in size and dried. The sample was chemically activated with 80% by 200 mL of phosphoric acid solution. The mixture was stirred at 85 °C for 4 h. After activation, the carbonization of the sample was done at 500 °C for 2 h. Produced AC was washed with distilled water and dried.

Potato peel: Moreno-Piraján and Giraldo (2011) used potato peel to obtain AC to remove copper (II) from an aqueous solution. Colombian potato peel was collected from cultivations, washed, and dried before beginning the process. The sample was impregnated with an aqueous solution of $ZnCl_2$ in the concentration of 160 wt%. The sample was then pyrolyzed in an argon atmosphere for 4 h. Kyzas and Deliyanni (2015) synthesized AC from potato peel to adsorb pharmaceutical effluents. The first method used was hydrothermal treatment. Another method for synthesizing AC was through chemical activation. The potato peel sample was treated with 2 M KOH solution and stirred overnight. After drying at 100 °C for 24 h, the mixture was carbonized at 600 °C under nitrogen for 2 h. Prepared AC was washed, dried, and ground. Bernardo et al. (2016) studied the effectiveness of waste potato peel AC for removing diclofenac. Chemical activation technique was used to obtain the charcoal. The potato peel waste was immersed in a saturated aqueous solution of K_2CO_3 in 1:1 and stirred for 2 h at room temperature. The activated sample was then dried at 100 °C for 24 h. The impregnated sample was then carbonized in an electric furnace at 700 °C for 1 h in a nitrogen atmosphere. Obtained AC was washed with distilled water and dried at 100 °C overnight.

Corncob: El-Sayed et al. (2014) assessed AC prepared from corncob using a chemical activation technique. Corncob was collected, washed with distilled water, and dried. After size reduction to 0.05 mm, the raw material was impregnated with phosphoric acid in a ratio of 1:2 (w/w) for 24 h and neutralized by washing with distilled water. The sample was then subjected to pyrolysis in the absence of air at 400 °C for 2 h. The prepared AC was washed and dried at 100 °C.

Bamboo waste: Odoemelam et al. (2015) fabricated bamboo dust and bamboo-based AC for the removal of lead (II) and cadmium (II) ions from aqueous solutions, discarded as industrial wastewater that gets accumulated in living tissues throughout the food chain. The waste bamboo sample was collected from bamboo tree, washed, cut into pieces, and sun-dried. One-half of the selection was ground and converted into AC through chemical activation. Bamboo dust was soaked in 0.5 M HNO_3 solution and stirred for 30 min at a temperature of 30 °C. Hayakawa et al. (2018) tested the adsorption ability of bamboo AC for adsorbing cesium and strontium. The sample was crushed and dried up to 3–6 months. Bamboo was carbonized in an alumina crucible at temperatures ranging from 400 to 1000 °C for 1 h. Charcoal was converted into activated charcoal using the gas activation technique. Air oxidation was carried out for 2 h at 270 °C in a kiln.

Rice straw: Ramangkoon et al. (2016) optimized the production of activated charcoal from rice straw for medical and pharmaceutical applications using a chemical activation process. Collected rice straw was cut into small pieces, dried, and sieved to 60-mesh particle size, carbonized at 400 °C for 2 h, and further impregnated using 85% phosphoric acid for 24 h. Recarbonization was done at 700 °C for 1 h, and then it was neutralized with distilled water and dried at 110 °C for 24 h. Babar et al. (2019) aimed to generate a low-cost and efficient substitute method of production of activated carbon from biomaterials. Their process started with washing the raw material, i.e., rice straw, and dehumidifying it at 105 °C for 24 h. The dried mass was impregnated with magnesium chloride in 1:1 proportion, kept for 2 h at room temperature, and dried for 48 h for activation. After that, the treated material was carbonized by pyrolysis at 550 °C for 2 h. Pattananandecha et al. (2019) fabricated high-performance activated charcoal for cosmetics and pharmaceutical applications using chemical techniques. Rice straw with the highest lignin content was selected, washed, cut into 60-mesh size particles, and dried at 110 °C for 24 h. The raw material was carbonized at 400 °C in a furnace for 2 h and cooled to room temperature. Activation was performed using 85% potassium hydroxide in a reflux ratio of 1:10 w/v at 70–80 °C for 2 h. Obtained activated carbon was washed with hot water to neutralize and dried at 110 °C for 24 h.

Apple fruit shell: Ashtaputrey and Ashtaputrey (2020) prepared activated charcoal from wood apple fruit shell to lower the concentration of dissolved pollutants in effluents. The sample was purchased from the local market, washed, cut into pieces, and oven-dried at 110 °C for an hour. Carbonization was done without oxygen at 300 °C for 1 h. Prepared charcoal was dried at 110 °C and ground to 100–200 mesh size. The sample was chemically activated using a 1 N aqueous solution of $ZnCl_2$ in the ratio of 1:5 ($ZnCl_2$:C) for 12 h. Prepared AC was turned into a paste and again carbonized at 300 °C.

Castor seeds: Ferreira et al. (2020) produced and characterized the adsorption performance of AC made from castor seeds. A laboratory press was used to convert grains into the cake. The dried cake sample was impregnated with 40% phosphoric acid in the ratio of 2:1 in favor of castor seed cake. The obtained cake was dried at 105 °C after resting for some time. The dried material was carbonized at 800 °C for 1 h. Kim (2004) used waste peach stones to produce granular activated carbon. The sample was crushed to 1.41–0.25 mm size. AC was formed by impregnating H_3PO_4 at 500 °C for 1.5 h.

Miscellaneous: Marichelvam and Azhagurajan (2018) attempted to adsorb one of the most hazardous materials, mercury, using AC made from the banana corm and neem leaves. Banana corm was cut dried at room temperature for a week and then under 106 °C for 16 h in a hot air oven. On the other hand, neem leaves were dried at 90 °C for 3 h. The sample was activated using phosphoric acid in the ratio of 2:1 and heated at 260 °C for 30 min. AC was then washed with distilled water and dried.

9.7 Conclusion

Like any other adsorbent, biomass AC finds various applications in the food processing, petroleum, pharmaceutical, and automobile industry. It is also used to remove pollutants and dyes from wastewater treatment plants. One of the significant advantages of AC derived from biomass is using waste material to synthesize something beneficial. Since biomass has low inorganic ash content, the production of AC is relatively environment friendly over AC from other raw materials. Conventionally, AC has been synthesized from coconut shells, coal, lignite wood, and animal bone. Still, due to the unavailability of these raw materials in some places, other biomass is used, which has shown remarkable results in quality and sustainability. Nowadays, agricultural wastes like rice straw, shells of almonds, hazelnut, olive pits, pistachio hull, corncob, banana corn, and many other by-products are used to produce AC.

It can be concluded that the use of biomass for the preparation of activated carbons is a cheap and straightforward way and that can be employed for adsorption of active industrial compounds such as organic, inorganic, and heavy metal. Further, activated carbon can be a good candidate as an electrode material for energy storage technologies. A detailed cost estimation (production, operation, and maintenance) would be beneficial to highlight the cost-effectiveness of the AC prepared from biomass.

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Part III

Biofuels and Biorefinery

Biodiesel from Biomass: Production of Sustainable Biodiesel Fuel

10

Perminder Jit Kaur, Praveen Kumar Sharma, and Shivani Chaturvedi

10.1 Introduction

Biomass availability sources have emerged as a potential alternative to ever-shrinking fossil fuel reserves. In present times, from the overall global energy demand, approximately 81% of the energy is being obtained from fossil fuels, which will negatively impact the environment and human health (Aderibigbe et al. 2021). According to the oil market report (2021) from the Organization of the Petroleum Exporting Countries, the global oil demand could rise from 90.5 to 96.5 million barrels per day (mb/day) from 2020 to 2021, which could be due to the inevitable industrial and anthropogenic overcome of the globally imposed COVID-19 lockdown courses of action taken in 2020. Likewise, utilization of diesel and gasoline for the first quarter of the year 2021 was around 24.0 and 26.3 mb/day, which can increase further. Also, by the year 2030, it is predicted that the oil consumption around the world will rise to 118 mb/day and could ultimately lead to depletion in the global crude oil reserve by 2060 (OPEC 2021; Bharti et al. 2021). In this sequence, India's utility for automobile fuel is more than 0.5. On average, India's annual consumption is about 450 kg/vehicle. Our dependency on fossil fuel-based energy in powering transportation, agriculture, and accommodation indicates

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an alarming situation and calls for immediate actions to preserve the ever-diminishing fossil fuel and search for a better and more efficient alternative to rendering the need without fail (Mohiddin et al. 2021). Fossil-based fuels produce an ample number of harmful products such as CO, NO_x, CO2, SO_x, and carbon specifically into the environment (Perera 2018; Kumar et al. 2020). Various global initiatives like the Paris Agreement signed by members (191) of the United Nations Framework Convention on Climate Change (UNFCCC) aim at reducing the global risks of climate change through constant attempts (UN 2015).

Thus, researchers are looking for a non-toxic, high-energy capacity, clean, and green alternative to fossil fuels. Biodiesel, on this note, is the most preferred biofuel to be utilized for its inexhaustibility; innocuous, high lubricating qualities; and cleaner-burning properties (Atabani et al. 2012; Kim et al. 2018; Bharti et al. 2021). Biodiesel is clean, cheap, and environment-friendly and emits fewer hydrocarbons, smoke, and toxic gases. Being produced from local resources, biodiesel is considered renewable. A high amount of excess oxygen allows complete combustion and lower emissions. First-generation raw materials like starch and potato through second-generation non-edible oil cakes, waste oils to third-generation algae, and energy crops can generate high-quality biodiesel through a low-cost, simple transesterification process at moderate reaction conditions. The process involves a reaction between triglyceride and alcohol in the presence of an acid or basic catalyst to produce fatty acid alkyl esters and alcohol (Kanwar Gaur and Goyal 2022; Nagappan et al. 2022). High cetane number, longer ignition delay, low ash value, better engine ignition, and emission performance have motivated researchers to explore different blend ratios of biodiesel in petrol (Gad and Ismail 2021; Suzihaque et al. 2022). Another pathway to produce biodiesel is through thermo-chemical route. Pyrolysis of biomass in specially designed reactors can produce biochar, syngas, and bio-oil of suitable properties. Feedstock type, reaction conditions, and reactor types can affect the relative proportions of products. To produce commercial-scale biodiesel to replace fossil fuel, interest in biomass, including agricultural waste algae-derived biofuel, has risen considerably (Ghesti et al. 2022).

To promote biofuel as a commercial fuel, policies are designed globally. The major bio-ethanol-producing countries are the United States and Brazil. The United States had created around 1557 petajoules with 38% of global biofuel in 2019 (Kohler 2019). India has also proposed a 20% ethanol blending in petrol and 5% biodiesel in the diesel by 2030 as per its National Policy on Biofuels, 2018 (Devi et al. 2021). American standard ASTM D7467 mentions the biodiesel to commercial diesel from 6% to 20%. Blends with 13% are allowed in Brazil, with the target of increasing to 15% by 2023 (Bukkarapu and Krishnasamy 2022).

The present chapter explores the various types of raw materials to be used for biodiesel production, their merits, and their limitations. Different pathways for converting feedstock to biodiesel generation, yield, and multiple factors affecting the quality of biodiesel produced are discussed here. The chapter also compares the performance of catalytic and non-catalytic transesterification processes. The chapter offers insight into technical, social, and financial barriers hindering the acceptance of biodiesel and the future scope of biodiesel as a commercial fuel.

10.2 Process for Production of Biodiesel

The waste biomass-derived biodiesel process can involve any of the two routes. The first pathway is the production of lipids through hydrolysis of cellulose and hemicellulose of biomass, which can be further processed to produce biodiesel. The second pathway involves the production of cheap and eco-friendly catalysts from waste biomass components, like stems, leaves, stalks, etc., to enhance the speed of the conventional transesterification process of multiple raw materials (Fig. 10.1).

10.2.1 Enzyme-Catalyzed Biodiesel Production

Biomass consists of lignin, cellulose, and hemicellulose, which are difficult to be converted into simple sugar using conventional methods. Lignocellulosic materials can undergo pretreatment (physical, chemical, or biological) to produce biomass of suitable properties. Pretreatment can involve physical, chemical, or biological methods. Mechanical treatments like milling, grinding, and steaming increase surface area and improve raw material conversion (Wang et al. 2021). Chemical treatment, including acid treatment, enhances cellulose decomposition efficiency. Alkali treatment is done to remove lignin altogether. Biological treatment methods like microbial treatment can be done in a low-cost, environment-friendly manner to degrade hemicellulose and lignin (Mahmood et al. 2019). Cellulase consists of endo-1,4-β-*glucanase*, *cellobiohydrolase*, and *β-glucosidase*, which can be converted into sugar to utilize biodiesel further. Oleaginous microorganisms including yeast, mold, and bacteria, under suitable conditions, can convert carbohydrates into microbial lipids, also known as single-cell oils (SCOs).

Yeast species such as *Meyerozyma guilliermondii* and *Rhodosporidium fluviale* have shown significant lipid production potential. Further, biodiesel can be produced using both catalytic and non-catalytic processes. Non-catalytic processes include treatments like emulsification, pyrolysis, and transesterification, among which transesterification is the most popular.

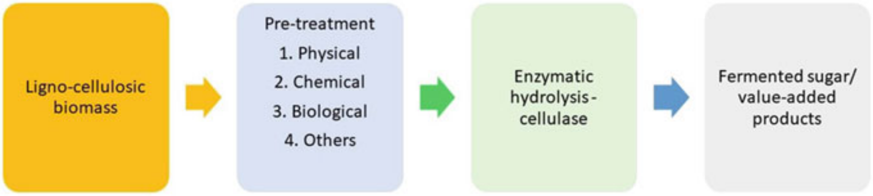

Fig. 10.1 General lignocellulosic biomass utilization process

10.2.2 Transesterification Process

The general procedure for oil extraction involves various common steps. The feedstock is pretreated to enhance oil yield during the pressing stage. Kernel removal and drying are carried out using stompers and mallets, followed by oil extraction. Figure 10.2 shows the general biodiesel production process.

10.2.3 Oil Extraction

Mechanical extraction can be done using a manual ram or an automated screw press. An oil yield as high as 91% on filtering and degumming can be achieved. The solvent extraction process involves using a solvent to extract oil from the seed. The most common solvent, n-hexane, can generate oil of 41% and 95–99% yield using *J. curcas* and *P. pinnata* seeds. There are associated environmental concerns related to wastewater treatment after the solvent extraction process. The enzymatic process uses an enzyme to extract oil from sources. Though the process is slow, it is still an attractive technique due to its eco-friendly nature and no volatile component emission. Recently, researchers have used a combination of solvent extraction and microwave-based hybrid processes to enhance the oil yield efficiency at low cost, time, and energy.

10.2.4 Transesterification

As shown in Fig. 10.2, the oil extracted from the seed is sent for the transesterification process, which is the heart of the biodiesel production process. Since reactants, oils, and alcohols are immiscible with each other, there is a need to mechanically agitate the vessel or increase the reaction time and temperature with additional costs. Reaction temperature, time, mixing intensity, and reactor geometry are the most significant parameters. The production can be done using both catalytic and non-catalytic methods. For the non-catalytic process, the transesterification of vegetable oil takes place above the critical temperature and pressure (temperature, 513 K methanol and 514 K ethanol and 10–45 MPa) (Da Silva and Oliveira 2014). However, high temperatures lead to increased energy consumption and are not economically feasible. The catalytic process utilizes biocatalysts or chemical

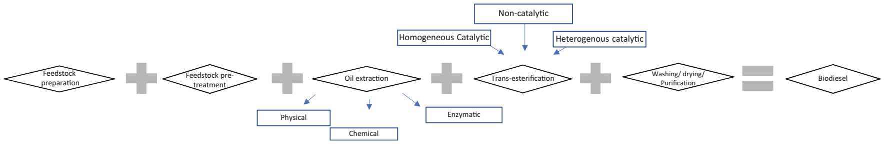

Fig. 10.2 General biodiesel production process

catalysts to transform the triglyceride molecules into fatty acid alkyl esters (FAAEs) (Nasreen et al. 2018; Gupta and Rathod 2021).

Catalytic processes can be further classified into various categories based on the types of material of construction, i.e., homogeneous or heterogeneous types. If a catalyst is soluble in the reactant, it becomes a simple, low-energy-consuming homogeneous catalyst. Certain limitations are associated with a low recovery rate and less reusability (Mohiddin et al. 2021), which prompted researchers to look for heterogeneous catalysts. Being produced from insoluble materials, they are easily detachable using simple centrifugation or filtration processes and are reusable many times. Recently biomass-derived heterogeneous catalysts have gained wide popularity among researchers worldwide (Cheng and Li 2018). Nanocatalysts, including nanoferrites synthesized from ceramic material, showcase tremendous advantages over traditional heterogeneous catalysts regarding their chemical, physical, structural, electrical, and mechanical characteristics (Thakur et al. 2020).

10.2.5 Homogeneous Catalysts

Homogeneous catalysis involves the application of catalysts present in its liquid form, mainly basic and acidic. Homogeneous catalysts such as acids (H_2SO_4, HCl, H_3PO_4, $AlCl_3$, $ZnCl_2$, etc.) and bases (NaOH, KOH, CH_3NaO, CH_3KO, etc.) are among the widely used catalysts. While homogeneous acid catalysts require high temperature and pressure (Marchetti et al. 2011), homogeneous base catalysts need milder conditions (Vyas et al. 2010). The drawbacks mentioned above notably showcase the inevitable difficulty in separation and reusability of the catalyst and restrict its significance and use in biodiesel's industrial-scale synthesis by using homogeneous catalysts (Bharti et al. 2021).

Homogeneous base catalysts accompanied by milder reaction condition like low temperature and pressure conditions, easy availability, and shorter reaction time (4000 times faster than acid-catalyzed transesterification) make homogenous base catalysts highly acceptable (Kawashima et al. 2009; Williams 2015). Generally, the base catalytic transesterification process undergoes at a minimum pressure (1.4–4.2 bar), temperatures (333–338 K), with a minimum concentration of catalyst (0.5–2 wt%), atmospheric pressure, average stoichiometric alcohol/oil molar ratio, and reaction times (typically 1 h) (Bhuiya et al. 2016).

The mechanism for the action of homogeneous base catalyst is given in Fig. 10.3. Verma et al. (2017) used both methanol and ethanol for the synthesis of Karanja biodiesel through KOH as a catalyst and reported the highest yield of 88.7% and 77% for methanolysis and ethanolysis, respectively, at a reaction temperature of 333 K with a molar ratio of 1:9 and 1.25 wt% of catalyst loading for 2 h. In another study, the waste soybean oil was transesterified with 7 wt% NaOH and gave 95% biodiesel yield with an oil-to-methanol molar ratio of 1:9, reaction temperature of 40 °C, and reaction time of 1 h 33 min (Tan et al. 2019). Another study reported that canola oil is transesterified using NaOH catalyst (3 wt%), yielding 85% biodiesel at

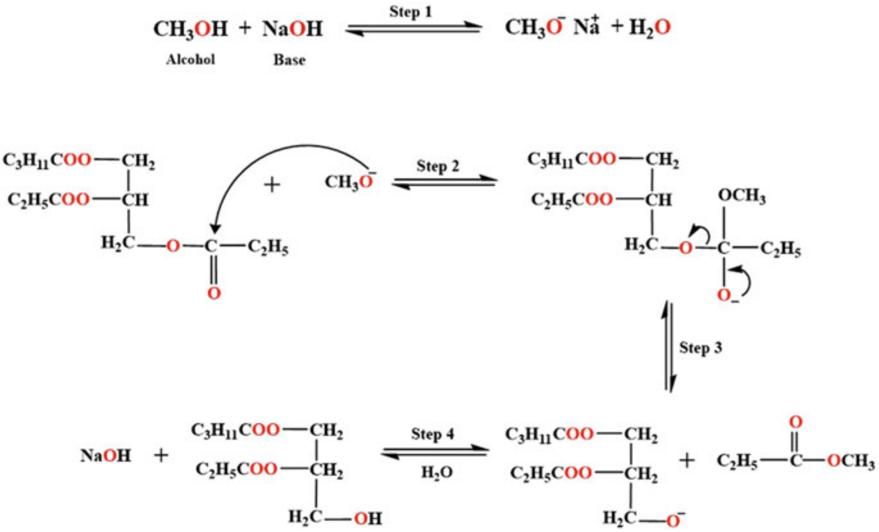

Fig. 10.3 Mechanism for base-catalyzed transesterification process. (Source: Kumar et al. 2021)

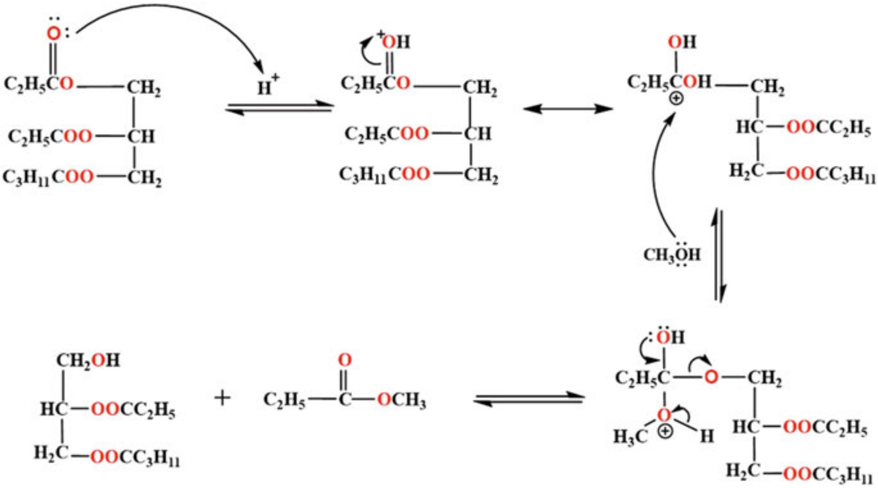

Fig. 10.4 Mechanism for acid-catalyzed transesterification process. (Source: Kumar et al. 2021)

the oil-to-methanol molar ratio of 1:6.5 at a slightly higher temperature of 70 °C for 2 h (Hariprasath et al. 2019).

The most commonly used acid catalysts are sulfuric acid, ferric sulfate, hydrochloric acid, and sulfonic acid (Atadashi et al. 2013). The acid-catalyzed reaction proceeds between triglycerides, alcohols, and an acid catalyst, producing glycerol and biodiesel. Figure 10.4 shows the homogeneous acid-catalyzed reaction mechanism. Unlike base catalysts, acid catalysts are more economically viable and insensitive to the oil's free fatty acid content. Sulfuric acid and hydrochloric acid are favored catalysts in this process (Lam et al. 2010). Oliveira et al. (2017) reported the yield of biodiesel as 93.5% using H_2SO_4 as a catalyst with oil to methanol ratio of 1:9 at a temperature of 70 °C. The alcohol-to-oil molar ratio is crucial in influencing the reaction.

10.2.6 Heterogeneous Catalysts

Heterogeneous catalysts are anti-corrosive and can be recovered quickly. This ease of recovery attributes to its different reactant phase systems, which assist an easy pathway for separating the catalyst from the reaction mixture through conventional separation techniques like filtration, sedimentation, and centrifugation (Diamantopoulos 2015). Examples of acidic heterogeneous catalysts are ZnO/I_2, ZrO_2/SO_{2-4}, TiO_2/SO_{2-4}, niobic acid, sulfated zirconia, amberlyst-15, and Nafion NR50. In contrast, CaO, $CaTiO_3$, $CaZrO_3$, CaO-CeO_2, $CaMnO_3$, $Ca_2Fe_2O_5$, KOH/Al_2O_3, KOH/NaY, Al_2O_3/KI, ETS-10 zeolite, and alumina/silica-supported K_2CO_3 are some examples of alkali heterogeneous catalysts (Leung et al. 2010).

A suitable heterogeneous catalyst must be mesoporous, highly stable, benign, and inexpensive (Changmai et al. 2020). It must also possess multi-functionality and strong, active sites, making it highly versatile and competitive (Chouhan and Sarma 2011). Presently, researchers are trying to make bifunctional heterogeneous catalysts that can be employed for both esterification and transesterification simultaneously, which could save energy, time, material, and production cost (Farooq et al. 2013; Mohiddin et al. 2021).

The commonly used solid catalysts are functionalized by sulfonated zirconia (SZ), Nafion resins, sulfonated saccharides, tungsten oxides, and organosulfur mesoporous silicas (Chopade et al. 2012). For instance, around 95% yield of biodiesel was obtained from neem oil at a temperature condition of 65 °C for a reaction time of 2 h with a catalyst loading of 1 and molar ratio of 9:1 (alcohol to oil) using sulfated zirconia as a catalyst (Muthu et al. 2010). Another study by Shu et al. (2010) reported the use of carbon-based solid acid catalyst at a temperature of 220 °C with a catalyst loading of 0.2 with the molar ratio of 16.8:1 (alcohol to oil) for 4.5 h using waste vegetable oil as a feedstock for the conversion of biodiesel which yielded to be 94.8%.

The heterogeneous alkali catalyst shows enhanced catalytic activity during transesterification under milder reaction conditions (Calero et al. 2014). Table 10.1 displays several types of base heterogeneous catalysts sued for the transesterification of lipids. Researchers have reported the complete conversion (100% conversion) to biodiesel of soybean oil using snail shell as a heterogeneous base catalyst at room temperature with the reaction time of 7 h at the oil-to-methanol molar ratio of 1:6 and a catalyst loading of 3 wt% (Laskar et al. 2018).

Several researchers experimented with kitchen waste as a heterogeneous base catalyst and found encouraging results. Likewise, researchers have obtained a biodiesel yield of 93% by transesterification of refined soybean oil at a temperature

Table 10.1 Effect of catalyst on soybean oil on conversion efficiency

Feedstock	Catalyst	Catalyst (wt%)	Reaction condition (*T* (°C)/ time)	Conversion (%)	MOA: MMEOH	Reference
Soybean oil	Oyster shells	25	65/5	96.5	1:6	Nakatani et al. (2009)
Waste soybean cooking oil	NaOH	0.5	55/2	68.5	1:3	Hossain and Mazen (2010)
Soybean oil	NaOH	1.3	40/1.33	95	1:9	Silva et al. (2011)
Soybean oil	Snail shell	3	RT/7	100	1:6	Laskar et al. (2018)
Refined soybean oil	Chicken eggshell	7	57.5/3	93	1:10	Goli and Sahu (2018)
Soybean oil	$MnCO_3$	2	180/1	98.1	1:21	Wan et al. (2018)
Soybean oil	Potassium methoxide	2	80/0.25	91	1:6	Celante et al. (2018)
Soybean oil	MgO supported on γ-Al_2O_3	5	60/6	60	1:6	Navas et al. (2018)
Soybean oil	*Brassica nigra* waste	7	65/0.42	98.79	1:12	Nath et al. (2019)
Sunflower oil	*Sesamum indicum* waste	7	65/0.67	98.9	1:12	Nath et al. (2020)
Soybean oil	*Moringa* leaves	6	65/2	86.7	1:6	Aleman-Ramirez et al. (2021)

of 57.5 °C and reaction time of 3 h with 1:10 to be the molar ratio of oil to methanol at a catalyst loading of 7 wt% (Goli and Sahu 2018). Using chicken eggshell as a heterogeneous catalyst at 57.5 °C for 5 h and the oil-to-methanol ratio of 1:13 with 8.5 wt% of catalyst loading reported 90.41% biodiesel yield (Kirubakaran and Arul Mozhi Selvan 2018).

10.2.7 Nanocatalysts

Along with the development of heterogeneous catalysts, which are recyclable, stable, highly selective, and efficient, demand has been growing simultaneously concerning its improvement or modification as a catalyst that can be used for biodiesel production. Nanocatalysis has emerged as a suitable option. According to the reports, the market value of nanocatalysts had reached up to USD 9.58 billion in 2020, which is further expected to reach USD 22.9 billion by 2027. Nanoscale heterogeneous catalysts with larger surface areas allow them to be an attractive candidate for transesterification reactions (Bharti et al. 2020, 2021). Their catalytic properties can be modified accordingly by simply making acceptable changes to the shape and size of the active phase of the nanomaterials (Somorjai and Materer 1994). Nanoferrites exhibit strong ferrimagnetic properties containing iron oxide as the prime component. They are classified as (a) spinel (MFe_2O_4), (b) garnet ($M_3Fe_5O_{12}$), and (c) hexagonal ($MFe_{12}O_{19}$), where M denotes transition metals like Mn, Fe, Co, Ni, Cu, and Zn (Bharti et al. 2020; Punia et al. 2020; Rana et al. 2015). The introduction of magnetic property into nanocatalyst helps with easier separation. It shows good recovery on applying an external magnetic field which facilitates the minor catalyst weight loss and high catalyst reusability compared to traditional separation techniques (Gardy et al. 2019). Amidst all the base nanocatalysts available to prepare biodiesel, CaO, zeolites, and hydrotalcite have received humongous attention. Among them, CaO has been extensively studied for its high activity, basicity, and milder reaction condition. Despite its advantages, it also shows some limitations in the recovery step of the catalyst from the reaction mixture, as during the process of a transesterification hydrogen bond is formed between the lattice oxygen species with methanol and glycerine, which increases the viscosity of glycerine and forms solid in suspension with CaO which hence inhibit the process of recovery (Kouzu and Haidaka 2012). Magnetic functionalized CaO helps overcome these limitations. Thus, a magnetic material is combined with the CaO and SrO samples to prepare a magnetic catalyst. This prepared catalyst was utilized to transesterify soybean oil into biodiesel by Zhang et al. (2016) and obtained a yield of 94.9% at 70 °C for 2 h with an oil-to-methanol molar ratio of 1:12 and 0.5 wt% of catalyst loading (Bashir et al. 2022). As the magnetic property of the catalyst allowed it to be recovered quickly after every cycle, it showed stability upon five reusable runs.

The biodiesel obtained using the oil extraction process possesses high viscosity and low volatility, contains polyunsaturated hydrocarbons, and is not suitable for use as a fuel. It needs further purification and modification to be used in vehicles (Table 10.2).

Table 10.2 Biodiesel processing technologies

Process	Specific reaction conditions	Advantages	Limitations	Reference
Ultrasonic	• Energy = 1.4 kWh/m^3 • Biodiesel yield = 99% • Alcohol-to-oil ratio = 4:1 to 15:1 • Frequency = 20–40 kHz • Catalyst = 1–6 wt% • Temperature = 40–65 °C • Time = 15–240 min	• Reduce reaction time and temperature • Low operation cost • Reduce catalyst amount • Increase yield of biodiesel production up to 99%	• Difficult to scale-up • Required specially designed equipment • High installation cost • Energy consumption	Topare et al. (2015), Bashir et al. (2022)
Microwave	• Energy = 500–800 W • Alcohol-to-oil ratio = 3:1 to 18:1 • Catalyst = 0.5–5 wt% • Reaction temperature = 40–100 °C • Reaction time = 0.05–1 h • Conversion yield = 80–100%	• Less time-consuming • Improve biodiesel yield • No pretreatment required • Cleaner products • Less heat loss	• Difficult to scale-up • Need strict control of the time of reaction • Not efficient for materials with high solids	Bashir et al. (2022), el Sherbiny et al. (2010)
Plasma	• Reaction temperature = 25–50 °C • Reaction time = milliseconds–2 min • Conversion yield = 78–100%	• Low reaction time • Less energy required	• Specially designed reactors require • High installation cost	Kongprawes et al. (2021)
Supercritical	• Pressure = 22.5–40 MPa • Temperature = 250–350 °C • Residence time ~ 20 min • Yield = 0–94.04% • Reaction time = 2–120 min	• Less reaction time • Clean and eco-friendly process • No pretreatment required	• High installation as well as running cost	Quesada and Olivares (2010)

10.3 Scope and Challenges for Biodiesel Usage

The properties of biodiesel are a vital function of the type of feedstock used, with non-edible oils and waste materials as the most promising for its preparation. As a sustainable option, biodiesel is producible in more significant amounts from vegetable oils and fats of animal origin. The choice of raw material for biodiesel production depends on the availability of bio-resources in that specific region. As shown in Table 10.3, based on research trends, it was found that while countries like Cuba, India, Malaysia, Mali, Mozambique, Pakistan, Peru, Tanzania, Thailand, and Zimbabwe have explored *Jatropha curcas*, similarly, oilseed palm was researched in Brazil, Iran, Malaysia, Mexico, Peru, and Thailand; rapeseed in Canada, Chile, China, Greece, Italy, and Turkey; sunflower in Argentina, Canada, Greece, Italy, and Turkey; *Pongamia pinnata* in Australia, Bangladesh, and India; *Callophyllum inophyllum* in Australia and Malaysia; soybean in Argentina, Canada, Italy, and the United States; fish oil in Iran; used cooking oil in Ireland; animal fat and fish residues in Norway and Bangladesh; and microalgae in China as feedstock materials (Alagumalai et al. 2021; Jayakumar et al. 2021). Computing biodiesel from biomass is an acceptable strategy for the future bioenergy-based economic development path.

Other factors like reaction temperature, reaction and holding time, types of catalyst used, and reactor configuration also affect the quality and yield of biodiesel. Different researchers have examined various sources and response conditions to maximize oil output. Optimizing reaction parameters is essential to obtain biodiesel at a low cost. Further experiments are underway to alleviate the properties of biodiesel. Using convention transesterification methods, biodiesel with properties compared to conventional diesel oil can be obtained. As shown in Table 10.4, the flashpoint of biodiesel is 171 °C, much higher than mineral diesel. Thus, they are highly safe to use. In addition to this, the cetane number of biodiesel is much higher

Table 10.3 The majority explored raw materials in different countries (Alagumalai et al. 2021; Jayakumar et al. 2021)

Raw material explored	Countries
Jatropha curcas	Cuba, India, Malaysia, Mali, Mozambique, Pakistan, Peru, Tanzania, Thailand, and Zimbabwe
Oilseed palm	Brazil, Iran, Malaysia, Mexico, Peru, and Thailand
Rapeseed	Canada, Chile, China, Greece, Italy, and Turkey
Sunflower	Argentina, Canada, Greece, Italy, and Turkey
Pongamia pinnata	Australia, Bangladesh, and India
Callophyllum inophyllum	Australia and Malaysia
Soybean	Argentina, Canada, Italy, and United States
Fish oil	Iran
Animal fat and fish residues	Norway and Bangladesh
Microalgae	China

Table 10.4 Pros and cons of using different catalysts

Classification	Pros	Cons	Examples	References
Heterogeneous base catalyst	• Upgraded selectivity • Anti-corrosive • Multi-utilizable and reusable • Showcase longer lifetime • Easily separable from product • Faster reaction rate than acid catalyzed	• The high molar ratio of -OH to oil • Fragile to FFA and oil • Diffusion limitation • Hygroscopic • Excess production of wastewater during purification • Poisoning of catalyst when exposed to ambient air • Leaching of functional species	CaO, $CaTiO_3$, $CaZrO_3$, CaO-CeO_2, $CaMnO_3$, $Ca_2Fe_2O_5$, KOH/Al_2O_3	Aderibigbe et al. (2021), Mohiddin et al. (2021), Velusamy et al. (2021), Tamjidi et al. (2021)
Heterogeneous acid catalyst	• Simultaneous occurrence of esterification and transesterification • Easy separation b/w product and catalyst • Recyclable, reusable, and regenerative • Suitable for low-grade oils	• Expensive and low rate of reaction • High-temperature conditions and extended reaction time • Unfavored side reactions • Larger energy requirement • Contaminated endpoint due to leaching at the active site	ZnO/I_2, $ZrO_2/SO_2{}^{-4}$, $TiO_2/SO_2{}^{-4}$, niobic acid, sulfated zirconia	Aderibigbe et al. (2021), Mohiddin et al. (2021), Velusamy et al. (2021), Tamjidi et al. (2021)
Homogeneous base catalyst	• Zero production of water during transesterification • 4000 times faster than acid catalyzed • Moderate reaction conditions and less energy required	• One-time use • Thin-skinned to FFA in oil • Extra step to remove catalyst • Saponification requires the presence of more >2 wt.% of FFA in oil • More waste H_2O is produced	NaOH, KOH, CH_3NaO, CH_3KO	Aderibigbe et al. (2021), Mohiddin et al. (2021), Velusamy et al. (2021), Tamjidi et al. (2021)

(continued)

Table 10.4 (continued)

Classification	Pros	Cons	Examples	References
	• Inexpensive, economically feasible, and widely available	• Reduced biodiesel yields due to saponification		
Homogeneous acid catalyst	• High biodiesel yield production • Avoidance of saponification can be achieved • Esterification and transesterification taking place at the same time • Thick-skinned to FFA and water in oil	• Require catalyst neutralization • Corrosive in nature • Lower rate of the reaction • Hard separation of catalyst and product • Additional step for catalyst removal	H_2SO_4, HCl, H_3PO_4, $AlCl_3$, $ZnCl_2$	Aderibigbe et al. (2021), Mohiddin et al. (2021), Velusamy et al. (2021), Tamjidi et al. (2021)
Nanocatalyst	• Eco-friendly and low toxicity • Easy magnetic separation • Good reactivity, selectivity, and optimum yield • Higher specific surface area • Easy alteration to the physical and chemical properties of the catalyst according to its selectivity and activity	• High in expense • Agglomeration and precipitation • Require high alcohol % • Low rate of reaction • Saponification catalyst deactivation	$Cs/Al/Fe_3O_4$, $KF/CaO–Fe_3O_4$, CaO/MgO, KF/Al_2O_3	Velusamy et al. (2021), Tamjidi et al. (2021), Chang et al. (2011), Boz et al. (2009), Feyzi et al. (2013), Hu et al. (2011)

than conventional diesel, indicating its high combustion efficiency (Mishra and Goswami 2018). Researcher investigations have shown that using the ultrasonic method in the traditional process of transesterification can lead to the production of biodiesel with better lower heating values, lower viscosity, and density at less reaction time (4 min) (Ponnappan et al. 2021). Similar experiments are underway globally to improve the properties of biodiesel to improve its utilization potential further. Table 10.4 shows the benefits and drawbacks of various catalysts.

The cetane number of biodiesel indicates its compatibility with engines, including smooth start and running, i.e., engine knock and nitrous oxide emissions (Abomohra et al. 2022). While high heating value (HHV) defines its calorific value, fuel's viscosity and blending ratio of biodiesel to diesel are the fundamental properties affecting the engine's performance. Table 10.5 shows the properties of biodiesel, including its kinematic viscosity, cloud point, and cetane number obtained from different sources, which are in the range mentioned by the American Society for Testing and Materials (ASTM) and European Standards.

Non-edible oils like palm oil and cottonseed oil are attractive options to prepare biodiesel of international standards. In addition to this, locally available and low-cost biomass feedstocks are also investigated as a potential source of biodiesel. However, the significant challenges with biodiesel are its high viscosity, leading to the formation of larger droplets, poor fuel combustion, and deposition of black smoke in the combustion chamber. The polymerization of unsaturated fatty acids at higher temperatures results in gumming and injection choking. Transesterification of oil is the most common method to reduce viscosity and improve engine efficiency. A few investigations have shown concerns like low stability against oxidation, lack of long-duration shelf life, high cetane number, and high flash point compared to fossil fuels. The studies have shown that lowering NO_x emission is still a challenge by using non-edible oils as substitutes in diesel engines.

Thus, biodiesel blending with petroleum fossil fuels has already been implemented worldwide. Various terms are used to define the proportion of biodiesel in petroleum. Bzz indicates the relative balance of biodiesel, where zz is the quantity of biodiesel in the blend. For instance, B20 and B80 terms are used to define 20% and 80% biodiesel.

10.4 Global Biodiesel Policies

In an attempt to foster the growth of biofuel production to improve the share of renewable energy, different countries have initiated various policy-level interventions like mandatory blending targets, tax exemptions, etc. The ethical issues with first-generation edible products have given impetus to research on biofuel production from non-edible oil cakes and waste biomass material. National biofuel policies of Brazil, India, and Indonesia are generally framed by leveraging the use of local resources like sugarcane, agro-waste, and palm oil, respectively (Saravanan et al. 2018; Lima et al. 2020; Halimatussadiah et al. 2021). Studies have shown that shells of groundnut, rubber seed, castor seed, sunflower, linseed, groundnut, and sesame seed can be used to produce biodiesel in Bangladesh annually. In addition, the country is reported to have a great potential to use non-edible waste animal skin to produce biodiesel (Mahmud et al. 2022).

Initially, the European Commission 2003 Biofuel Directive to increase the use of biofuel and other renewable fuels to 5.75% has impacted both production and consumption of biofuel in European nations. While biofuel policies in Brazil were driven by the petroleum fuel shortage, the US policies were framed to reduce greenhouse gas emissions in the framework. The Canadian Environmental Protection Act Bill C-33 (Canada), Renewable Fuel Standard (RFS2) (the United States),

Table 10.5 Properties of biodiesel compared to US and European Standards

Biodiesel type/standard	Kinematic viscosity (mm^2/s)	Cloud point (° C)	Cetane number	HHV (MJ/kg)	Oxidation stability (h)	Reference
ASTM D6751	1.6–6.0	–	>47	–	>3	Zahan and Kano (2018)
EN 14214	3.5–5.0	–	>51	–	>6	Zahan and Kano (2018)
Diesel	2.5–5.7	−10 to −5	45–55	42–45.9 (calorific value)	–	Ashraful et al. (2014)
Mineral diesel	2.956		46	45.34		Pali and Kumar (2016)
Karanja biodiesel	6.56	8	–	35.82 (calorific value)	–	Khan et al. (2018)
Palm oil biodiesel	4.42–4.76	–	59.9–62.8	37.2–39.91	–	Zahan and Kano (2018)
Cotton seed biodiesel	4.0–9.6	–	41.2–59.5	37.5–41.68	–	Zahan and Kano (2018)
Jatropha oil	4.84	2	51–52	39.63	–	el Sherbiny et al. (2010), Singh et al. (2021), Aigba et al. (2021)
Sal seed methyl ester	5.89		63.5	39.65		Pali and Kumar (2016)
Kusum methyl ester	5.19		57.86	41.6		Pali and Kumar (2016)
Sterculia foetida biodiesel obtained by conventional transesterification process	4.1		64	38.13 (lower heating value)		Ponnappan et al. (2021)
Sterculia foetida biodiesel obtained by ultrasonic stirring transesterification process	3.8		67	38.48 (lower heating value)		Ponnappan et al. (2021)
Protosiphon botryoides	6.41	−2.62	51.59	41.51	5.52	Abomohra et al. (2022)
Chlorella pyrenoidosa	0.14	−2.51	51.64	41.50	3.79	Abomohra et al. (2022)
Scenedesmus dimorphus	3.63	–	32.9	40.2	5.6	Abomohra et al. (2022)

National Alcohol Program Protocol (Brazil), EU Directive 2009/28/EC (European Union), National Policy on Biofuels 2018 (India), and National Policy on Biofuels (Malaysia) are some of the critical global policies targeted at supporting research and development activities and commercialization of the same. In Germany, the Biofuel Quota Act, 2007, had set a target of 4.4% biodiesel in diesel, which was supported by many other policy initiatives like targeting a share of 18% for renewables to total energy share (Saravanan et al. 2018).

Key instruments adopted in the United States to promote biofuel production are supporting the feed crop supply, which include incentivizing farmers to grow biomass feedstock through the Biomass Crop Assistance Program (BCAP). Likewise, the Biorefinery Assistance Program assists biorefineries by providing easy loans (Saravanan et al. 2018). Import tariffs also play a significant role in protecting national industries from the external competition (Sorda et al. 2010). Technology, policies, environmental sustainability, and economics are the pillar of success for biofuel implementation programs.

Overall, the success of these policies depends on competition from other fuels and faster implementation of these policies. Issues related to efficient land use, soil health, and biodiversity need to be addressed through multifaceted, efficient policies encompassing these dimensions.

10.5 Conclusion and Future Direction

Biofuels are fuels obtained from biological sources and take much lesser time to form than fossil fuels. It can play a critical role in mitigating climate change, improving global energy security, and strengthening local economies. Four generations of fuels have been tested under lab and industrial-scale conditions. There are ethical issues associated with the first and second generations of raw materials where edible feedstock is used for biodiesel generation. Thus, more focus should be given to the application of third and fourth generations of fuels, which can serve the dual purpose of waste utilization and energy generation. With more advanced technology like synthetic biology-based raw materials, supercritical oil extraction, and ultrasonic treatment, plasma reactors are tested on a laboratory scale to improve the final product yield and quality.

The potential of biodiesel to replace conventional fuel is very high. Already many nations have adopted biodiesel blends with diesel oil. For many years, international and national policy-makers are also making efforts to reduce fossil fuel usage. Their focus is to encourage low-carbon technologies, and develop energy-efficient technologie. The reduction in environmental CO_2 was observed due to biodiesel in the place of fossil fuels. It may be so because the ratio between CO_2 emitted from biodiesel combustion is lesser than the CO_2 utilized by the plants for photosynthesis (Lapuerta et al. 2008). SO_2 emission was also lower using biodiesel (Basha et al. 2009). Newer techniques like particulate traps, catalysts, and recirculation of exhaust gas can also further improve the efficiency of biodiesel-based vehicles. Though sulfate and aromatic compound emissions are very low, research efforts are still underway to improve engine performance and reduce nitrous oxide emissions from biodiesel-based fuels.

With the collective efforts from researchers across the globe in advanced reactor configuration, along with the use of third and fourth generations of biofuel and optimization of reaction parameters, the scope of biodiesel as a low-cost, eco-friendly, and sustainable fuel is very high.

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Bioethanol Production from Agricultural Biomass: Sources of Cellulose, Pretreatment Methods, and Future Prospects

11

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11.1 Introduction

Global warming is one of the environmental issues which has emphatic and inevitable impacts on our planet as well as all the life forms existing on the planet. Multiple lines of evidence have strongly established that combustion of fossil fuels leading to emissions of greenhouse gas results in global warming. Fossil fuel consumption by the world's transportation sector is nearly 60%, which eventually leads to depletion of natural resources and generation of massive pollution (Aditiya et al. 2016).

India is considered as third biggest oil importer in the world. It has consumed almost 3.3 million tons of fuel estimated in 2020–2022. The United States Department of Agriculture (USDA) stated that India's average blending of ethanol in petrol rises up to 5.8% in 2019. It was also reported that the USA continues to be the biggest ethanol supplier and ethanol import in India from the country grows up to 750 million liters. Visualizing the above parameters of fuel consumption, we see that there's an urgent need to acquire low-cost, clean, alternative, and renewable energy, which can be achieved by production of biofuels to replace fossil fuels (Gonçalves et al. 2016). This will not only help in reducing environmental impact by fossil fuel usage but also contribute to energy self-sufficiency.

Bioenergy with lesser greenhouse gas emission assures phasing out the fossil-derived energy making bioenergy a substantial contributory of clean and efficient energy simultaneously avoiding depletion of fossil fuels. Bioenergy obtained traditionally by combustion of biomass and its modern substitutes such as biogas, biofuels, biorefineries, etc. allows to gain energy security and economic growth in addition to stabilizing the environment (Fischer and Schrattenholzer 2001; Menon

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and Rao 2012; Popp et al. 2014; Sadhukhan et al. 2018; Jeswani et al. 2020; Muh et al. 2020; Kaniapan et al. 2021; Manikandan et al. 2022).

Different types of lignocellulosic biomass available can be categorized into three categories as primary sources (sugarcane, sugar beet, fruits) produced as crop, secondary sources (starchy crops, straw, bagasse, and rice husks) obtained from residue of crops, and tertiary sources (municipal wastes, wood trimmings, sludge from sewage treatment). Laboratory and industrial ethanol is generally produced by acid-catalyzed reaction of ethylene or obtained by fermentation where microorganisms such as yeast and bacteria are used to metabolize the sugars producing ethanol and CO_2 (Kang et al. 2014). Producing bioethanol mainly involves fermentation of simple sugar and starch which are mainly derived from polysaccharides, and the ethanol generated is generally first-generation bioethanol. These substrates need to be fermented in a highly efficient manner which is quite expensive and non-sustainable in nature as these fuel sources are used as an important part of global food supply (Uçkun Kiran and Liu 2015; Battista et al. 2016). Production of bioethanol from lignocellulose biomass (second-generation biofuel) is sustainable and cost-effective which accounts for potential renewable energy sources (Jørgensen et al. 2007; Kang et al. 2014; Cutzu and Bardi 2017).

Lignocellulosic biomass generated from agricultural, industry, forestry, or municipal waste acts as a precursor for the production of lignocellulosic or 2G bioethanol. In recent years, it is found that environmental pollution is increasing due to the improper disposal of agro-industrial waste. This waste includes agricultural by-products such as straws, leaves, and husk as well as waste produced from food processing industries such as fruit peels, oil cakes, plant residues, etc. (Sadh et al. 2018). The bioethanol obtained from renewable resources such as crops, starch, and sugar helps in the reduction of greenhouse gas emission and when blended with road transport fuels leads to reducing air pollution. Bioethanol produced shows 94% less greenhouse gas emissions when compared to gasoline. It was also reported that for producing 1000 L bioethanol from lignocellulosic feedstocks, 2.6 mg of CO_2 emission is saved (Aditiya et al. 2016; Mohapatra et al. 2017). The energy content of bioethanol is approximately 40% lower than gasoline, and oxygen content is 35% higher that enable a cleaner combustion and the emission of less toxic substances (Ahmed et al. 2016).

Bioethanol serves as a promising alternative as well as renewable and sustainable liquid biofuel, successful in dealing with environment quality and today's global energy crisis (Aditiya et al. 2016).

Worldwide bioethanol is mainly used as transportation fuel. Bioethanol has advantages like renewability, it is less toxic than other fuels, it has particulate free burning nature, and lower VOCs and NO_x pollutants are emitted by its emission (Cutzu and Bardi 2017). Steps such as pretreatment, fermentation, and distillation are needed to turn lignocellulosic biomass into ethanol (Fig. 11.1). Various methods used for pretreatment and fermentation should be appropriate and effective to achieve high bioethanol yield.

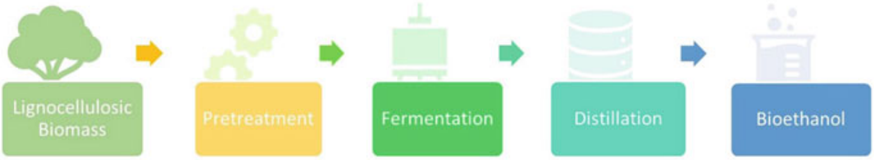


Fig. 11.1 Bioethanol production process flow

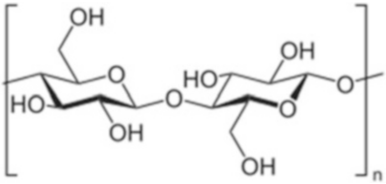
11.2 Source of Cellulose

11.2.1 Structure

An organic compound "cellulose" with chemical formula $(C_6H_{10}O_5)_n$ is a polysaccharide that consists of thousands of D-glucose units linked by β(1 → 4) linkage. The long chains of anhydro-D-glucopyranose units (AGU) are present where each molecule has three -OH groups per AGU, with the exception of the terminal ends. One end is the reducing end with D-glucose unit, and the other end is a non-reducing end with C4-OH group. Cellulose contributes to the structure of cell walls of plants, many algae, and oocytes. Molecular structure of cellulose has significant features like hydrophilic nature having contact angle of 20–30°, degradability range, and chemical variability as it has a high reactive -OH group. Due to these properties, cellulose is stated as an abundant polymer in nature. The content of cellulose varies in different substrates, e.g., wood contains 40–50%, dried hemp consists of approximately 57%, and cotton fibers consist of 90% cellulose. Some bacterial species are also able to secrete cellulose, and they produce one of the purest forms of cellulose. A strain of *Clostridium* bacteria TU-103, found in waste produced by zebra, is able to convert almost any form of cellulose to butanol which is a biofuel (Kulkarni Vishakha et al. 2012; Gupta et al. 2019; Seddiqi et al. 2021; Butnariu and Flavius 2022; Nisa et al. 2022).

Few additional properties of cellulose are that it is insoluble in water and other organic solvent, odorless, chiral, and biodegradable. Pulse tests given by Krumm et al. (2016) showed that the melting temperature was 467 °C. The carbon, hydrogen, and oxygen contents in cellulose are 44.44%, 6.17%, and 49.39%, respectively (Chen 2014; Krumm et al. 2016). Studying cellulose (Fig. 11.2) is important because it has various uses, out of which biofuel production from cellulosic biomass is taking advancement rapidly, as it is a homopolymer of glucose.

Fig. 11.2 Structure of cellulose



Another polysaccharide which comprises 20% biomass of plants is hemicellulose. Unlike cellulose, they are made up of units of sugars like xylose, mannose, arabinose, galactose, and glucose. The chains of hemicellulose are shorter 500–3000 sugar units, and they are branched. Hemicellulose also plays an important role in biofuel production along with cellulose (Chen 2014).

11.2.2 Types of Cellulose

The material that produces cellulose is called cellulosic material. According to the sources, cellulose can be categorized into plant cellulose, bacterial cellulose, algal cellulose, wood cellulose, and non-wood cellulose, and all these sources of lignocellulose biomass which have potential to be used as a substrate for ethanol production are shown in Fig. 11.3.

11.2.2.1 Plant Cellulose

Cellulose is the main part of the cell wall of plants. Most of the higher plants' cellulose has a crystalline structure with a very long length but a narrow width of only a couple of nanometers (Šturcová et al. 2004). Plant cellulose is a mesh-like, tough material giving structural support to make cell wall. Cellulose is categorized into four different types of polymorphs, that is, celluloses I, II, III, and IV. The types

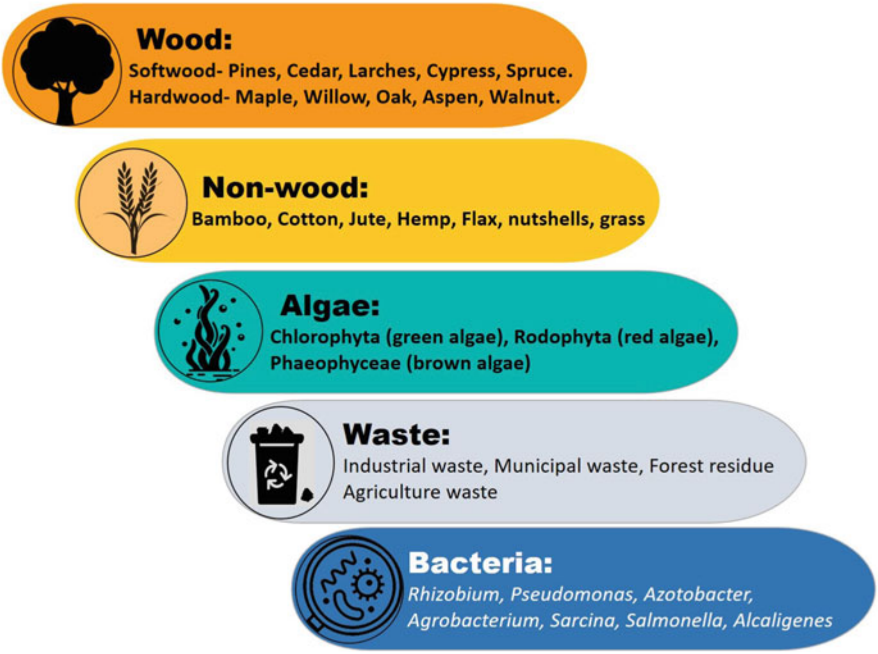


Fig. 11.3 Common sources of cellulose

of cellulose that are produced by plants are of categories I and II, and they are called as native cellulose that is found in two different crystalline forms. Type I cellulose is less stable thermodynamically than type II. Type II cellulose is mainly found in marine algae which is formed when type I cellulose is reacted with sodium hydroxide. When types I and II are treated with liquid ammonia, it produces type III crystalline form, which if further heated produces type IV cellulose (Lavanya et al. 2011).

11.2.2.2 Cellulose from Wood

Wood is one of the major sources of cellulose. Both softwood and hardwood contain cellulose and hemicellulose. Softwood contains 40–45% of cellulose, while hardwood contains 45–47% of cellulose (Kang et al. 2014). Examples of wood cellulose are aspen (*Populus tremuloides*) and cottonwood (*Populus trichocarpa*); both contain 56.5% and 52.0% of cellulose, respectively (Wayman 1958).

11.2.2.3 Cellulose from Non-wood

Non-wood biomass includes plants with weak steam; it also includes corncob, husk, nutshells of fruits, and agricultural and garden waste. Based on the output, bamboos are considered as the most abundant non-wood sources. Non-woody plants are gaining popularity as alternative sources of cellulose due to low lignin content, high cellulose yield, and relatively short rotation period leading to low production costs (Pennells et al. 2019). The valorization of non-wood agricultural residues is also beneficial with respect to reducing the burden of disposal of waste.

11.2.2.4 Bacterial Cellulose

Bacterial cellulose is gaining importance recently as a source of producing biofuel. Microorganisms usually make microbial cellulose, which is a source of pure cellulose. Due to its high purity and unique physical and chemical properties, it has many uses in many industries, such as the food and biomedical industries. It can also be used to make biobased polymers and nanocomposites (Lahiri et al. 2021).

Bacterial cellulose is naturally produced; many studies focus on enhancing the cellulose growth from culture in laboratory. These approaches have led to tailorable microbial cellulose, and desired properties can be achieved. Bacterial cellulose has almost the same formula like plant but has different properties like high purity and greater tensile strength and hydrophilicity and is more volatile than plant cellulose as it can be produced in lab. It can be grown in any shape because it has high movability at the time of formation. *Gluconacetobacter xylinus*, a Gram-negative bacterium, can synthesize cellulose (conventionally known as *Acetobacter xylinum*). *Agrobacterium*, *Acetobacter*, *Rhizobium*, *Azotobacter*, *Sarcina*, *Alcaligenes*, and *Pseudomonas* can also produce bacterial cellulose (Dien et al. 2003; Kumar et al. 2019; Lahiri et al. 2021).

11.2.2.5 Algal Cellulose

Apart from the above, seaweeds have emerged as a source of cellulose and a major contributor in third-generation bioethanol production. Cellulose microfibrils are present in the cell wall of green, red, and brown seaweeds to give skeletal support to the microalgae. The members of Ulvales, Cladophorales, Ulotrichales, and Bryopsidales contain significant amount of cellulose which is predominantly an α-allomorph type with negligible or no lignin content. Algal cellulose is mainly comprised of two different crystalline structures Iα and Iβ. These both celluloses are structured by parallel glucan chains in a flat-ribbon conformation, with alternating glucosyl units locked in opposite orientations by intramolecular hydrogen bonds. These intramolecular hydrogen bonding hold the chains together in flat sheets. Algal cellulose Iα is a triclinic unit cell. It has one chain with conformation- and hydrogen-bonding-different glycosyl residues (Nishiyama et al. 2003; Šturcová et al. 2004).

11.2.2.6 Animal Cellulose

An uncommon source of animal cellulose is tunicates. It is the only animal species that produces cellulose as skeletal frame in the tunic tissues. Tunicate-derived cellulose is composed purely of cellulose I allomorph making it superior to cellulose obtained from plants in terms of aspect ratio, surface area, crystallinity, and mechanical properties (Dunlop et al. 2020).

Cellulosic materials from different sources like plant cellulose, bacterial cellulose, algal cellulose, wood cellulose, and non-wood cellulose are popular substrates for bioethanol production. Mostly agricultural residues and sugary crops are considered as good sources of cellulose, but it can be extracted from sources such as sugarcane, corn, rice straw, and wheat straw (Lavanya et al. 2011). A list of sources with their composition of cellulose, hemicellulose, and lignin components is summarized in Table 11.1. For instance, cellulose content in agricultural waste such as wheat and corn straws ranges from 30% to 40% of biomass with least amount of lignin content making it a preferred substrate for bioethanol production. Similarly, cardoon plant also has high cellulose content but is accompanied with high hemicellulose and lignin content which means it needs to undergo additional pretreatment for optimum bioethanol production; however, high hemicellulose and lignin fraction make it valuable in paper and pulp production. In the case of waste generated in the food industry, the cellulose content ranges between 12% and 39%. As evident from the table, about 40–50% of bagasse is cellulose, but it is essential to reduce the lignin proportion to facilitate sugar hydrolysis and fermentation. In wood, it is reported that the cellulose content of hardwood and softwood is comparable with each other; however, higher lignin in softwoods makes it resistant to hydrolysis in comparison to hardwoods. A comparison of some seaweed-based cellulose is also described in Table 11.1. The cellulose contents in different seaweed species range from 35% to 56% with an average being 42.26%. It is also reported that cellulose prepared from seaweed has higher crystallinity index in comparison to other lignocellulose biomass. The chemical composition of lignocellulose biomass represented in the table can assist in deciding the energy-efficient pretreatment, hydrolysis, and fermentation parameters for obtaining maximum bioethanol yield.

Table 11.1 Sources of cellulose

	Content (%)			Reference
Used substrate	Cellulose	Hemicellulose	Lignin	
Agricultural source				
Rice straw	32.0	24.2	29.6	Takano and Hoshino (2018)
Cardoon *Cynara cardunculus*	41.9 ± 0.0	12.8 ± 0.7	14.9 ± 0.1	Fernandes et al. (2015)
Banana rachis	26.1	11.2	10.8	Guerrero et al. (2018)
Banana pseudo-stem	20.1	9.6	10.1	Sarkar et al. (2012)
Wheat straw	35–45	20–30	8–15	
Coconut shell	15–27	18–40	41–45	Danso-Boateng et al. (2022)
Oak wood	38–46	19–30	22–29	
French oak	22–50	17–30	17–30	
Rice straw	32–47	19–27	5–24	Sarkar et al. (2012)
Rice husk	32.67	31.68	18.81	Ma’ruf et al. (2017)
Corn straw	42.6	21.3	8.2	Sarkar et al. (2012)
Industrial				
GK-coba	24.14	12.60	11.30	Khalil et al. (2015)
Mn-1054	26.14	17.20	5.62	
Ramada	24.31	12.72	5.34	
Mn-4508	20.18	15.19	7.20	
SS-301 (Sweet sorghum *Sorghum* varieties)	22.13	11.73	5.19	
Orange peels	13.61 ± 0.6	6.10 ± 0.2	2.10 ± 0.3	Ververis et al. (2007)
Lemon peels	12.72 ± 0.5	5.30 ± 0.2	1.73 ± 0.2	
Wood and forest				
Hardwoods	45–47	25–40	20–25	Kang et al. (2014)
Softwoods	40–45	25–29	30–60	
Grasses	25–40	35–50	–	
Switch grass	40–45	30–35	12	
Municipal				
Waste office paper	52.42 ± 1.24	9.48 ± 0.86	15.08 ± 1.32	Annamalai et al. (2020)
Waste newspaper	34.97 ± 1.48	9.55 ± 0.63	21.72 ± 1.26	
Cardboard	61	12	118	Ioelovich (2014)
Packaging paper	60	11	7	
Napkins	58	6	4	
Blotting paper	81	6	4	
Newspaper	38	15	21	
Office paper	62	5	1	

(continued)

Table 11.1 (continued)

Used substrate	Content (%)			Reference
	Cellulose	Hemicellulose	Lignin	
Weed				
Algal biomass	7.10 ± 0.2	16.30 ± 0.5	1.52 ± 0.2	Ververis et al. (2007)
Imperata cylindrica	44.4 ± 0.1	31.1 ± 0.0	6.7 ± 0.0	Premjet (2018)
Amaranthus viridis	37.4 ± 0.1	34.2 ± 0.0	5.1 ± 0.1	
Sida acuta	56.0 ± 0.3	16.0 ± 0.4	6.8 ± 0.1	
Rottboellia cochinchinensis	41.6 ± 0.7	28.6 ± 0.4	7.5 ± 0.1	
Sorghum halepense	44.4 ± 0.1	25.8 ± 0.2	6.6 ± 0.5	
Eragrostis amabilis	39.7 ± 0.4	29.6 ± 0.2	7.2 ± 0.2	
Cyperus imbricatus	35.6 ± 0.1	32.3 ± 0.3	4.7 ± 0.3	
Cenchrus echinatus	35.8 ± 0.6	31.8 ± 0.4	6.3 ± 0.3	
Urena lobata	43.5 ± 0.3	11.4 ± 0.7	9.6 ± 0.1	

11.3 Pretreatment

Pretreatment is a necessary step before forwarding the substrate for the fermentation process. Pretreatment accounts for more than 20% of ethanol production costs and is a costly capex procedure. It also affects biomass conversion steps (Pant et al. 2022). Any pretreatment method aims to break down cellulose, hemicellulose, and lignin into smaller fragments for enzymatic hydrolysis and other biorefining processes, increasing product yield (Sharma et al. 2019). This is mainly required because the original form is very complex that cellulase enzymes are not able to hydrolyze it into fermentable sugars. So, the pretreatment is a very important step before proceeding further for better yield (Oyegoke et al. 2022). The molecular structure of lignins determines the strong resistance of plant biomass to breakdown processes, which limits its use as a raw material in bioconversion processes such as cellulose bioethanol production. Lignins protect biomass from hydrolysis by forming a physical barrier between polysaccharides and hydrolytic enzymes (lignin-polysaccharide complexes) and inhibiting the activity of binding enzymes (Mikulski and Kłosowski 2022). The ideal pretreatment should promote sugar production or the ability to produce sugars after enzymatic digestion, reduce carbohydrate degradation or loss, prevent by-products that impede hydrolysis and fermentation, be cost-effective, and be environmentally friendly (Li et al. 2022).

The pretreatment is mainly used for size reduction of substrate for better extraction of hemicellulose, cellulose, starch, etc. before hydrolysis to get substantial amount of reducing sugars. This is a much better approach for respective enzymes to hydrolyze the pretreated substrate into fermentable sugars as the original form of sugars is difficult to hydrolyze because of its complex structure. Also, it helps in

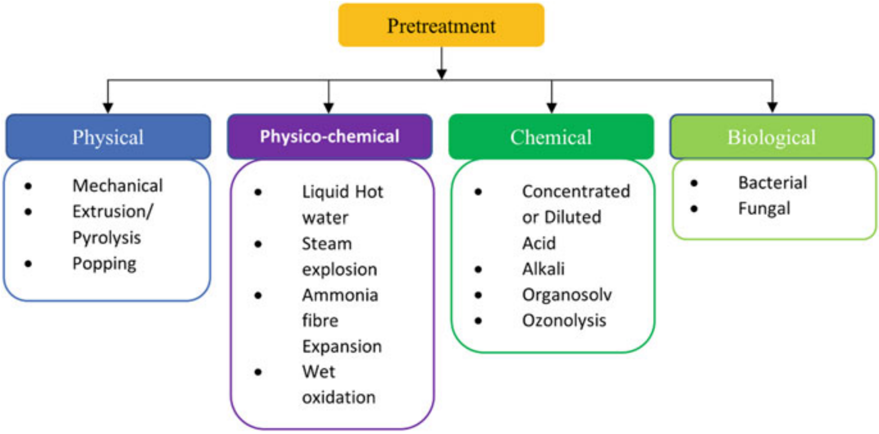


Fig. 11.4 Biomass pretreatment methods for bioethanol production

bringing down the degree of crystallization which is present in the cellulose fibers (Mosier et al. 2005; Sanchez and Cardona 2008; Sharma et al. 2019; Ummalyma et al. 2019; Zhao et al. 2022). The pretreatment for lignocellulosic material is considered to be successful; it is important to select the substrate accordingly. The selected material for fermentation should have good fermentation capability, low solid waste production, high ability to digest the pretreated residue, minimum heat and power requirements, the efficacy should be maintained in case of low moisture, decreasing the size of substrate should not be much required, minimal quantity of toxic generation, able to retain good sugar concentration, able to recover the amount of lignin and operating conditions and cost should be maintained (Alvira et al. 2010; Maurya et al. 2015). The pretreatment changes the properties of the substrate in different ways. Physical, chemical, physicochemical, and biological methods can be used for pretreatment, depending on the forces and amount of energy used in each process (Fig. 11.4). Few studies reported that combination of these processes results in a better yield (Banerjee et al. 2009; Mohapatra et al. 2017; Oyegoke et al. 2022). However, each pretreatment technique has its own benefits and drawbacks (Sharma et al. 2019).

11.3.1 Physical Pretreatment

The physical pretreatment mainly focuses on reducing the size of substrate and crystallinity in cellulose matrix. The physical pretreatment includes mechanical and extrusion treatment methods. Physical pretreatment is a pre-step to co-processing, optimizing equipment and conditions before scale-up, and minimizing costs (Li et al. 2022).

11.3.1.1 Mechanical

Mechanical pretreatment reduces particle size (10–30 mm after chipping, 0.2–2 mm after milling or grinding) to increase biomass surface area. It also decreases the crystalline nature of lignocellulose feedstock and reduces the extent of polymerization of hemicellulose, cellulose, etc. Various milling, grinding, and chipping methods contribute in reducing the physical size of the particle and to improve the lignocellulosic material digestibility. However, this method consumes a very high amount of energy and not efficient economically (Alvira et al. 2010; Maurya et al. 2015).

11.3.1.2 Extrusion/Pyrolysis Treatment

The extrusion method was utilized to produce gaseous products and residual char. The pretreatment is basically practiced at high temperatures, i.e., above 300 °C, followed by blending and shearing. This makes the chemical and physical modification in cellulose structure. Screw speed and barrel temperature may interrupt the lignocellulosic structure, causing fiber defibrillation, fibrillation, and shortening and enhanced carbohydrate arability to enzyme attack (Maurya et al. 2015; Rastogi and Shrivastava 2017).

11.3.1.3 Popping Pretreatment

Popping pretreatment employs heat and pressure to enhance cell wall enzyme accessibility (Nguyen et al. 2017). This technique is similar to water-impregnated steam explosion, which combines the mechanical forces of a rapid explosion with hydrolysis in high-temperature water and acetic acid generated from acetyl groups in the biomass. As biomass is generated by the pretreatment, there is a “pop-out.” In contrast to this process, the equipment used for popping pretreatment is a fairly simple system made up of a direct burner, a rotary reactor, and no steam generator. This method has a lot of advantages over other ways of doing things. For example, it has a much smaller effect on the environment and a higher saccharification efficiency than commonly used methods with similar properties. They are not suitable for a scale-up procedure, because of significant capital costs and pressure (Choi et al. 2013; Wi et al. 2013; Jang et al. 2021).

11.3.2 Physicochemical Pretreatments

The use of physicochemical processes is preferable over the use of chemical methods since they are more environmentally friendly. Despite this, the process becomes more involved, which may result in an increased energy requirement (Li et al. 2022).

11.3.2.1 Liquid Hot Water

The liquid hot water method, also known as hydrothermal pretreatment, incorporates both physical and chemical pretreatment techniques. In this, the lignocellulosic substrate is added in liquid at high temperature in range from 160 to 240 °C, pressure above 5 MPa, and time that varies for about an hour or more. It generally does not require any sort of rapid decompression, and no additional chemical or catalysts need to be added. Hot water can remove up to 80% of hemicellulose from herbaceous feedstocks and improve enzymatic digestibility. The advantages of this method are that it has good pH maintenance which reduces unnecessary degradation of polymers, it has high ability to recover pentose sugar, less inhibitors are formed, and no corrosion-resistant materials and chemicals are needed. This method requires a lot of energy and water, so it's not commercially viable (Alvira et al. 2010; Yu et al. 2010).

11.3.2.2 Steam Explosion

Steam explosion, or autohydrolysis, is the most common pretreatment for lignocellulosic biomass. In this method, chopped biomass is subjected to high-temperature (160–260 °C) and high-pressure saturated steam (20 min) followed by a sudden release of pressure, which causes autohydrolysis of hemicellulose acetyl groups. This results in the segregation of individual fibers which destroy the structural cell wall. Due to steam explosion, the ability of enzymes to do hydrolysis is improved, there is lesser impact on nature, fewer chemicals are required that are not hazardous, and yield of sugar is increased, making it an acceptable method by industries. However, the process has few drawbacks: it is not preferred for softwoods, the hemicellulose content and lignin content are not degraded properly, there is generation of inhibitory materials, and this process is expensive as it requires more equipment for the addition of acid into chamber (Martín et al. 2002; Pan et al. 2005).

11.3.2.3 Ammonia Fiber Expansion

Ammonia fiber explosion is one of the physical and chemical pretreatments for biomass that are based on ammonia. In this, the lignocellulosic biomass is treated with liquid ammonia for the period of 30–60 min and at relatively moderate temperature (90–100 °C) and then sudden pressure release. After ammonia pretreatment at high pressure and temperature, lignin structure changes, increasing water holding capacity and causing cellulose swelling and phase change, improving the digestibility and reactivity of residual carbohydrates. The other ammonia-based pretreatment methods include soaking aqueous ammonia and ammonia recycle percolation. It has advantages as it enhances the area of reaction for enzymes causing increased digestibility. In this method, less amount of toxic compounds and inhibitors is formed. It is not preferred as this method does not work effectively with biomass containing a high amount of lignin; the amount of hemicellulose and ammonia is reduced largely which then affects the amount of sugar produced (Maurya et al. 2015; Rastogi and Shrivastava 2017).

11.3.2.4 Wet Oxidation Pretreatment

Wet air oxidation is the sub-critical oxidation of organics or oxidizable inorganics at high temperatures (125–320 °C) and pressures (0.5–2 MPa). Wet air oxidation is a promising alternative pretreatment method for fractionating lignocellulose into a solubilized hemicellulose fraction and a solid cellulose-rich fraction with minimal inhibitor formation, allowing improved enzymatic hydrolysis of the pretreated material for subsequent ethanol fermentation. Wet air oxidation opens cellulose's crystalline structure, solubilizes hemicellulose, and degrades lignin into CO_2, H_2O, and carboxylic acids. Deacetylating hemicellulose produces carboxylic acids. At temperatures above 170 °C, adding oxygen makes the reaction exothermic, reducing energy use. Wet oxidation generates acids from hydrolysis and oxidative reactions. It has been shown to be an effective technique for solubilizing hemicelluloses and lignin, as well as increasing cellulose digestibility. It is the most extensively utilized method for producing ethanol, followed by simultaneous saccharification and fermentation. The only thermal energy necessary for WAO is the difference in enthalpy between the incoming and outgoing streams; consequently, minimal fuel is required. Although the initial investment for wet air oxidation is greater than that of other pretreatment techniques, the operational costs are essentially limited to the energy used to compress the air (Alvira et al. 2010; Banerjee et al. 2009).

11.3.2.5 Oxidative Pretreatment

During oxidative pretreatment, H_2O_2 or peracetic acid ($C_2H_4O_3$) is added to water-suspended biomass as H_2O_2 is a popular oxidizer. Studies show that 1–2% H_2O_2 at 25–30 °C can dissolve half the lignin and most of the hemicellulose. To increase cellulose accessibility, this pretreatment process eliminates hemicellulose and lignin from biomass. During pretreatment, electrophilic substitution, side chain displacement, alkyl/aryl ether linkage breakage, and oxidative aromatic nucleus cleavage may occur. The main disadvantage is that this process is costly due to the high cost of H_2O_2, and high-efficiency reaction vessels that can withstand such conditions are required (Maurya et al. 2015).

11.3.2.6 CO_2 Explosion

Supercritical carbon dioxide, which has traditionally been used as an extraction solvent, is now being investigated for non-extractive applications due to its many benefits. The method is based on using CO_2 as a supercritical fluid, which is a gaseous fluid that is compressed to a density resembling liquid at temperatures higher than its critical point. Lignin can be effectively removed under supercritical pretreatment conditions, improving substrate digestibility. Co-solvents like ethanol, when added, can enhance CO_2 delignification at high pressure. Carbonic acid is produced when CO_2 and water react, facilitating the breakdown of polymers. Because CO_2 molecules are the same size as water and ammonia, they can fit through the lignocellulose's tiny pores. High pressure facilitates this mechanism. After the CO_2 pressure is released explosively, the structure of cellulose and hemicellulose is disrupted, and the substrate's available surface area to enzyme attack rises. Supercritical CO_2 is widely used as a non-extraction solvent due to its environmental acceptability, non-toxicity, low cost, easy recovery, and non-flammability. CO_2 forms carbonic acid in water, accelerating hydrolysis. CO_2 explosion is more cost-effective than ammonia expansion and produces fewer inhibitors than steam explosion. High pressure is required (Kim and Hong 2001; Alvira et al. 2010; Maurya et al. 2015).

11.3.2.7 Microwave Pretreatment

Microwave irradiation is a commonly utilized method due to its great heating efficiency and simple operation. Since microwave-based pretreatment frequently involves both thermal and non-thermal effects, it might be considered a physicochemical process. Microwave pretreatment improves starch digestibility, which can increase enzyme accessibility. Submerging the biomass in diluted chemical reagents and exposing the resulting slurry to microwave radiation for 5–20 min of pretreatment. This alternative energy generates hot nuclei by interacting with the polar molecules of the solvent, which is usually water. It has the potential to change the ultrastructure of cellulose by decomposing lignin and hemicelluloses and increasing the enzymatic sensitivity of lignocellulosic materials. Thus, the reactions may be carried out more rapidly and with improved yields and selectivity. The heating is done by the rotation of the dipoles, in which the polar molecules try to line up in the rapidly changing electromagnetic field caused by the microwaves, and by ionic conduction, which is the instantaneous superheating of the ionic substance caused by friction between the ionic molecules caused by the motion that creates the electric field. The main benefit of this method is that the reactions happen quickly and the mixture is heated evenly. The pretreatment of biomass with the help of microwaves could be a good way to save time, energy, and the formation of inhibitors. It could be thought of as one of the most promising ways to change the native structure of cellulose by breaking down lignin and hemicelluloses, making it more sensitive to enzyme hydrolysis. The sugar production from the substrate could be increased by combining microwave technology with the addition of additives (Maurya et al. 2015; Harahap et al. 2022; Mikulski and Kłosowski 2022; Oyegoke et al. 2022).

11.3.2.8 Ultrasound Pretreatment

Ultrasound has been used to get hemicelluloses, cellulose, and lignin out of lignocellulosic biomass, but less research has been done on how easily lignocellulosic materials can be broken down by water. Even though there hasn't been much research on ultrasonic pretreatment of lignocellulose, some researchers have shown that ultrasonic pretreatment makes saccharification of cellulose work better. Higher enzymatic hydrolysis yields after ultrasound pretreatment might be because the introduction of ultrasound field into the enzyme processing solution causes cavitation effects that greatly speed up the movement of enzyme macromolecules toward the substrate surface. Also, the mechanical impacts caused by the collapse of cavitation bubbles make it easier for enzymes to work on solid substrates. Cavitation works best at 50 °C, which is the best temperature for many enzymes (Sun and Tomkinson 2002; Alvira et al. 2010).

11.3.3 Chemical Pretreatment

Chemical pretreatment increases biomass hydrolysis. Acids, alkalis, organic solvents, and ionic liquids break down lignocellulosic biomass. Due to its simplicity and efficiency, chemical pretreatment is widely employed in industry. Chemical pretreatment can produce inhibitors and environmental pollution (Li et al. 2022).

11.3.3.1 Concentrated or Diluted Acid

Acid pretreatment is most widely used method because of its high efficiency. Acid pretreatment solubilizes hemicellulose and lignin and makes cellulose more enzyme-accessible. Acid pretreatment can be done with concentrated or diluted acid, but concentrated acid produces inhibitory chemicals. Acids remove hemicellulose or lignin from cellulose to increase glucose recovery. Concentrated acids are toxic, corrosive, and hazardous, necessitating corrosion-resistant equipment. However, when these chemicals are used at high temperatures, large amounts of breakdown products are formed. They can also corrode equipment, pollute residues, and harm the environment, among other things. Higher concentrations of these compounds reduce reaction times and eliminate the need for enzymes, but low concentrations require higher temperatures and pressures to obtain optimal hydrolysis efficiencies. One of the drawbacks of using concentrated chemicals is the need to neutralize the samples after they have been treated, which raises the overall expense of the process (Mosier et al. 2005; Maurya et al. 2015; Velazquez-Lucio et al. 2018).

At an industrial scale, diluted acid pretreatment is the best choice. There are two ways to do dilute acid pretreatment: at a high temperature (>180 °C) for a short time and at a lower temperature (>120 °C) for a longer time (30–90 min). Acid that has been diluted seems to be a better way to treat lignocellulosic biomass before it is used in industry. This has been studied for a wide range of lignocellulosic biomass. Organic acids like fumaric and maleic acids are emerging as potential cellulose hydrolysis enhancers for ethanol synthesis (Alvira et al. 2010; Maurya et al. 2015; Rastogi and Shrivastava 2017; Velazquez-Lucio et al. 2018).

With dilute sulfuric acid, which is also the most extensively used acid, high hydrolysis yields have been reported. H_2SO_4, H_3PO_4, NH_3, $C_2H_4O_3$, $C_2H_2O_4$, HCOOH, CH_3COOH, and $C_4H_4O_4$ have all been investigated (Maurya et al. 2015).

11.3.3.2 Alkali Treatment

Alkaline chemistries are better at pretreating agricultural wastes and herbaceous crops. Alkaline pretreatment removes lignin from biomass by breaking the ester bonds that hold lignin and xylan together. This leaves more cellulose and hemicellulose in the fractions, which is similar to how soda or kraft pulping works (McIntosh and Vancov 2010).

The alkaline treatment entails the application of alkali, often sodium, potassium, calcium, or ammonium hydroxides, to biomass under ambient conditions. Pretreatment with alkali can be done in a wide range of periods, from seconds to days, at room temperature. Because of the swelling caused by the NaOH, the cellulose's internal surface area expands, while the degree of polymerization and crystallinity decreases. This causes the lignin structure to break. It has been observed that lowering the lignin concentration of hardwood from 24–55% to 20% with NaOH increases digestibility from 14% to 55%. The primary benefit of this method is the effective elimination of lignin from biomass. If you want anything that works, NaOH is your best bet. When compared to other methods, it was found to be superior in expanding usable interior space. However, softwoods with a lignin level higher than 26% showed no reaction to dilute NaOH. Alkaline pretreatment [NaOH/Ca$(OH)_2$], which helps get rid of lignin, can be made more effective by adding air or oxygen. However, the substantial processing expenses incurred after the initial purchase of lime or other hydroxides make the entire process prohibitively expensive. Washing the calcium and sodium salts used in the process uses a lot of water. Furthermore, they are challenging to eliminate (Mosier et al. 2005; Alvira et al. 2010; Maurya et al. 2015).

This procedure removes acetyl and uronic acid from hemicelluloses, increasing enzyme accessibility. Hydrolysis of ester bonds between xylan and hemicellulose residues also occurs. This technique improves cellulose digestibility and lignin solubilization while solubilizing little cellulose and hemicellulose as compared to acid pretreatment. It has been demonstrated that alkaline pretreatment of biomass prior to fermentation can result in greater saccharification yields. Pretreatment with an alkaline solution at high temperatures breaks down hemicelluloses into sugar monomers, reduces cellulose crystallinity, and increases biomass porosity, resulting in faster enzymatic hydrolysis. Sodium hydroxide is primarily used in the alkaline-based technique. Alkaline pretreatment reduces sugar deterioration and is cost-effective because many caustic salts can be recovered and/or regenerated. This approach is distinguished by the induction of solvation and saponification reactions, which result in the formation of pores in the cell wall. This allows intracellular chemicals to escape and reduces starch polymers, cellulose, and starch crystallinity (Maurya et al. 2015; Wang et al. 2016; Mohapatra et al. 2017; Velazquez-Lucio et al. 2018; Yang et al. 2019).

11.3.3.3 Organosolv

Organosolv extracts lignin from lignocellulosic biomass using organic or aqueous solvents with inorganic acid catalysts. Acetone, methanol, ethanol, ethylene glycol, triethylene glycol, and tetrahydrofurfuryl alcohol are being used. Some organic or aqueous organic solvents can be used as catalysts at higher temperatures with or without organic acids. In some studies, hemicellulose bonds are broken using acid catalysts (HCl, H_2SO_4, oxalic, or salicylic). In a two-stage fractionation, it has been proposed to combine the organosolv process with prior acid hydrolysis to separate the fiber's hemicellulose and lignin. It is possible to achieve high lignin removal (70%) and minimal cellulose loss (less than 2%). The addition of acid typically results in a high yield of xylose. By raising the process temperature (above 185 °C), this acid addition can be avoided for a satisfactory delignification. An important application of the organosolv process is the extraction of high-quality lignin, a product with added value. Due to the effective removal of lignin, this process has demonstrated high levels of enzymatic hydrolysis of treated biomass (around 90%). The main benefit of the organosolv process, when compared to other chemical pretreatments, is the recovery of relatively pure lignin as a by-product (Mosier et al. 2005; Maurya et al. 2015; Mohapatra et al. 2017; Alvira et al. 2010; Joy and Krishnan 2022).

Solvent and catalyst costs are the process's main drawback. Solvents' high commercial price is another industrial consideration. Solvent recovery reduces operational costs. Organic solvents are flammable and can cause fires and explosions if used improperly. Solvents may inhibit enzymatic hydrolysis and fermentative microorganisms which raises costs. Organic solvents also stop enzymatic hydrolysis from occurring, so they have to be taken away for enzymatic hydrolysis to work. Solvents need to be taken out of the system using the right extraction and separation methods, such as evaporation and condensation. Solvents should also be recycled to cut down on operational costs. So, getting rid of organic solvents also comes with an extra cost. For economic reasons, ethanol and methanol, which have low molecular weights and low boiling points, are the best solvents (Mosier et al. 2005; Alvira et al. 2010; Maurya et al. 2015; Mohapatra et al. 2017; Rastogi and Shrivastava 2017).

11.3.3.4 Ozonolysis

In the last few decades, ozonolysis pretreatment has been shown to be effective by breaking down the lignin polymer and making the hemicellulose in lignocellulosic biomass slightly more soluble. During the process, the substrate is kept in a reaction vessel, and the ozone gas is passed through it. There could be packed beds, fixed beds, or stirred semi-batch reactors inside the vessel. Both the amount of water and the type of biomass are very important. It can be used to break up the structure of things like wheat straw, bagasse, pine, peanut, cotton straw, rye straw, and poplar sawdust. The next step, enzymatic hydrolysis, works better when there is less lignin in the wood. Compounds with conjugated double bonds and high electron densities in their functional groups react quickly with ozone. So, since lignin has a lot of C=C bonds, it is most likely to be oxidized when lignocellulosic materials are exposed to ozone. When ozone attacks lignin, it releases water-soluble, low molecular weight compounds, mostly organic acids like formic and acetic acid, which can cause the pH to drop from 6.5 to 2. Ozonolysis has been used to treat agricultural wastes like wheat straw and rye straw to increase the yield of enzymatic hydrolysis in both cases. Most of the time, ozonolysis is done at room temperature and pressure, and it doesn't leave behind any toxic residues that could affect the hydrolysis and fermentation that come next. More research is needed to make ethanol from ozone-treated lignocellulosic materials. The process can be too expensive because of high ozone requirement (Garcia-Cubero et al. 2009; Alvira et al. 2010; Maurya et al. 2015; Rastogi and Shrivastava 2017).

11.3.3.5 Ionic Liquid Pretreatment

Ionic liquids are a new type of solvent that is effective, is safe for the environment, and can be used to turn lignocellulosic feedstocks into fuels and chemicals. This is because ionic liquids can break down and separate biomass efficiently. Ionic liquids have gotten a lot of attention as possible biomass pretreatment agents because they have "green" properties like not being volatile or flammable, being chemically and thermally stable, having a wide electro-chemical range, having high ionic conductivity, being able to be recycled, and being able to dissolve a wide range of things. Ionic liquids are a group of melted salts with unique physical and chemical properties. They have shown a lot of promise. This pretreatment process uses ionic liquids with a biomass-to-ionic liquid weight-to-weight ratio of 1:10 and temperatures between 100 and 150 °C. Antisolvents like water, methanol, and ethanol use soluble biomass to regenerate, which is then broken down by enzymes to make fermentable sugars. Ionic liquids behave similarly to salt, which consists of large organic cations and small inorganic anions. At low temperatures, they are liquids (room temperature). Because ionic liquids contain anions such as chloride, formate, acetate, and alkyl phosphonate, they can form hydrogen bonds with cellulose at high temperatures. Ionic liquids have a lot of potential for pretreating lignocellulosic biomass and making substrates that can break down more than 90% of cellulose (Maurya et al. 2015; Nargotra et al. 2018; Das et al. 2021a, b).

However, ionic liquids can be used as pretreatment agents; they are more expensive and aren't as good at getting rid of lignin and hemicelluloses as other methods. This limits how widely they can be used. Even though the dissolved material was able to settle out, there are still problems with the cost, recycling, and biocompatibility of ionic liquids for further processing. Some choline-based aprotic ionic liquids have been studied and shown to be compatible with both enzymes and microbes. This enables the development of a one-pot reaction system, in which all process steps are performed in a single vessel without separation. Some protic ionic liquids have been called low cost, and this is mostly because they are easier to make. Ionic liquids like 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) have a special way of breaking down complex polysaccharides and getting rid of lignin at room temperature (Nargotra et al. 2018; Das et al. 2021a, b).

Ionic liquids that are still in the biomass could stop hydrolytic enzymes from working and stop fermentation from happening further down the line. It could change how much sugar and biofuel are made in the end. Flash distillation can be used to get ionic liquids back from antisolvents after they have been regenerated, so they can be used again. For ionic liquids to be used on a large scale, energy-efficient ways to recycle them must be found. Before using them in biomass pretreatment, it is also important to think about how toxic they are to enzymes and fermenting microorganisms (Maurya et al. 2015).

11.3.4 Biological Pretreatment

One crucial approach for digesting lignocellulosic biomass is biological processing. Given that it is carried out naturally without the use of chemicals, biological pretreatment is regarded as a "green" technology. Numerous researchers have used different microbes, and this zero-pollution strategy has drawn a lot of interest since it improves the pace of fermentation and enzymatic saccharification without requiring a substantial financial input. Low energy consumption and minimal to no waste stream output are the key advantages. It may be used for on-farm wet storage to produce biofuels from lignocellulosic biomass at a low cost. The biggest advantages of biological pretreatment over other methods are that there is no chemical recovery after pretreatment, the cost of treatment further down the line is low, and it is easy to use, uses less energy, is good for the environment, and makes less toxic materials like furfural and hydroxymethylfurfural. For biological pretreatment, microorganisms that release a variety of cell wall-degrading enzymes have been utilized successfully. This method primarily employs fungus and bacteria, or their enzymes, and is highly dependent on a variety of factors, including the culture medium, culture duration, strain type, generated enzymes, and degradation processes. These microbes include ruminant bacteria, wood rot fungus, and symbiotic bacteria that can coexist with some invertebrate animals (e.g., termites, earthworms). Through the use of ligninolytic enzymes, wood rot fungi such as white rot, brown rot, and soft rot can partially break down or alter lignin. Cellulolytic and hemicellulolytic systems, which are primarily in charge of hydrolyzing the biomass ingested by their hosts, can be produced by symbiotic bacteria in animal rumens or the digestive tracts of termites (Li et al. 2022; Narayanaswamy et al. 2013; Wan and Li 2013).

Cellulolytic and hemicellulolytic bacteria are typically used to hydrolyze cellulose and hemicellulose into monomeric sugars in biological pretreatment. When the fermentation process and the breakdown of lignocellulosic biomass are initiated simultaneously, bioproducts such as different enzymes, lactate, acetate, organic acids, etc. are produced as well as biofuels such as ethanol, hydrogen, methane, furfural, etc. Several elements impact a biological pretreatment's success. This includes things about the substrate like biomass composition, inoculum concentration, aeration rate, moisture content, incubation time, incubation temperature, pH, and microbe species. For successful lignin and hemicellulose removal from biomass, an appropriate microbial consortium must be used. Optimal incubation temperature, pH, and time vary by biological consortium. Aeration helps oxygenate, remove CO_2, maintain humidity, dissipate heat, and distribute metabolic volatiles (Sharma et al. 2019; Ummalyma et al. 2019; Sindhu et al. 2016).

It is common practice to use a solid-state fermentation technique to carry out biological pretreatment. Biological pretreatment is more time-consuming than thermochemical pretreatments because microorganisms, especially fungi, need more time to completely colonize and degrade biomass feedstocks. Because of this, it is less likely that a processing plant will use this technique for on-site pretreatment of lignocellulosic biomass. However, bacteria's need for carbohydrates for their own growth and metabolism is a problem that must be addressed when using microbes in pretreatment. Consequently, lignin-degrading microorganisms are chosen for biological pretreatment. However, as compared to the status quo of pretreatment technologies, biological pretreatment has the potential to significantly lessen negative environmental effects and energy consumption. Furthermore, pretreated biomass residues obtained by fungal pretreatment applied as an on-farm wet storage pretreatment would have significantly greater cellulose digestibility than pretreated biomass residues obtained using ensilages that utilize lactic acid bacteria for fermentation (Wan and Li 2013; Li et al. 2022).

11.3.4.1 Bacterial Pretreatment

Numerous microorganisms produce diverse biomass-degrading enzymes utilized in biological pretreatment. The selection of the best bacteria strains for the pretreatment of lignocellulosic biomass, followed by enzymatic hydrolysis and fermentation, is an important part of making biofuel. Compared to lignin, cellulose and hemicellulose are relatively simpler to break down (Sharma et al. 2019). Bacteria degrade lignin less effectively than fungi, but they're more adaptable, fast-reproducing, and useful. *Bacillus* spp., *Rhodococcus* spp., and *Pseudomonas* spp. are the predominant bacteria capable of degrading lignin from termite gut, calf stomach, soil, and compost. Bacterial pretreatment of lignocellulosic biomass has great potential for future industrial applications, but there are many unresolved issues, such as low lignin degradation efficiency and unclear metabolic network pathways and enzyme regulatory mechanisms (Li et al. 2022). Despite the fact that the breakdown of lignin by microorganisms has been studied extensively in fungi and less so in bacteria, scientists are very interested in bacterial lignin degradation due to recently discovered bacterial peroxidases, laccases, and β-etherases that can be used to degrade lignin (Sharma et al. 2019).

11.3.4.2 Fungal Pretreatment

Fungi are widely recognized microorganisms due to the cooperative influence of their enzymes on the decomposition of lignocellulosic waste. Fungi are abundant in nature, and many of them produce useful enzymes that break down plant matter such cellulolytic, hemicellulolytic, and ligninolytic. Because filamentous fungi are abundant and can be isolated from numerous sources, including soil, living plants, and lignocellulosic waste, they are widely utilized. In contrast, lignin's complex delignification route is proving to be a significant roadblock in the way of studying and choosing the most effective fungal strain. By destroying the cell wall structure of lignocellulosic biomass, white-rot fungi are the best microorganisms for the pretreatment of the majority of lignocellulosic materials, according to the findings of these studies. As the hyphae of white-rot fungi grow and erode the cell wall structure of lignocellulosic biomass, they parasitize the wood system's cell cavities. To gain access to lignocellulose, the white-rot fungus secretes laccase, lignin peroxidase, manganese peroxidase, and other peroxidases. Diverse white-rot fungi can degrade 30–70% of lignin from various lignocellulosic biomasses in 7–80 days (Sharma et al. 2019; Alvira et al. 2010; Maurya et al. 2015; Li et al. 2022).

Several white-rot fungi, such as *Ceriporia lacerata*, *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, *Cyathus stercoreus*, *Pycnoporus cinnabarinus*, and *Ceriporiopsis subvermispora*, produce lignin peroxidases, which are enzymes that break down lignin. Few white-rot fungi like *Trametes versicolor* and *Ceriporiopsis subvermispora* can break down both lignin and whole cellulose (cellulose and hemicellulose). This means that cellulose recovery is low. To get closer to a biological pretreatment of lignocellulose that is cost-effective and improve the hydrolysis so that ethanol yields can be increased, more basidiomycetes fungi that can delignify plant material quickly and efficiently need to be studied and tested (Alvira et al. 2010; Maurya et al. 2015; Sindhu et al. 2016; Li et al. 2022).

To get closer to a biological pretreatment of lignocellulose that is cost-effective and improve the hydrolysis so that ethanol yields can be increased, more basidiomycetes fungi that can delignify plant material quickly and efficiently need to be studied and tested (Alvira et al. 2010; Maurya et al. 2015). Due to process bottlenecks, such as low sugar yields, poor feedstock capacity, lengthy fungal pretreatment time, and sterilization requirements, the pretreatment of fungi on a biorefinery scale does not appear to be economically viable at the current state of technology; significant process improvements are still required to meet product cost targets. White-rot fungi have the ability to degrade a variety of materials, making it particularly challenging to screen strains when utilizing various lignocellulosic biomasses. In addition, selecting a fungal strain that can efficiently degrade lignin and recover cellulose remains challenging, and its commercial application has not advanced (Sharma et al. 2019; Li et al. 2022).

There are a number of benefits to using biological pretreatment over other pretreatment methods. The primary problems with this method are that it takes a long time and the sugars could be taken by the microorganisms for their own growth. The economics of a process can be improved by using it with the combined pretreatment process, combining a biological process with physical and chemical approaches to shorten the pretreatment time (Ummalyma et al. 2019).

11.3.5 Combined Pretreatment

The physical, chemical, and biological pretreatments of lignocellulosic biomass for biofuel applications have been thoroughly examined. Numerous variables affect the degradability of biomass, including lignin concentration, cellulose crystallinity, and lignin-cellulose bonds. Consequently, a single pretreatment procedure does not produce the desired outcomes due to its intrinsic limitations and limited working modes. In addition, a single pretreatment technique is impractical in terms of cost and efficiency. Combination pretreatment was reported to be more successful than chemical and biological pretreatment alone, according to studies. Combinational pretreatment is an effective method for the development of sophisticated biomass pretreatment systems (Wang et al. 2016; Das et al. 2021a, b).

11.4 Biomass Fermentation

Numerous microbes are capable of converting biomass into ethanol. Bioethanol is currently regarded as the most important biofuel for the future. It is manufactured through chemical synthesis or fermentation and is subject to major industrial development around the world (Ahmed et al. 2016).

When lignocellulosic biomass is chosen for ethanol fermentation, it needs to be hydrolyzed to glucose before fermentation. Producing ethanol requires microorganism in various ways. Microorganisms are capable of the conversion of sugars to bioethanol mainly in two ways: firstly, by glycolysis, in which two pyruvate molecules are formed by one monosaccharide, by releasing two NAD+, and secondly, by fermentation under anaerobic conditions, NAD+ will be regenerated by transfer of two electrons from NADH to acetaldehyde (which is an intermediate formed during decarboxylation of pyruvate) forming ethanol (Maicas et al. 2002; Balat 2011; Munjal et al. 2012).

The most successful ethanol production is acquired by microbes such as yeast *Saccharomyces cerevisiae*. In bioethanol production, other microorganisms such as *Escherichia coli*, *Zymomonas mobilis*, *Thermoanaerobacter ethanolicus*, *Pichia stipitis*, *Klebsiella oxytoca*, *Candida shehatae*, *Mucor indicus*, etc. were also studied. But a good replacement for *S. cerevisiae* has not yet been found. The most efficient bacterial nanocellulose producers belong to *Komagataeibacter* genus, which synthesize high amounts and food-grade cellulose (Florea et al. 2016; Bušić et al. 2018).

Although all the enlisted organisms are capable of ethanol production, the wild-type strains produce much less amount of ethanol and thus are inadequate to fulfill the requirement as a viable alternative for bioethanol production. To overcome the restrictions in the utilization of microbes to their full potential, all the above microbes are tailored to improvise hyper-cellulolytic activity, fermentation capacity, uptake of substrate, resistance to stressor, and valorization of multiple biomasses. Several methods such as random and site-directed mutagenesis, protoplast fusion, gene editing, genome editing, metabolic engineering, cell surface engineering, etc. have made it possible to inculcate necessary traits in the microbes allowing us to solve the challenges associated with them and ramp up the ethanol production (Lugani et al. 2020).

Fermentation is a crucial step in the bioethanol production process because bioethanol is made by converting carbohydrates (starch and cellulose) into ethanol with the aid of microorganisms. After the substrate has been pretreated, the lignin is removed so that it can be fermented easily. Combination processing methods, such as simultaneously saccharifying and fermenting, simultaneously saccharifying and co-fermenting, and consolidated bioprocessing, can be used to add value and possibly save money. Using an integrated biorefinery method, the waste from making bioethanol can be used to make biochemicals, fertilizer, heat, and energy, among other things (Velazquez-Lucio et al. 2018; Dhungana et al. 2022). During the fermentation process, yeast cells absorb a portion of the sugar and turn the remainder into glycerol, acetaldehydes, and lactic acid (Braide et al. 2016).

Lignocellulosic biomass is an abundant and readily available ethanol source as it can be used locally without competing with food (Guerrero et al. 2018). The best way to turn lignocellulosic materials into bioethanol is decided by how much it costs, how it affects the environment, and how well it uses energy. There are celluloses, hemicelluloses, lignin, and soluble polar and non-polar polysaccharides in lignocellulosic materials. Even though producing ethanol from lignocellulosic materials is hard, it can replace making bioethanol from food products (Braide et al. 2016). Starchy crops (corn, wheat, barley), sugar crops (sugarcane, sugar beet, sorghum, fruits), and cellulose crops (stems, leaves, trunks, branches, husks) are all acceptable options for alcoholic fermentations (Cutzu and Bardi 2017). Through metabolism, microorganisms are grown in these materials to turn sugars and starches into ethanol (Tran et al. 2019). Yeasts, especially those from the *Saccharomyces* species, are the most common microorganisms used in the alcoholic fermentation process. Industrial bioethanol production is best when it has a high ethanol yield; a high ethanol tolerance; a high ethanol productivity (>5.0 g/L/h); the ability to grow in simple, cheap, and undiluted media; and the ability to grow in the presence of inhibitors, at a low pH, or at a high temperature (Cutzu and Bardi 2017).

Recent studies have explored using microorganisms to convert biomass into ethanol. Braide et al. (2016) achieved maximum percentage ethanol yield of 6.72% (sugarcane bagasse), 6.23% (sugarcane bark), 6.17% (cornstalk), 4.17% (corncob), and 3.45% (cornhusk) at 72 h of fermentation and at pH 3.60, 3.82, 4.00, 3.64, and 3.65, respectively (Braide et al. 2016). García-Torreiro et al. (2016) used a sequential SSF system to produce ethanol, conducting the saccharification process first for the first 24 h before inoculating *P. tannophilus* to begin the fermentation. The white-rot fungus *Irpex lacteus* was used to pretreat the materials. Final ethanol yields for wheat straw, corn stover, barley straw, and corncob were 79 ± 14, 102 ± 8, 91 ± 2, and 106 ± 10 (mg ethanol/g dry substrate), respectively, after 94 h of SSF. Final ethanol concentrations after 94 h of SSF were 12.5 ± 0.8, 13.5 ± 1.0, 10.8 ± 0.2, and 11.5 ± 1.1 g/L (García-Torreiro et al. 2016). Also, by cultivating the cellulase-producing *Streptomyces* sp. T3-1, a technique developed by Hsu et al. (2011), can significantly increase the hydrolysis efficiency of corncob-based cellulosic material. After 2 days, the fermentation process was complete, with the glucose having been nearly completely depleted and ethanol having reached a maximum concentration of 24.6 g/L (Hsu et al. 2011). Also, Selvakumar et al. (2022) chemically pretreated corncobs using H_2SO_4 and CH_3COOH in varied ratios. *Saccharomyces cerevisiae* hydrolysates were fermented at 30 °C and 200 rpm for 4 days. This study suggests binary acid pretreatment for lignocellulosic biomass (Selvakumar et al. 2022). Densifying lignocellulosic biomass with alkaline chemicals, corn stover yielded 21.4 g of ethanol per 100 g of corn stover, which was increased using a standard steam autoclave. Without washing or detoxifying the pretreated biomass, 70.6 g/L of ethanol was produced (Chen et al. 2021). Cabral et al. (2016) prepared coconut fibers with alkali pretreatment, hydrolyzed them enzymatically, and then fermented them with *Saccharomyces cerevisiae*. Despite significant cellulose loss (4.42% for the fiber and 17.9% for the original content), alkaline (5% NaOH) pretreatment solubilized lignin (80%), making coconut fibers a viable raw material for 2G ethanol production trials. Eighty-seven percent of the sugars were converted through enzymatic hydrolysis, and 81% of the hydrolysate substrate was used in ethanolic fermentation, yielding a 59.6% efficiency for sugar to ethanol conversion (Cabral et al. 2016). Choi et al. (2015) established a unique method for producing bioethanol from single-source citrus peel waste (orange, mandarin, grapefruit, lemon, or lime) or citrus peel waste combined with other fruit waste (banana peel, apple pomace, and pear waste). According to the study, yeast fermentation produced higher ethanol concentrations (14.4–29.5 g/L) and yields (90.2–93.1%) than immobilized cell reactor fermentation alone (Choi et al.

2015). In addition, Guerrero et al. (2018) tested fermentation with 0.25 g/L *S. cerevisiae* cells and no mineral salt addition. PSSF (8 h) and SSF fermentation configurations yielded 4.8% and 4% (v/v) ethanol solutions from banana rachis and pseudo-stem, respectively, indicating 87% and 74% of maximal ethanol production (Guerrero et al. 2018). Moreover, by using banana pseudo-stem as a source for the bioethanol production by *S. cerevisiae* NCIM 3570, Ingale et al. (2014) investigated crucial aspects of the pretreatment of fungi with *A. ellipticus* and *A. fumigatus* for the saccharification of cellulosic substrate for the manufacture of ethanol. The fermentation of 4.1 g/L cellulosic hydrolysate resulted in a maximum yield of 84% and productivity of 0.024 g/h, yielding 17.1 g/L of ethanol after 72 h (Ingale et al. 2014).

Sherpa et al. (2022) researched sugarcane top bioethanol. Separate fermentation produces 3.76% (v/v) ethanol in 48 h, while SSF produces 5.69% (v/v) ethanol in 30.67 h. To boost fermentation efficiency, a partially consolidated bioprocessing method was developed. This process combines pretreatment and saccharification with laccase and cellulase enzyme mixes, followed by co-fermentation with *S. cerevisiae* and xylose-fermenting yeast AKBR 212. This method produced 7.57% ethanol in 24.30 h (Sherpa et al. 2022). The effects of popping pretreatment on saccharification and fermentation for individual and mixed biomass were investigated by Nguyen et al. in 2017 (coffee husk, cassava stem, and coconut coir) versus simultaneous saccharification and fermentation vs. separate hydrolysis and fermentation. Better than simultaneous fermentation and hydrolysis was simultaneous saccharification. Popping pretreatment enhanced both individual and mixed biomass saccharification efficiency (Nguyen et al. 2017). Wang et al. (2016) investigated the impact of pretreatment with diluted sulfuric acid, ultrasound-assisted alkali, and high pressure-assisted alkali on cotton stalk bioethanol production. Cotton stalk produced the highest reducing sugar yields (271.70 mg/dry biomass) and ethanol yields (45.53%) when high pressure was used to assist the alkali pretreatment. High pressure-assisted alkali pretreatment was proven effective for cotton stalk ethanol generation (Wang et al. 2016). The impact of hydrotrope as a pretreatment method on rice straw for bioethanol production is examined by Devendra and Pandey (2016). Rice straw was delignified using sodium cumene sulfonate and sodium xylene sulfonate as hydrotropes. While sodium cumene sulfonate hydrolysate could be fermented (with *Saccharomyces cerevisiae*) to produce 0.74% weight percent (w/v) of ethanol with a conversion efficiency of 73.5%, sodium xylene sulfonate hydrolysate could only produce 0.4% w/v ethanol with a conversion efficiency of 79.6% when standard glucose was used as the control (Devendra and Pandey 2016). With this, Yadav et al. (2011) attempted a study to produce bioethanol from rice straw by co-culturing of *S. cerevisiae* and *P. stipitis* in a way that allows both hexose and pentose sugars to be turned into ethanol at the same time. The concentration of ethanol was discovered to be 12 g/L by co-culturing OVB 11 (*Saccharomyces cerevisiae*) and *Pichia stipitis* NCIM 3498. The yield, volumetric ethanol productivity, and fermentation efficiency were each found to be 0.33 g/L h, 0.4 g/g, and 95%, respectively (Yadav et al. 2011). Moreover, Battista et al. (2016) recovered hydrogen and bioethanol from olive mill wastewater and olive pomace mixture using *Saccharomyces cerevisiae* anaerobic fermentation.

Pretreatments (ultrasonic pretreatment, basic pretreatment, and calcium carbonate addition). Basic pretreatment reduced polyphenol content in the reaction medium and led to cellulose hydrolysis, which increased ethanol concentration from 2.50 g/L to over 10.00 g/L, increasing the process 2.33-fold (Battista et al. 2016).

Ishola et al. (2013) developed simultaneous saccharification, filtration, and fermentation (SSFF) to produce lignocellulosic ethanol. The fermenting organism and the enzymes can be utilized under ideal conditions with SSFF, and the fermenting cultures can be recycled for several cultivations. At 68 and 72 h of fermentation, SSFF and simultaneous saccharification and fermentation (SSF) produce roughly the same quantity of ethanol, 84.2% and 85.3% of the theoretical output, respectively (Ishola et al. 2013). Raja Sathendra et al. (2019) used a hydrothermal method and a chemical method to remove lignin from palm wood that had already been treated. *Trichoderma reesei* MTCC 4876 was used to break down palm wood that had already been treated. After that, *Kluyveromyces marxianus* MTCC 1389 used palm wood hydrolysate to make bioethanol. Artificial neural network with a 5-2-1 topology was also used to find the best values for process parameters. At artificial neural network's best conditions of 45 °C temperature, 156 rpm agitation rate, pH 5, substrate concentration of 8% (v/v), and inoculum size of 3.2% (v/v), the experimental bioethanol yield was 22.90 g/L (Raja Sathendra et al. 2019). Kumar et al. (2022) evaluated humic acid on alkaline pretreatment of Kentucky bluegrass biomass to extract 70.1% lignin and biocomponents. 7.5% (w/v) pretreated biomass and 16 FPU/g cellulase produced 0.55 g/g reducing sugars. Yeast fermentation of biomass hydrolysate produced 76.6% (w/w) ethanol (Kumar et al. 2022).

In addition, Yang et al. (2019) use alkali-catalyzed hot liquid water pretreatment of bamboo to produce bioethanol using *Saccharomyces cerevisiae*. Maximum bioconversion was achieved using 0.5% NaOH aqueous at 170 °C, separate enzymatic hydrolysis, and fermentation, providing 4.8 g/L ethanol (Yang et al. 2019). In the presence of *Saccharomyces cerevisiae*, Ahmed et al. (2016) use a solar batch fermenter to produce bioethanol from common date palm waste (Ahmed et al. 2016). In order to improve pretreatment conditions and increase sugar recovery yield for both cotton straw and sunflower straw, Yildirim et al. (2021) used a central composite design of response surface methodology. By fermentation with *S. cerevisiae*, the maximum ethanol concentration, ethanol yield, and ethanol productivity for cotton straw were 7.21 g/L, 0.41 g/g, and 0.10 g/L h, respectively, at the end of the study. For sunflower straw, these values were 8.05 g/L, 0.40 g/g, and 0.11 g/L h (Yildirim et al. 2021).

Nazar et al. (2022) examined the ligninolytic activity of *Bacillus ligniniphilus* L1 laccase for bioethanol generation from rice straw. Bacterial laccase increased rice straw cellulase hydrolysis, yielding 15.8 mg/mL glucose, 21.8 mg/mL reducing sugar, and 22.3 mg/mL bioethanol (Nazar et al. 2022). Tiwari et al. (2022) used *Klebsiella oxytoca* ATCC 13182 to produce bioethanol from rice husk. After 48–72 h of incubation at pH 7, 36 °C, bioethanol production can reach 32.61 0.45 g/L. Acid and biological pretreatment (especially with *Aspergillus niger*) increased bioethanol production by 1.47 times (47.98 ± 1.25 g/L) (Tiwari et al. 2022). A camel rumen endo-1,4-xylanase was described and tested on agricultural wastes. Rajabi et al. (2022) examined the contribution of endo-1,4-xylanase on *B. subtilis* AP ethanol production in an SSF system. The enzyme increased ethanol production (p 0.001) to 7.3 g/L with a yield of 26.8% from wheat bran (Rajabi et al. 2022). Ziaei-Rad et al. (2021) use [TEA][HSO_4] to pretreat wheat straw. Three-hour pretreatment biomass yielded 43.1 g/L and 84.34% of the theoretical maximum yield after 48 h of fermentation. 10.76% of the biomass was untreated (Ziaei-Rad et al. 2021).

From Table 11.2, it was showed that *Saccharomyces cerevisiae* is mostly utilized for bioethanol production from a wide range of agricultural residues. However, more research is required to increase the yield of bioethanol through the utilization of various non-explored agricultural biomasses, easy and low-cost pretreatment methods, and new and modified microorganisms.

11.5 Green Energy Generation in India

Even though renewable energy is strongly emphasized globally and numerous initiatives aim to replace fossil fuel-based energy system, several countries still heavily depend on fossil fuels. Despite the fact that most of the countries are committed to shift to renewable power, the surging energy requirement reduces the transition from fossil fuel to non-fossil fuel energy resources. Although the share of renewables has improved to 28.3% of the global electricity in 2021, it is not up to the mark in agriculture, building, industry, and transport sector (Chaturvedi 2022; REN21 2022).

Amid these events, world policy makers have set new models, adapted novel norms, and proposed ambitious programs which are boosting the shift to renewable-based energy systems. All these landmark policies and programs are steadily gaining impetus as reflected by the escalating share of renewable energy in total energy demand globally. Figure 11.5 is global maps representing some of the leading countries in biofuel production, the USA and Brazil being the world's biggest biofuel producers (15,000 and 7500 million gallons, respectively). World map of biofuel productivity is changing radically due to integration between different energy sectors and availability of energy storage options. This has allowed countries such as Europe, Indonesia, Germany, India, and China to be clustered as top countries in biofuel production (Chaturvedi 2022; REN21 2022).

Despite being listed in the top countries in biofuel production, as depicted in Fig. 11.6, in India, significant share of energy is still extracted from fossil fuels, followed by hybrid energy systems; however, contribution of renewable energy in total final energy demand remains low.

To suffice the energy needs, India has adopted new business models to reduce draining out of fossil fuels and accelerated installation of power capacity and grid connect. India has launched green energy corridor project and renewable energy hybrid projects and introduced schemes such as PM KUSUM, Roof Top Solar (RTS) Programme, and Solar Parks to achieve the clean energy target. The country is working on enhancing domestic manufacturing of energy equipment, generating

Table 11.2 Various substrates used for fermentation for the production of bioethanol

Substrate used	Pretreatment	Microorganism used	Bioethanol yield	Reference
Corn stover Barley straw Corncob Wheat straw	White-rot fungus *Irpex lacteus*	*Pachysolen tannophilus* (CETC 1426)	13.5 ± 1.0 g/L after 94 h of SSF 10.8 ± 0.2 g/L after 94 h of SSF 11.5 ± 1.1 g/L after 94 h of SSF 12.5 ± 0.8 g/L after 94 h of SSF	García-Torreiro et al. (2016)
Sugarcane bagasse Sugarcane bark Corncob Cornstalk Cornhusk		*Saccharomyces cerevisiae*	6.72% 6.23% 6.17% 4.17% 3.45%	Braide et al. (2016)
Corn stover	NaOH (0.2 g/g)	*Saccharomyces cerevisiae* CRD51	70.6 g/L	Chen et al. (2021)
Corncob	0.5% (v/v) H_2SO_4	*Streptomyces* sp. T3-1	24.6 g/L after 2 days of fermentation	Hsu et al. (2011)
Corncob	H_2SO_4 + CH_3COOH	*Saccharomyces cerevisiae*	24.6 mg/mL (maximum bioethanol concentration)	Selvakumar et al. (2022)
Coconut husk fiber	5% NaOH	*Saccharomyces cerevisiae*	97%	Cabral et al. (2016)
Cotton stalk	Untreated NaOH LZ-K2	*Saccharomyces cerevisiae* YPH499	26.46% 41.28% 42.01%	Malik et al. (2021)
	Untreated NaOH LZ-K2	*Pachysolen tannophilus* 32691	21.83% 29.88% 27.26%	
	Untreated NaOH LZ-K2	*Saccharomyces cerevisiae* YPH499 and *Pachysolen tannophilus* 32691	38.50% 56.47% 54.73%	

Cotton straw Sunflower straw	Dilute acid	*Saccharomyces cerevisiae*	0.41 g/g 0.40 g/g	Yildirim et al. (2021)
Sugarcane tops	Laccase and cellulase enzymes	*Saccharomyces cerevisiae*	3.76% (v/v) in 48 h	Sherpa et al. (2022)
		Saccharomyces cerevisiae and xylose-fermenting yeast AKBR 212	7.57% (v/v) in 24.30 h	
Citrus peel waste	–	*Saccharomyces cerevisiae* KCTC 7906	90.2–93.1%	Choi et al. (2015)
Date palm waste	–	*Saccharomyces cerevisiae*	–	Ahmed et al. (2016)
Olive oil waste	Ultrasonic pretreatment, basic pretreatment, $CaCO_3$ addition	*Saccharomyces cerevisiae*	5.36 ± 1.23 g/L 9.01 ± 0.51 g/L 4.65 ± 0.30 g/L	Battista et al. (2016)
Wheat bran	Artificial seawater + 0.3% HCl	*Bacillus subtilis* AP	26.8% (7.3 g/L)	Rajabi et al. (2022)
Wheat straw	Ionic liquid, $[TEA][HSO_4]$	–	84.34% (43.1 g/L) after 48 h	Ziaei-Rad et al. (2021)
Rice straw	Sodium cumene sulfonate Sodium xylene sulfonate	*Saccharomyces cerevisiae*	0.74% w/v 0.4% w/v	Devendra and Pandey (2016)
Rice straw	–	Bacterial laccase from *Bacillus ligniniphilus* L1	22.3 mg/mL	Nazar et al. (2022)
Rice straw	H_2SO_4	Co-culture of *Saccharomyces cerevisiae* OVB 11 and *Pichia stipitis* NCIM 3498	96.01% after 48 h	Yadav et al. (2011)
Rice husk	Acid and biological pretreatment (*Aspergillus niger*)	*Klebsiella oxytoca* ATCC 13182	47.98 ± 1.25 g/L	Tiwari et al. (2022)
Cardoon *Cynara cardunculus*		Two strains of *Saccharomyces cerevisiae*: 1. NCYC 1119—SHF 2. PYCC 2613—SSF	1. ~18.5 g/L in SHF 2. ~18.7 g/L in SSF (Yield given)	Hsu et al. (2011)

(continued)

Table 11.2 (continued)

Substrate used	Pretreatment	Microorganism used	Bioethanol yield	Reference
Banana Lignocellulosic waste (Rachis, pseudo-stem)	Acid-catalyzed steam explosion	*Saccharomyces cerevisiae*	For rachis: 48.0 ± 0.1 g/L (in SHF at 120 h) 46.2 ± 3.5 g/L (in SSF at 72 h) 48.3 ± 1.2 g/L (in PSSF (8 h)) at 72 h) 46.1 ± 1.4 (in PSSF (12 h)) at 72 h) For pseudo-stem: 42.0 ± 0.9 g/L (in SHF at 120 h) 40.1 ± 2.2 g/L (in SSF at 72 h) 41.8 ± 0.9 g/L (in PSSF (8 h) at 80 h)	Guerrero et al. (2018)
Banana pseudo-stem	Milling + 1 N NaOH	*S. cerevisiae* NCIM 3570	84% in SSF	Ingale et al. (2014)
Spruce chips	–	*Saccharomyces cerevisiae*	84.2% in SSFF 85.3% in SSF	Ishola et al. (2013)
Mixed biomass (coffee husk, cassava stem, coconut coir)	Popping	*Saccharomyces cerevisiae* KCTC 7906	77.3% in SSF (pretreated) 21.7% in SSF (non-pretreated)	Nguyen et al. (2017)
Palm wood	3% sulfuric acid, 3% nitric acid, and 3% phosphoric acid separately	*Kluyveromyces marxianus* MTCC 1389	22.90 g/L at 84 h of fermentation	Raja Sathendra et al. (2019)
Kentucky bluegrass	Alkaline pretreatment	Yeast	76.6% (w/w)	Kumar et al. (2022)

Cotton stalk	Raw	*Saccharomyces cerevisiae*	29.63%	Wang et al. (2016)
	Dilute H_2SO_4		26.27%	
	Ultrasound-assisted alkali		32.57%	
	High pressure-assisted alkali		45.53%	
Bamboo	NaOH	*Saccharomyces cerevisiae*	4.84 g/L	Yang et al. (2019)

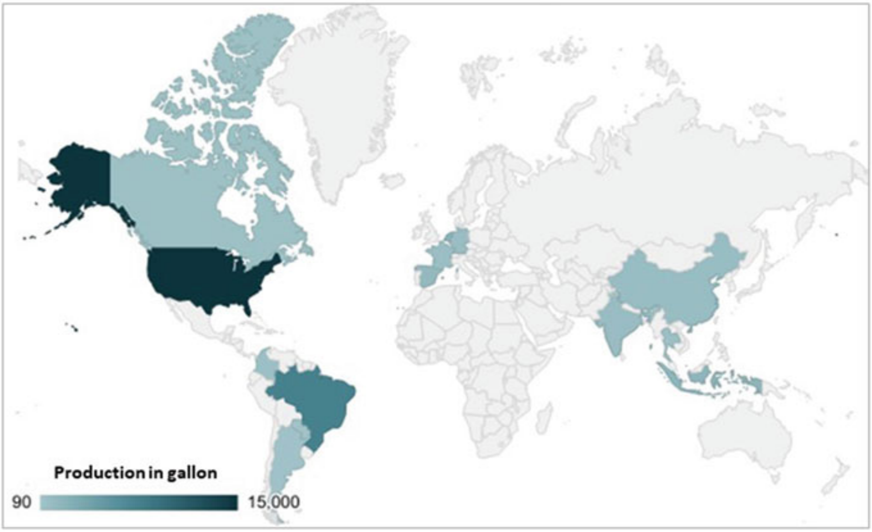


Fig. 11.5 Global map showing top leading countries in biofuel production (billion gallons) (Statista 2022)

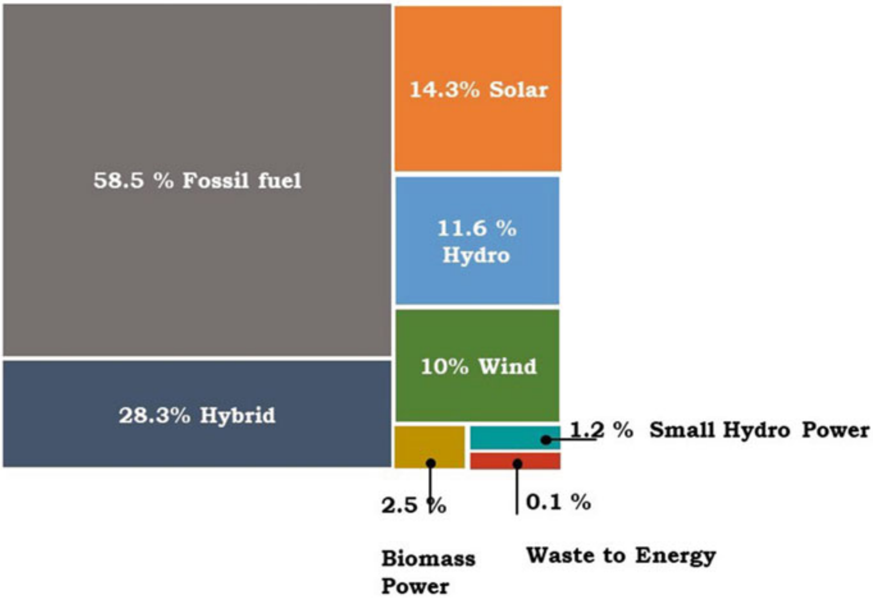


Fig. 11.6 Fossil fuel and non-fossil fuel generation capacity installed in India (CEA 2022)

skilled energy labor, and giving attractive incentives to provide clean energy. The Government of India aims to develop at least one city in each state as solar city and has set a target of 175 GW of renewable energy capacity by the year 2022, out of which 114 GW is already achieved till June 2022. India is well on its way to achieve about 40% cumulative electric power installed capacity from non-fossil fuel-based energy resources by 2030 (Chaturvedi 2022; REN21 2022).

11.6 Future Prospects

The production of advanced bioethanol from lignocellulosic biomass has undergone extensive research and development over the past few decades, and as a result, this biofuel is now an essential part of meeting the expected future demand for bioethanol. Cellulosic ethanol still needs to be fully commercialized, though, so higher production yields and lower costs are still needed. To maximize the use of lignocellulosic biomass sources and increase the sustainability of the conversion process, innovative and sophisticated technologies are required at each stage of the process (Duque et al. 2021). Traditional ethanol feedstocks including molasses, sugarcane juice, corn, etc. have societal and economic obstacles (Kumar et al. 2009). Genome engineering and cell wall modification are currently cutting-edge techniques for feedstock modification. There is currently no industrially viable pretreatment method for the removal of lignin that is both affordable and effective enough to meet the demand for bioethanol globally (Lamichhane et al. 2021). One microorganism modified with genes or microbial consortia reduces costs, but another problem is microbe survival and co-utilization of pentose and hexose carbohydrates. Now, researchers are developing modified strains that can break down polysaccharides and utilize carbohydrates even when hazardous substances are present (Devi et al. 2022).

Pretreatment technology provides a practical way to separate the main lignocellulose constituents and reveal the cellulose that is present (Zhao et al. 2022). The best bioethanol can be made from feedstock if the feedstock is pretreated first. There are different kinds of pretreatment. They can be either physical or chemical, and their strength can vary. The best type of pretreatment is one that doesn’t cost much and makes a lot of bioethanol (Oyegoke et al. 2022).

It is still necessary to create more sophisticated pretreatment technologies that can regulate mechanisms, adjust to the special characteristics of various types of biomass, and keep costs low (Mosier et al. 2005). It is crucial to lose as little sugar as possible, increase the concentration of solids as much as possible, and keep the price of reactors and other equipment low in order to further reduce the cost of the pretreatment step in the conversion of biomass into ethanol (Alvira et al. 2010). Investigating technologies that enable pretreatment and saccharification to occur simultaneously in the same vessel will result in cost savings, energy reductions, and process simplification (Li et al. 2022).

The low conversion efficiency of the technique has prevented widespread commercialization even though the proof of concept has already been established. It is possible to use a native single bacterium, a genetically altered organism, or a consortium (Singhania et al. 2022). So, the economic, ecological, and environmental effects of making and using bioethanol are something that should be looked at when trying to find a balance between the quality and harmony of the natural environment, the quality of life, and economic growth (Piwowar and Dzikuć 2022).

11.7 Conclusion

In the recent past, increased civilization and industrialization has led to the attenuation of fossil fuels and natural substances, thereby causing global warming. In this situation, there is an urgent need to explore alternate fuels. There are various lignocellulose materials listed in this chapter which can be valorized into not only first-generation and second-generation bioethanol but also the third-generation bioethanol produced in fair amount using algae. The chapter has made an attempt to summarize different technologies involved in the production of bioethanol. Some of the steps discussed here include pretreatment and hydrolysis methods which allow to obtain better yield or contribute toward generating almost negligible waste. Further, vast diversity of microbes available with different characteristics can be used as per need and can also be combined with each other for better bioethanol production. There are yet several areas of research in this field which are being explored all around the world to find the most efficient and effective way of producing bioethanol contribution to global energy demand. Cleaner and greener production of bioenergy is important for sustainable development, and this substitution will surely be an important factor in increasing the health of our Mother Nature.

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A Novel Mango (*Mangifera indica* L.) Seed Waste-Based Biorefinery Scheme

12

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Abbreviations

AA	Antioxidant activity
AP	Alkaline pretreatment
ASCN	Acetic acid nanocellulose
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibrils
Crl	Crystallinity index
EH	Enzymatic hydrolysis
FCNP	Spherical formic acid nanocellulose
HPLC	High-performance liquid chromatography
HSCN	Homogenized acetic acid nanocellulose
HSHO	High shear homogenization-assisted organosolv
MCC	Microcrystalline cellulose
MCDA	Multi-criteria decision approach
MSH	Mango seed husks
MSK	Mango seed kernels
Mw	Molecular weight
OE	Organosolv extraction
SCNP	Sulfuric acid nanocellulose
TPC	Total polyphenol content
XGN	Xyloglucan
XLN	Xylan

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12.1 Introduction

Globally, mango processing plants generate over 25 million tons per annum of mango waste consisting mainly of seeds and peels. The mango seed waste amounts to over 1 million tons per annum (Torres-León et al. 2016; Anta et al. 2020a). However, the mango seeds (35–55% of the mango fruit) (Kittiphoom 2012) have low economic value applications with uses limited to animal feed; otherwise, they are dumped in landfills (Anta et al. 2018, 2020b). There is an opportunity to exploit the mango seed based on its composition, for higher economic returns. The seed's outermost layer, the husk (MSH), comprises mainly cellulose, hemicellulose, and lignin, whereas the inside stone (the kernel (MSK)) is rich in polysaccharides mainly starch and hemicelluloses and some organic acids, proteins, polyphenolic (flavonoids, gallates, ellagic acid, mangiferin, gallotannins, etc.) and cellulose (Kittiphoom 2012; Cordeiro et al. 2014a; Hamaio et al. 2016; Torres-León et al. 2017).

The biorefining of the MSK is often focused on the extraction of single products such as polyphenols (unbound form), starch, proteins, and fats and oils while leaving out hemicellulose, cellulose, and lignin (Sogi et al. 2013; Torres-León et al. 2017). Similar to the MSK, the biorefining of the MSH despite being rich in lignin (up to 21.0%), hemicellulose, and cellulose (up to 55%) (Henrique et al. 2013; Cordeiro et al. 2014a; Andrade et al. 2016) is limited to the production of products such as nanocellulose, bioethanol, or activated carbon (Andrade et al. 2016; Ganeshan et al. 2016; Dzigbor and Chimphango 2019) as single products. However, with careful selection of process conditions and strategic optimization, it is possible to recover a combination of these components from the MSH, leading to the full utilization of the mango seed waste, which would expand the product spectrum. The increase in the number of products obtained from the mango seed waste has numerous techno-economic and ecological gains (FitzPatrick et al. 2010).

Nanocellulose is an emerging high-value product that can be produced from mango waste. Nanocellulose has a unique combination of morphological, mechanical, and thermal properties (Habibi 2014; Shatkin et al. 2014; Rajan et al. 2020; Wang et al. 2020; Ahankari et al. 2021), which render it suitable for many novel applications including as a food packaging material. The CNC has other numerous nonfood applications such as reinforcement agents and nanofillers in biocomposites (Li et al. 2015; Du et al. 2017; Svärd et al. 2017). Notably, the annual growth of the nanocellulose global market is increasing at compounded rate of 21.3% with an estimated increase of $486 million by 2023 (Markets and Markets 2020). Consequently, there is a growing number of industries for the commercial production of nanocellulose in regions such as North America and Europe producing cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) (Miller 2015; Shatkin et al. 2015).

The commercial CNC currently on the market is produced from wood. However, wood has many competing uses including papermaking and construction (Delepierre et al. 2021). However, second-generation (2G)-agro-industrial wastes are emerging as suitable alternatives to wood because they are characterized by reduced lignin content and mechanical fibrillation is easily achieved, thus, reducing CNC production energy requirements (Anwar et al. 2014; Garcia et al. 2017; Rajinipriya et al. 2018). Feedstocks such as microcrystalline cellulose (MCC) that are rich in highly crystalline cellulose (cellulose content >65% and crystallinity >55%) are considered the most suitable feedstock for producing CNC. Notably, the MCC can easily be produced from the MSH upon the removal of hemicellulose, lignin, and polyphenols, which are amorphous compounds (Silvério et al. 2013; Hamid et al. 2016; Oun and Rhim 2016).

The common processes for generating cellulose-rich material from biomass require pretreatments with high selectivity for the amorphous components to obtain a cellulose-rich material (Nuruddin et al. 2011; Henrique et al. 2013; Li et al. 2015). In the conventional approaches, the amorphous components are disposed in downstream processes without any recovery (Henrique et al. 2013; Li et al. 2015) despite the economic value they possess. The diversified properties of the hemicellulose, starch, polyphenols, and lignin warrant their recovery in the downstream processes for high-value applications. Therefore, there is a need for selection of appropriate pretreatment/fractionation processes that can form part of an integrated biorefinery to allow the recovery of these compounds in high yields and usable forms. To improve the efficiency of the process, it is inevitable to strategically optimize the sequential steps for the selective extraction of the individual products in high yields. Such multiproduct biorefineries could potentially improve the economic returns of the mango processing plants (Egüés et al. 2013; Svärd et al. 2017) with environmental and social benefits from reduced waste disposal and job creation, respectively, from the additional value chains.

The mango seeds have two types of hemicelluloses, which are predominantly xylans (XLN) and xyloglucans (XGN) (Tharanathan et al. 2006; Siacor et al. 2021). Therefore, extraction processes can be tuned to obtain hemicellulose extracts with varying ratios of the XGN and XLN to suit requirements for different end uses such as the formulation of barrier films, active packaging films, and coatings (Schnell et al. 2017; Svärd et al. 2017). For example, hemicellulose extracts with a high XGN content are suited to produce self-supporting smooth films compared to having a high XLN content (Bello and Chimphango 2022). However, a very high XGN content reduces hemicellulose dissolution leading to brittleness in films, whereas a very high XLN increases flexibility and the films hydrophilicity (Bello and Chimphango 2022). Therefore, the hemicelluloses can be extracted to have a suitable composition of XGN and XLN for use in producing films that are smooth, hydrophobic, and flexible. Furthermore, the antioxidant activity emanating from the polyphenols (bound or unbound) can be used in food applications for their health benefits and in nonfood applications to slow down oxidation processes (Dorta et al. 2012a; Dorta et al. 2012b; Quirós-Sauceda et al. 2014).

The starch, which is the predominant component of the MSK, constitutes an alternative feedstock for energy production and for other advanced uses such as biocomposite formulations, after some modifications to reduce the inherent hydrophilicity (Silva et al. 2019; Siacor et al. 2021). Additionally, the lignin and the cellulose components, which are present in high amounts in the MSH, can be recovered for various applications. For example, the phenolic groups present in the lignin fraction make lignin a diverse feedstock for use in the preparation products such as phenol-formaldehyde resins (El Mansouri and Salvadó 2006; Egüés et al. 2013; Svärd et al. 2017), whereas the cellulosic fraction can be used as a matrix in biocomposites formulations or can be subjected to controlled hydrolysis to produce cellulose nanoparticles such as the cellulose nanocrystals (CNC). Therefore, the economic exploits of the mango seed are inevitable but would require developing methods that can selectively extract the polyphenols, starch, hemicellulose, lignin, and cellulose from the mango seed to deliver multiproduct streams in high yields and purity than just single-product streams with compromised quality. When such methods are integrated into the fruit processing plants, they would constitute enablers for developing innovative waste management strategies through the establishment of sustainable waste-based biorefineries, thus making the mango processing industries more robust and resilient to global market fluctuations (FitzPatrick et al. 2010).

The challenges of recovering multiple products in integrated biorefineries include the inhibitory effects and the overlapping optimal extraction conditions for some of the components, which affect the efficiency and selectivity of the extraction processes (Bharimalla et al. 2015). For example, the viscosity resulting from the high starch contents of the MSK (≈32–65%) (Sonthalia and Sikdar 2015; Saeaurng and Kuakpetoon 2018; Tesfaye et al. 2018) could be a limiting factor during the solid-liquid separation (Liu et al. 2016b) of co-extracts due to mass transfer problems. Similarly, the complexes that can form between the polyphenols (both unbound and bound) and proteins can hinder starch extraction (Daiber 1975; Kock et al. 1985) whereas the cross-linkages between the lignin and the carbohydrates (hemicellulose and cellulose) would limit chemical and enzymatic hydrolysis and negatively affect the quality of the lignin and the carbohydrates. Therefore, highly selective pretreatment/fractionation methods for the products of interest are needed (Huijgen et al. 2012) to improve the performance of integrated biorefineries.

There are various pretreatment methods for lignocellulosic materials that have been studied (Guragain et al. 2016; Minjares-Fuentes et al. 2016). However, most of the methods are not cost-effective. Therefore, there have been continued efforts to reduce production costs by finding ways of increasing the product yields and reducing resource consumption, e.g., energy and material consumptions (Matsakas et al. 2018). For example, in CNC production, most of the pretreatments have been directed toward obtaining highly crystalline cellulose-rich material as a starting feedstock. The conventional Kraft and bleaching pretreatment processes have been the most common routes for obtaining such materials but at the expense of recovering the hemicellulose, lignin, and other compounds as valuable components because of the degradation they suffer under these conditions. Consequently, compounds such as lignin and hemicellulose present in the black liquor are burned for fuel (Nuruddin et al. 2011; Henrique et al. 2013; Li et al. 2015). Alternatively, lignocellulosic materials are pretreated using alkaline-, acid-, enzymatic-, thermo-chemical-, and ionic liquid-based methods. The choice of the methods is dependent on the type of feedstock and the desired product attributes for the end-use applications (Brienzo et al. 2009; Egüés et al. 2013; Rabetafika et al. 2014; Bello and Chimphango 2021). The costs associated with the different pretreatment and processing options and their effectiveness in pretreating the lignocellulosic materials (Deepa et al. 2011; Zhou et al. 2018) justify the need for optimization for increased economic returns through expansion of the MSK and MSH product spectrum (Yoo 2012; Dorta et al. 2013; Rabetafika et al. 2014; Ceaser 2019; Matsakas et al. 2019).

In establishing integrated biorefineries, it is logical to first extract components such as polyphenols, starch, and hemicellulose that are prone to degradation under severe conditions (Akowuah and Zhari 2010; Dorta et al. 2012b; Galili and Hovav 2014; Werner et al. 2014; Mehmood et al. 2018; Mugwagwa and Chimphango 2019). However, such severe conditions are required for delignification to facilitate enzymatic and chemical conversions of the cellulose into CNC (Guo et al. 2013; Castro et al. 2017).

Starch is a water- and alkali-extractable compound from biomass. Alternatively, specific enzymes can be used to selectively extract the starch (Correia et al. 2012; Koegelenberg and Chimphango 2017; Ceaser 2019). The starch yields from water extraction processes are comparatively low (≈59%) (Cordeiro et al. 2014a; Sonthalia and Sikdar 2015; Silva et al. 2019) compared to chemical or enzymatic methods. On the other hand, the application of the chemical methods such as alkaline methods can lead to the co-extraction of the hemicellulose and lignin, which reduces their yields and quality, thus, compromising the performance of the biorefinery. Highly specific enzymes can be selective for the starch, thus, reducing the risk of co-extraction or degradation of the other components (Zheng et al. 2020; Peña et al. 2012). Up to 100% selective starch removal has been achieved in other studies (Ceaser 2019). Thus, the enzymatic starch extraction from MSK is the preferred method to acidic-, alkaline-, and water-based methods for the integrated biorefinery.

The pretreatment or fractionation processes that are alkaline—or organosolv—are considered effective for the fractionation of agro-residues into high-value products (Chimphango et al. 2012; Makhetha 2016; Nitsos et al. 2016). For instance, the alkaline pretreatments (AP) using calcium, sodium, and potassium hydroxides, mainly in their mild form, are considered the most effective and selective methods for the extraction of hemicellulose with reduced lignin contamination (Liu et al. 2016b). However, increasing the alkalinity in the AP process increases delignification, thus causing lignin contamination (Egüés et al. 2013; Seok et al. 2016; Svärd et al. 2017). The extraction of hemicellulose that is free of lignin contamination could be a desirable attribute for hemicellulose targeting the formulation of biocomposite films for food packaging. In addition, the solid residues from the mild alkaline process are rich in cellulose and lignin, a characteristic that allows them to be fractionated further in the downstream processes of the multi-step biorefinery process (Liu et al. 2016b).

Organosolv pretreatment (OP) that is based on a single organic solvents or mixture of organic solvent is selective for lignin removal. Therefore, the OP can operate at temperatures above or below 185 °C when uncatalyzed or catalyzed with a base or acid catalysts for delignification of the biomass (Zhao et al. 2009; Guragain et al. 2016). In some cases, delignification of the biomass is achieved using alcohol-based (ethanol, methanol) and polyols-based (ethylene glycol, glycerol, and xylitol) methods (Agbor et al. 2011; Zhou et al. 2018). However, the lignin produced by the OP at high temperatures is prone to recondensation, which causes structural and morphological heterogeneity and reduces reactivity during modification and application under acidic conditions. The severity of the OP conditions influences the degree to which the hemicellulose and cellulose degrade into their monomeric forms or derivatize into products such as furfural and 5-hydroxymethylfurfural, respectively, when acid is used as a catalyst under high temperatures (Huijgen et al. 2012). Alternative pretreatment methods (steam explosion, ultrasonication, and high-pressure homogenization) can be used to reduce the severity of the OP process conditions (e.g., <150 °C) resulting in improved selectivity for lignin extraction and recovery of the cellulose-rich solid residues (Iskalieva et al. 2012; Terán Hilares et al. 2018; Matsakas et al. 2019; Bello and Chimphango 2021). Therefore, a combination of organosolv and high shear homogenization (HSHO) is considered as an effective strategy for improving the quality of the lignin that can be extracted from the MSH. The low-pressure conditions combined with the shear effects increase the surface area for extraction more than achieved with other known physical processes (Zhao et al. 2013; Madison et al. 2017).

12.2 Development of Mango Waste-Based-Multiproduct Biorefinery Scheme

12.2.1 Selection of Products

The mango processing plant producing products, such as fruit juices, generates by-products in the form of peels and seeds (Fig. 12.1). The focus in this biorefinery is on the seed component because of the extended product range that can be obtained. The MSH's potential product combinations include cellulose, hemicellulose, and lignin. The product range can further be extended by the fractionation of the MSK into about six additional products including starch and non-starch carbohydrates (hemicellulose and cellulose), fatty acids, proteins, and polyphenols (Kittiphoom 2012; Cordeiro et al. 2014b; Hamaio et al. 2016; Torres-León et al. 2017). Since the conventional biorefining of the MSK neglects the lignocellulosic components (hemicellulose, cellulose, and lignin) in favor of the products such as starch, fat and oils, polyphenols (mainly the unbound), and proteins (Sogi et al. 2013; Torres-León et al. 2017), the proposed integrated biorefinery considers both lignocellulosic and non-lignocellulosic components as valuable products. However, the selection of the product combination to be fractionated is based on a multi-criteria decision approach (MCDA) that considers multiple factors such as the proportions of the component in the composition of the waste, market/potential market value, compatible extraction conditions to the subsequent product in the biorefinery scheme, and the novelty of the end-use applications. Therefore, selection of the products targeted for the described biorefinery scheme is based on the MCDA

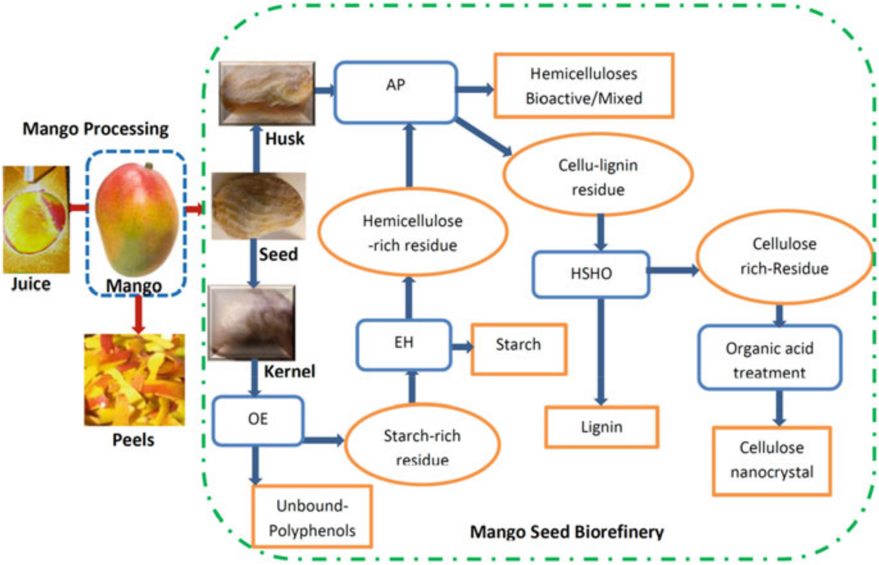

Fig. 12.1 Fractionation routes in a multi-step biorefinery for valorizing mango seed waste. Note: *EH* enzymatic hydrolysis; *OE* organosolv (ethanol/water mixture) process, *AP* alkaline process, *HSHO* high shear homogenization-assisted organosolv process

that includes several attributes for the unbound polyphenols, starch, bioactive hemicellulose, lignin, cellulose-rich solids, and nanocellulose (Table 12.1).

12.2.2 Fractionation Sequence

The sequential process consists of three main process steps for the recovery of unbound polyphenols, starch, and hemicelluloses bound with polyphenols (termed as bioactive hemicellulose), lignin, and cellulose-rich residues (Fig. 12.1).

12.2.2.1 Mango Seed Kernel Fractionation

Unbound Polyphenols

The mango seeds are first separated into MSH and MSK. The MSK is milled before the extraction of unbound polyphenol through solvent extraction (Fig. 12.1), which is chosen among other methods (Soxhlet and maceration) because of its ease of operation and recovery efficiency of products from various feedstocks (Dorta et al. 2012b; Lim et al. 2019) and the potential for recycling.

Notably, mixed organic solvents are often preferred for the extraction of unbound polyphenolic compounds from MSK to pure organic solvents. Therefore, in the described sequential process, ethanol/water mixtures are chosen as suitable extraction solvents to comply with good food manufacturing practices (Dorta et al. 2012b,

Table 12.1 Multi-criteria decision approach for selecting bioproducts and treatment conditions in integrated mango seed waste biorefinery

Product	Product selection criteria	Treatment/ fractionation method	Treatment process selection criteria
Polyphenolic compounds	Content in feedstock, multiple end uses and commercial value	Organosolv extraction	Solvent recovery; safe for food manufacturing
Mango kernel starch	Content in feedstock and multiple end uses	Enzymatic treatment	Substrate for further valorization
Bioactive hemicellulose	Content in feedstock, the potential for novel end-use applications and market value	Alkaline pretreatment	Suitable for formulating active food packaging; minimizes hemicellulose degradation
Cellu-lignin solid residue	Feedstock chemical composition	Alkaline pretreatment	Surface area and chemical and enzyme accessibility
Mixed hemicellulose	Content in feedstock, novel end-use applications and commercial value	Alkaline pretreatment	Custom functionalization thermal stability in biocomposite
Lignin	Content in feedstock, novel end-use applications and market value	High shear homogenization-assisted organosolv pretreatment	Low-temperature requirement
Cellulose-rich solid residue	Feedstock composition novel end-use applications and commercial value	High shear homogenization-assisted organosolv pretreatment	Increased cellulose recovery, raw material to produce cellulose nanoparticles
Nanocellulose	Unique mechanical properties, diverse applicability, and market value	Organic acid-based hydrolysis (uncatalyzed)	Thermal stability, nanocellulose, benefits from synergetic effect with AP-HSHO, hydrophobicity

2014; Lim et al. 2019). The commonly used extraction conditions for MSK unbound polyphenol include ethanol concentration of 50% v/v (Dorta et al. 2013; Torres-León et al. 2017; Lim et al. 2019) and temperatures of up to 100 °C with reaction times reaching 12 h (Akowuah and Zhari 2010; Dorta et al. 2012b; Galili and Hovav 2014; Abdel-Aty et al. 2018; Lim et al. 2019; Mugwagwa and Chimphango 2019). However, polyphenolic compounds are prone to degradation at temperatures above 70 °C, thereby increasing the risk of losing their bioactivity (Lim et al. 2019).

One of the objectives for the described biorefinery is to selectively extract unbound polyphenols while preserving the other MSK components, which are extracted in the subsequent stages. However, there is a trade-off on the extraction conditions for the unbound polyphenols if the co-extraction with the other components is to be minimized. Therefore, the selection of the process conditions for extracting polyphenolic compounds takes into consideration the conditions required for effective starch extraction.

It is well-known that the solubility of MSK starch in water and in organic solvent at low temperatures is quite limited (Sonthalia and Sikdar 2015; Saeaurng and Kuakpetoon 2018; Tesfaye et al. 2018) and that the starch gelatinizes at temperatures between 78 and 82 °C (Sonthalia and Sikdar 2015; Saeaurng and Kuakpetoon 2018; Tesfaye et al. 2018), which is also the temperature range at which co-extraction and degradation of polyphenols and hemicellulose can occur (Siacor and Taboada 2013; Saeaurng and Kuakpetoon 2018). Additionally, some hemicelluloses that are water-extractable, such as the XGN, can be extracted at such temperature ranges under alkaline or dilute acid conditions. Consequently, there is a risk of depolymerizing the hemicelluloses, which might not suit applications requiring the hemicelluloses to be in polymeric form. Furthermore, contamination and loss of functional properties can occur, therefore limiting their application as components of biocomposite films (vom Stein et al. 2011; Pius 2017).

The temperature under which the OE occurs should consider the thermal stability of the polyphenols. The unbound MSK polyphenols degrade during solvent extraction at temperatures between 75 and 100 °C (Akowuah and Zhari 2010; Lim et al. 2019; Mugwagwa and Chimphango 2019; Siacor et al. 2020). Therefore, temperatures during OE processing of MSK for polyphenol extraction should be limited to 60 °C. Such temperatures would in turn prevent gelatinization of the MSK starch (Saeaurng and Kuakpetoon 2018). Furthermore, there is an advantage for operating at such moderate temperatures because evaporation of the extraction medium is prevented, considering that the boiling point of ethanol is 78 °C. Evaporation of the reaction agents can have detrimental effects on the extraction yields and bioactivity of the extracted products (Galili and Hovav 2014). Another consideration is the duration of the treatment. It is critical to perform the pretreatment in the shortest time possible to minimize the degradation of the products. Therefore, the reaction time is limited to 1 h (Lim et al. 2019; Islam et al. 2021) which would prevent degradation and at the same time save production costs.

The selected conditions target the retention of lignin and cellulose in the solid residue because they are less severe to break down the hydrogen, ester, and ether bonds (Harmsen et al. 2010; Bello and Chimphango 2021). Therefore, the extraction conditions for the MSK (ethanol concentrations and temperatures) are optimized to find the best compromise conditions for obtaining high yield and quality for the selected bioproducts (Bello 2022). Thus, the yields and quality attributes of the OE extracts need to be constantly monitored for better performance. The optimization target is obtaining unbound polyphenols with high TPC and AA and retaining in the residue, the hemicellulose, starch, lignin, and cellulose in a non-degraded form. The residue forms a raw material for fractionation in the subsequent downstream stages.

Starch

The presence of the starch in the MSK limits the extraction of hemicellulose and lignin because of increased viscosity during the extraction process. High viscosity would result in mass transfer limitations. Therefore, in the multi-step process

(Fig. 12.1), destarching of the solid residue obtained from the OE of MSK is inevitable. The destarching would release the starch mainly as simple monomeric sugars. The destarching can be achieved by various methods including alkali, water, and enzymatic treatments (Correia et al. 2012; Koegelenberg and Chimphango 2017; Ceaser 2019). In extracting the starch using water, up to 59% starch removal can be achieved (Cordeiro et al. 2014b; Sonthalia and Sikdar 2015; Silva et al. 2019), which is lower than the destarching that can be achieved using alkaline methods (e.g., of up to 98%) (Correia et al. 2012). However, in the proposed biorefinery process, the water and alkali starch extractions are not sufficient to enhance the extraction of other products because less than 60% starch is removed (in the case of water extraction). In addition, there is a possibility of hemicellulose and lignin co-extractions due to the nonselective nature of these methods. Hence, starch is obtained at low yields, and with reduced quality. Consequently, the EH is rendered as a method of choice in the integrated biorefinery scheme for hydrolyzing the starch. The use of the enzymes is advantageous because enzymes are highly selective to the product and specific to the substrate. Hence, there is a possibility of achieving a complete removal of the starch from starch-rich feedstocks (Ceaser 2019). Therefore, in the integrated biorefinery, the OE solid residues are subjected to a two-stage enzymatic treatment (Fig. 12.1) using a combination of enzymes with complementary activities (Bello 2022). However, the high MSK starch content (≈40 wt%) may require repeating the EH several types for effective starch extraction. The efficiency and effectiveness of the EH process can be monitored by checking the residual starch in the solid residues and the monomeric sugars released in the hydrolysate. Furthermore, the quality of the resulting destarched MSK solid residue can be determined by measuring the content of the lignocellulosic components (Aguedo et al. 2012; Torres-León et al. 2019). The destarched MSK now becomes a feedstock for the downstream processes (Fig. 12.1).

Hemicellulose

The MSK is rich in bioactive substances such as polyphenols in either bound or unbound forms (Galili and Hovav 2014); the extraction conditions for the hemicellulose in the multi-step biorefinery process are chosen to preserve the bound polyphenols. Therefore, during the hemicellulose extraction step of the destarched MSK, the focus is on extracting the hemicellulose while ensuring a high cellu-lignin solid recovery (Liu et al. 2019; Zheng et al. 2020). Polyphenols bound to hemicellulose can be extractable in alkali solvents, which also favor the dissolution of the hemicellulose (Liu et al. 2019). Bound polyphenols have been extracted under alkaline conditions of up to 8 M NaOH for reactions that take place for as long as 4 h at temperatures as high as 60 °C (White et al. 2010; Acosta-estrada et al. 2014; Zheng et al. 2020). On the other hand, the extraction of hemicelluloses can take place under alkaline conditions (≤2 M) at temperatures as high as 80 °C for a period of ≤6 h (Bataillon et al. 1998; Matavire 2018). Therefore, the extraction of hemicellulose enriched with bound polyphenols in alkali solvents is possible by manipulating the extraction conditions (Galili and Hovav 2014).

Therefore, the objective of the AP stage in the biorefinery scheme is to recover the bioactive hemicellulose (hemicellulose bound with the polyphenols) from the destarched MSK (Fig. 12.1). The AP conditions enable a high cellulose and lignin content to be preserved in the cellu-lignin solid residues. Thus, the AP in the biorefinery is a compromise between the conditions described by Kim et al. (2006) and those of White et al. (2010), which provide alkaline conditions ranging from 1 M to 4 M NaOH and temperatures ranging from 25 to 90 °C for reactions times as low as 0.25 h and as high as16 h. These ranges can be manipulated to suit the extraction of hemicellulose with bound polyphenol. Under these AP conditions, it is important to set targets of yield compromises for the bioactive hemicellulose to achieve the desirable lignin and cellulose contents in the cellu-lignin solid residues. Bello (2022) showed that the destarched MSK can be treated in alkaline solutions of NaOH concentrations of 2 M or lower with 20 mM sodium borohydride ($NaBH_4$) added, at various temperatures of 90 °C or lower and reactions times of 4 h or lower for a predetermined solid loading (e.g., 10%wt). The optimum process conditions should give the highest yield, TPC, and AA of the extracted hemicellulose and the highest lignin and cellulose content retention in the cellu-lignin solid residues (Bello 2022).

12.2.2.2 Mango Seed Husk Fractionation

The MSH has a significant amount of cellulose, hemicellulose, and lignin (Bello and Chimphango 2022). Therefore, the sequential mild AP-HSHO targets the extraction of the hemicellulose-, lignin-, and cellulose-rich residues with reduced degradation at each stage.

Hemicellulose

The MSH is milled before subjected to the AP for the recovery of mixed hemicelluloses (XGN & XLN) in polymeric form while minimizing the degradation of the cellu-lignin solid residues (Fig. 12.1). The solid residues generated at this stage become raw material for the subsequent stage (Fig. 12.1). The factors considered in this step include temperature, NaOH concentration, and reaction time because of their effects on the hemicellulose extractability and quality attributes (purity, *Mw*, and thermal stability) (Vena et al. 2013a; Makhetha 2016). The recovered hemicellulose can be evaluated for its suitability as a component in self-supporting biocomposite film. The solid residues are analyzed for cellulose and lignin contents (Table 12.1). Therefore, acid treatments are avoided to prevent the degradation of the hemicellulose into monomeric sugars (Pius 2017). Extractions using water as an alternative method are avoided because of low yields (4–7%) (Svärd et al. 2017).

The AP is associated with high hemicellulose yields (up to 90%) and for the extraction of hemicelluloses with high *Mw* (Brienzo et al. 2009; Kochumalayil et al. 2010; Escalante et al. 2012). Such hemicellulose extract is considered desirable for superior functional properties of hemicellulose-based films formulated using the extract. In addition, there is selective cleavage of acetyl groups over the cleavage of glycosidic linkages when the process is performed under less severe AP conditions (Liu et al. 2016a; Pius 2017; Svärd et al. 2017; Shao et al. 2019).

The extraction of hemicellulose, in particular of XLN, under alkaline (0.5–2 M NaOH) conditions with temperatures above 40 °C has been reported (Hutterer et al. 2016). The XGN, on the other hand, is water-extractable at approximately 3 h (Kozioł et al. 2015; Bashir et al. 2016; Minjares-Fuentes et al. 2016) and alkaline-extractable when subjected to alkaline conditions ranging from 1 M NaOH to as high as 4 M NaOH with processing times as high as 16 h (subject to a particular type of biomass and XGN) (Renard et al. 1995; Busato et al. 2001; Kai and Petkowicz 2010). However, at a higher severity, The AP can result in co-extraction of the lignin and other phenolic compounds (Jiang et al. 2014; Garcia et al. 2017).

Purity is one of the desirable attributes for hemicellulose used in film development. However, the lignin and uronic acids present in the hemicellulose extract could also serve as natural plasticizers in speciality films (Egüés et al. 2013; Svärd et al. 2015). To take advantage of the lignin's plasticizing effect, hemicellulose extracts with less than 80% purity (contaminated mainly with lignin) have been used in the formulation of hemicellulose-based films (Egüés et al. 2013; Svärd et al. 2015; Aadil et al. 2016). However, despite the benefits that the lignin brings, its presence results in opaque films, which may not be desirable for certain applications. Therefore, the AP process conditions in the proposed biorefinery scheme are chosen for optimization to allow selective extraction of hemicellulose, thus limiting the lignin contamination to $\leq 20\%$.

The milder AP treatment conditions allows hemicellulose to be extracted in polymeric form (high molecular weight) and with high purity (minimum lignin content) (Egüés et al. 2013; Karp et al. 2014; Seok et al. 2016). The degree of delignification during this stage of the process depends on the AP severity and temperature conditions. High severity can result in excessive delignification and peeling reactions of the cellulose sugars (Karp et al. 2014). Generally, peeling is minimized if the process temperatures are <100 °C (Chimphango et al. 2012). Extractions performed with temperatures >150 °C and under severe alkaline (pH 14) result in cleavage of glycosidic linkages in hemicellulose (Krawczyk 2013). The addition of sodium borohydride ($NaBH_4$) to the reactants is done to prevent the peeling reactions (Chimphango et al. 2012). Based on Vena et al. (2013a) and Makhetha (2016) and through preliminary investigations, the AP optimal conditions can be found by varying the alkali concentrations from 1 to 2 M NaOH, temperatures from 40 °C to as high as 90 °C and process durations ranging from 2 h to as high as 4 h. Optimizing the AP enables identification of trade-offs for the extraction conditions that can give high yields of the hemicellulose extracts with reduced XGN (a low XGN/XLN ratio) content and residual lignin and uronic acids.

The hemicelluloses are after the AP recovered by ethanol precipitation (Fig. 12.1). The ethanol used in precipitating the hemicellulose is recovered for reuse, which has the potential to reduce the production costs. The resulting solid residue, rich in lignin (cellu-lignin), becomes the raw material for the subsequent stage that mainly targets the recovery of the lignin and cellulose (Fig. 12.1).

Lignin

The solid residues recovered after the extraction of the hemicellulose are subjected to HSHO to facilitate the extraction of lignin and produce solid residues rich in cellulose fibers (Fig. 12.1). The organosolv pretreatment/fractionation (OP) process generates lignin with increased purity and is less modified compared to technical lignins such as the Kraft and lignosulfonate lignins (Norgren and Edlund 2014). Therefore, the optimization of this step targets conditions that upgrade the lignin for applications such as resin production. The HSHO increases the crystallinity (Crl) of the solid residue, which favors CNC production in the next step (Fig. 12.1). In addition, the organic solvents and their aqueous mixtures are known to be effective lignin extraction agents and are easy to recover for reuse using simple distillation (Nitsos et al. 2016; Matsakas et al. 2019). However, performing the OP extractions at temperatures as high as160 °C in the presence of acid catalysts makes the lignin prone to recondensation, which has negative consequences on the lignin's quality and functionality (Agbor et al. 2011; Wildschut et al. 2013; Raita et al. 2017; Kim et al. 2018). Consequently, various rigorous modification processes are needed to increase the functionality of the extracted lignin.

Lignin yields and quality can be boosted by combining the OP with physicochemical/mechanical techniques such as steam explosion (Beisl et al. 2017; Matsakas et al. 2019). In this biorefinery scheme, the OP is combined with high shear homogenization (HSHO). In this combined process, the process parameters considered for optimizing the extraction conditions include ethanol concentration, temperature, and the duration required for homogenization (Bello and Chimphango 2021). The suitability of the lignin for manufacturing of phenol-formaldehyde resin production is determined from the degree of modification required to functionalize it and purity. The quality of the remaining solid residue is analyzed based on the cellulose content and crystallinity required for CNC production using non-catalyzed organic acids (Fig. 12.1).

Cellulose Nanocrystals

The most common method for CNC production is the conventional sulfuric acid-based treatment because it produces CNCs that disperse easily in water (Wang et al. 2020). However, the CNCs produced through the sulfuric acid route have reduced thermal stability making them not suitable for the formulation of biocomposites produced via simple melt blending (Braun and Dorgan 2009; Xie et al. 2019). Conversely, organic acids are used to produce CNC (Fig. 12.1) with increased thermal stability. However, organic acid-based CNC production method requires inorganic acid catalysts such as HCl and sulfuric acid at extended reaction times (Liu et al. 2016a; Du et al. 2017; Xie et al. 2019). Thus, mechanically assisted non-catalyzed organic acid-based treatments have many advantages over the sulfuric acid-based method.

High shear homogenization treatment following the AP treatment can improve the yield and quality of the CNC. Increasing the purity and surface area, and maintaining the Crl within the range of 50–90%, are achievable in the multi-step biorefinery process when AP is followed by the HSHO. The process enables the production of CNC using non-catalyzed organic acids from the cellulose-rich pulp. The CNC produced consists of cellulosic fibers with diameters within 10 μm (Bello 2022). The approach bypasses the need for pulping and bleaching of lignocellulosic biomass before sulfuric acid hydrolysis that is often practiced in conventional CNC production processes. Organic acids such as formic and acetic acids are preferred because of the potential to recycle and reuse them, thus saving on production costs. The organic acid process parameters (acid/pulp ratio and processing time) are optimized for high CNC yield, uniform morphology, ζ-potential, functional groups (formate or acetyl groups), and Crl among other attributes (Bello 2022).

12.2.3 Characterization of Mango Seed Waste and Products

Procedures and equipment used in determining the compositions of the mango seed waste and the fractionated products are described in Table 12.2.

Table 12.2 Evaluation of mango seed bioproducts

Component	Parameters and characterization method
Hemicellulose	• Sugar composition (high-performance liquid chromatography (HPLC)) • Linkages (nuclear magnetic resonance (NMR) spectroscopy, and gas chromatography-mass spectroscopy (GC-Ms)) • Molecular weight (Size exclusion chromatography (SEC)) • Functional groups and structural changes Fourier (transform infrared spectroscopy (FTIR)) • Thermal stability (thermogravimetric analyzer (TGA)) • Antioxidant activity (DPPH-radical scavenging and Folin-Ciocalteu method) • Molecular weight (Zetasizer with dynamic light scattering (DLS))
High purity lignin	• Chemical composition (HPLC) • Structural changes and purity (FTIR) • Molecular weight (SEC) • Elemental composition (X-ray photoelectron spectroscopy (XPS))
Cellulose-rich fibers	• Crystallinity (X-ray diffraction (XRD)) • Morphology and particle size (SEM and Zetasizer) • Structural changes (FTIR)
Cellulose nanoparticles	• Crystallinity (XRD) • Morphology and particle size (SEM + STEM) • Structural changes (FTIR) • Surface charge (Zeta-potential) and polydispersity, DLS, Zetasizer
Polyphenols	• Antioxidant activity (DPPH-radical scavenging) • Total polyphenol content (Folin-Ciocalteu method)
Hemicellulose-based films	• Thermal stability (TGA) • Mechanical properties (Instron machine)

12.3 Implementation of the Mango Waste Multi-step Integrated Biorefinery

12.3.1 Sequential Mango Seed Kernel Fractionation

There is a potential to recover over eight bioproducts from the mango waste. In the proposed integrated biorefinery (Fig. 12.1), polyphenols, starch, and hemicellulose containing bound polyphenols are recovered from MSK. The distribution of these components in MSK is reflected in Fig. 12.2 and their potential yields under the described optimum conditions are presented in Table 12.3. It is technically a challenge to achieve selective extraction of these components due to their varying and overlapping optimal extraction conditions. Therefore, product yields, molecular weight, and purity are often compromised. The sequence of product extraction in the proposed biorefinery scheme, thus, OE is performed first followed by EH and AP (Fig. 12.3) together with the strategic optimization of the extraction conditions at each of the fractionation stages, are the factors that enable selectivity for the selected bioproducts (polyphenols, starch, and hemicellulose, respectively) from the MSK while increasing the recovery of the solid cellu-lignin residues (Table 12.3).

Fig. 12.2 Composition of mango seed kernel

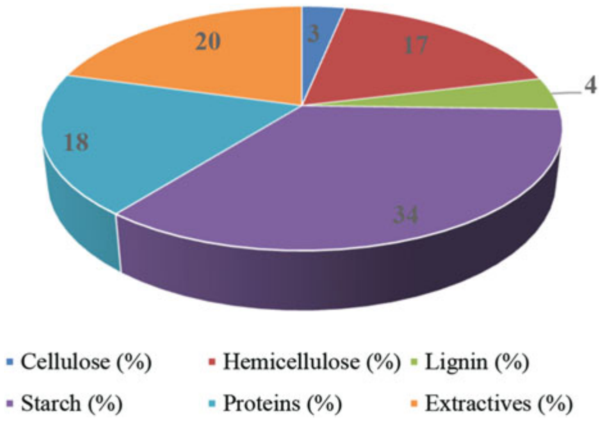

Table 12.3 Yield and properties of bioproducts from mango seed kernel

Product	Yield (%)	Purity (%)	TPC (mg GAE/g)	AA (%)	Molecular weight (g/mol)
Unbound polyphenols	–	–	>90	>80	–
Starch	>90	–			–
Bioactive hemicellulose	50–60	>75	30–40	>50	>10,000

Source: Bello (2022)
TPC total polyphenol content, *AA* antioxidant activity

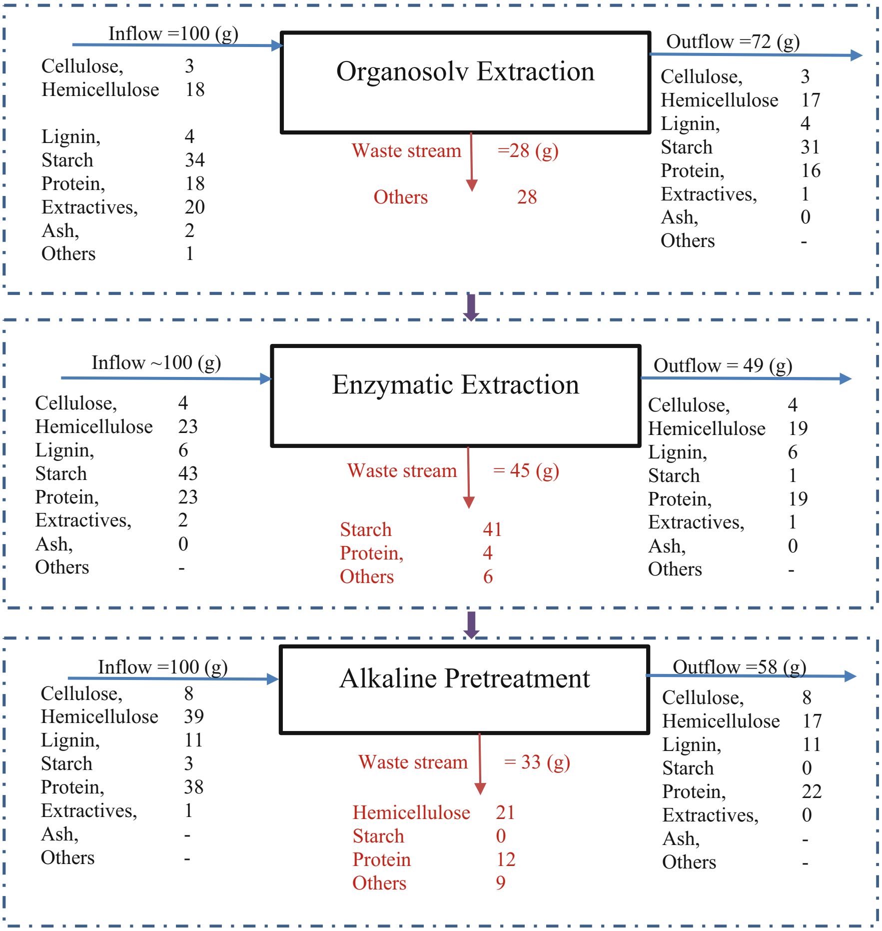

Fig. 12.3 Mango seed kernel material balance at each sequential stage. The values shown are in grams (g)

In the biorefinery scheme, the unbound polyphenols in the MSK are recovered first under optimized OE conditions that maximized TPC and AA of the polyphenols and the retention of the cellulose, lignin, hemicellulose, and starch contents in the solid residues (Table 12.4).

The OE optimized conditions (~65% v/v ethanol and 54 °C), TPC of over 90 mg GAE/g, and AA of over 80% of the extract are achievable (Bello 2022) (Table 12.3). The preservation of the other components such as the starch and non-starch carbohydrates and lignin in the solid residue is evident from the material balance (Fig. 12.3). The TPC and AA values obtained are comparable with literature values (Soong and Barlow 2004; Lim et al. 2019). The optimal ethanol concentrations in the literature are lower than the ones prescribed for the biorefinery scheme. The differences in the optimal ethanol concentrations are because the fractionation

Table 12.4 Component recovery rate at different stages of mango seed kernel sequential fractionation

Composition	Organosolv extraction (%)[a]	Enzymatic hydrolysis (%)[a]	Alkaline pretreatment (%)[a]
Cellulose	98	98	92
Hemicellulose[a]	94	84[a]	~100
Lignin[a]	98	~100[a]	96
Starch	92	~100	2
Protein	91	98	91
Extractives	7	34	8
Ash	9	14	–
Others	–	–	–
Total	72.23	94	92

[a] Based on solid and liquid streams

objectives are different. In the proposed biorefinery scheme, the objective is to optimize conditions for polyphenol extraction as well as for subsequent extraction of cellulose, lignin, hemicellulose, and starch from the remaining solid residues. In most studies, one or more objectives are pursued; however, these are for single products. Notably, the cost implications of using relatively higher ethanol concentration than in conventional processes should be weighed against the economic benefits to be obtained from the multiple products.

The removal of the unbound polyphenol increases the polysaccharide and lignin contents in the solid residues and at the same time makes it easily accessible to chemical and enzymatic attacks during the subsequent fractionation (Vena 2013). Thus, the OE stage is an important stage for improving the performance of the subsequent fractionation stages. Over 90% of the content of the remaining compounds are retained in the solid residues (Table 12.4). The degree of retention is greater than the values reported (≥20% losses) in the literature (Bello 2022). The solids were recovered from the OE when subjected to an enzymatic treatment, and over 95% removal of the starch is achieved while retaining over 80% of the other compounds, non-starch carbohydrates (cellulose and hemicellulose), and lignin in the destarched residue (Table 12.4). The enzymatic hydrolysis (EH) breaks down the starch into glucose that can be used as a feedstock for biofuel production or for lactic acid production. The importance of the EH in this multi-step integrated biorefinery is facilitating the release of hemicelluloses from the residues.

The degree of destarching projected in Fig. 12.3 is comparable to literature (Ceaser 2019). Clearly, the EH is selective for the starch; thus there is minimal degradation of the cellulose, hemicellulose, and lignin expected after the EH treatment (Table 12.4) attributed to the enzyme's substrate-specificity (Peña et al. 2012). However, the degree of retention of the hemicellulose is the least (Fig. 12.3), because hemicelluloses is extractable at the conditions where starch gelatinizes (Ceaser 2019). Previous studies have shown the co-extraction of hemicellulose such as XGN with starch in extraction systems that use water (Tharanathan et al. 2006; Bashir et al. 2016). Therefore, the EH would require simultaneous optimization of extraction conditions for starch and retention of the hemicellulose in the solid residue.

Subjecting the destarched MSK solids to AP (Fig. 12.1) targets the extraction of hemicellulose with antioxidant potential (hemicellulose containing bound polyphenols) (Kostalova et al. 2014). The methods for recovering bound polyphenols from MSK are not well established compared to the recovery of free polyphenols (Liu et al. 2019; Zheng et al. 2020). Therefore, the most usable form of bound polyphenols is through hemicellulose applications. The optimum AP conditions (1 M NaOH and temperature and time of <50 °C and 3 h, respectively) (Bello 2022), resulted in ≥50% hemicellulose dissolution from MSK (Table 12.2). The AP retained a cellu-lignin solid residue with >90% cellulose and lignin contents (Table 12.4).

The optimized AP conditions enable the recovery of bioactive hemicellulose of high purity, i.e., with minimal lignin contamination (Table 12.4). Furthermore, the hemicellulose exhibited *Mw* of about 110,000 g/mol with TPC content between 30 and 40 mg GAE/g (Table 12.3). The AA levels obtained are within the 48–80% range for bioactive hemicellulose (Ebringerová et al. 2008). The yield of the hemicellulose can be enhanced by using other techniques such as high-pressure reactors (Vena et al. 2013b; Pius 2017). Overall, the multi-step biorefinery process is an effective strategy for increasing the biorefinery product spectrum of the MSK and has the potential to diversify the product streams with a great efficiency as shown by the material balance (Fig. 12.3) and the degree of MSK component recovery (Table 12.4).

12.3.2 Fractionation of Mango Seed Husk

The conditions in the multi-step biorefining of the MSH involving a sequential AP step followed by HSHO pretreatment, are optimized to generate a solid residue with attributes suitable for nanocellulose production. The optimization of the biorefinery scheme is stepwise, with the optimization of the AP conditions targeting the fractionation of the MSH into hemicellulose extracts with varying XLN/XGN complexes while preserving lignin and cellulose-rich solids. The target is to extract ≥50% hemicellulose and retain ≥80% of the cellulose and lignin in the solids recovered after the initial step (Fig. 12.1). The choice of the products is justified by the MSH composition (Fig. 12.4). Therefore, the influence of each condition at each extraction step on the properties of targeted products, as well as the properties of the products obtained in the subsequent stages, needs to be predetermined.

The conditions at the AP stage ensure that the hemicelluloses extracted have potential application in the formulation of biocomposite films that are thermal stable. In addition, the lignin and the cellulose-rich solid residues extracted in the subsequent stage are suitable for producing phenol-formaldehyde resins, as well as cellulose nanocrystals, respectively (Fig. 12.1).

In the proposed setup, the optimized AP can have a recovery of ≥50% of the hemicellulose with different XGN and XLN compositions. The severity of the AP

Fig. 12.4 Mango seed husk composition

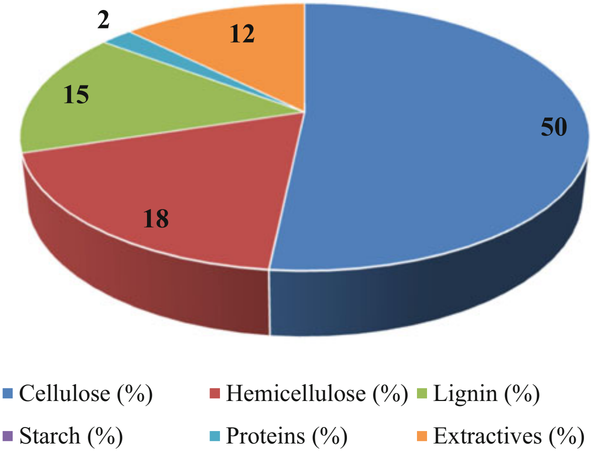

Table 12.5 Yields and properties of bioproducts recovered from mango seed husk in integrated biorefinery

Product	Yield (%)	Purity (%)	Molecular weight (g/mol)	$T_{\max}$ (°C)
Hemicellulose	46	79	70,189	330
Co-lignin	3	44		
HSHO lignin	70	96	3247	298
Non-assisted organosolv lignin	69	95	–	–

T_{max} maximum degradation temperature during thermal gravimetric analysis

conditions is mainly responsible for tuning the composition, e.g., XGN/XLN ratio and the functional properties (solubility and thermal stability) of the hemicellulose extracts (Bello and Chimphango 2022). Increasing the AP severity favors XLN dissolution over XGN dissolution (Bello and Chimphango 2022). The AP optimization strategy minimized XGN/XLN ratios and increased purity while increasing *Mw* and thermal stability. The hemicellulose extracts with a XGN/XLN ratio of 0.13 and lignin and uronic acids contamination of less than 16% are recovered when the AP conditions are optimized to less than 2 M NaOH at temperature of less than 90 °C for process durations of less than 4 h (Bello and Chimphango 2022). Biocomposites made with pure XLN are thermally labile and brittle (Bello and Chimphango 2022). Thermostability improvements require the addition of polyol-based plasticizers and polymers with high molecular weights (Egüés et al. 2013; Shankar et al. 2015; de Carvalho et al. 2019).

Hemicelluloses extracted at these conditions have the potential to be thermostable and exhibit molecular weights of up to 70,000 g/mol (Table 12.5), associated with XGN moiety presence (Simi and Abraham 2010; Rabetafika et al. 2014; Kozioł et al. 2015; Svärd et al. 2015). The *Mw* is higher than the *Mw* of pure xylan (27,235 g/mol) used in biocomposite film development (Bello and Chimphango 2022). A purity of

Table 12.6 Component recovery rate at different stages of mango seed husk sequential fractionation

Composition	Alkaline pretreatment (%)	AP-HSHO-treated MSH (%)
Cellulose	95	83
Hemicellulose	92**	83**
Lignin	124**	103[a]
Protein	84**	34
Extractives	86	90
Ash	48**	93**
Others	16	8
Total	95	85

AP alkaline pretreatment, *HSHO* homogenization-assisted organosolv pretreatment, *MSH* mango seed husk

[a] Based on solid and liquid streams; ** Determined based on the combination of content in the solid residue and in the solution

about 80% (Table 12.5) is achievable, which compares well with literature values (≥80% purity) (Ceaser 2019).

The optimized AP process conditions for the integrated biorefineries (Fig. 12.1) show the potential to innovate the downstream applications of the MSH bioproducts. In addition, the MSH offers a unique opportunity for establishing strategic biorefineries that would enhance the sustainable use of biomass waste materials while introducing advanced biomaterials for novel applications. Multi-step biorefining of any biomass material containing mixed hemicellulose in their compositions can be explored following a similar strategy as described, to diversify their applications. Recovering the hemicellulose that has been extracted can be a challenge. However, in the proposed biorefinery scheme, about 90% of the hemicellulose extracted is recovered (Table 12.6).

Notably, the extracted hemicellulose contains some lignin. Thus, lignin-hemicelluloses complexes (co-lignin) containing ≈20% lignin (Table 12.5) are formed and become a residue from the hemicellulose precipitation process. Similar co-lignin recovery levels have been reported in the literature (Deepa et al. 2011). The lignin-hemicelluloses complexes are coproducts of the biorefinery scheme with unique properties for novel applications.

The partial removal of the lignin at the AP stage is advantageous for reducing recalcitrance which inhibits the enzyme and chemical reactions during fractionation. Thus, there is a potential to reduce the severity of the process conditions in the subsequent stages (Varavadekar et al. 2009). MSH processed at the optimized AP conditions retains 95% of the cellulose and lignin in the solid residues (Table 12.5). The reduced degradation is confirmed by the material balance (Fig. 12.5). There is a minimal change between the input and output streams (about 7% and 5% for cellulose and lignin, respectively). The material balance in Fig. 12.5 shows that about 44% of the input hemicelluloses is retained, which suggests AP's selectivity for hemicelluloses.

The MSH solid residues' recovered post-AP treatment is treated with the novel HSHO for the extraction of the lignin and recovery of the cellulose-rich solids with

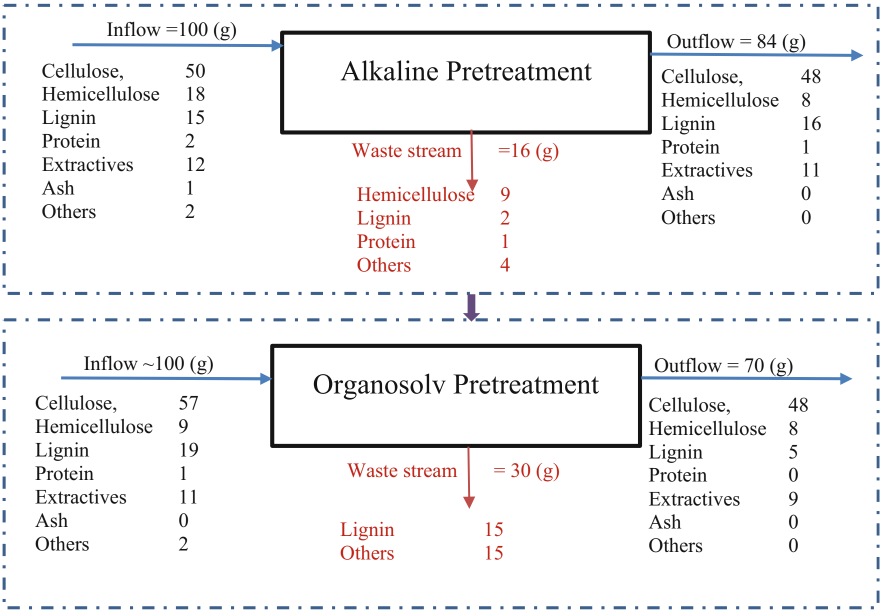

Fig. 12.5 Mango seed husk material balance at each sequential stage; values shown are in grams (g)

attributes suitable for CNC production. The conditions for performing the HSHO process such as the concentration of the ethanol used, the operating temperature, and the duration for the homogenization are optimized for selective lignin dissolution while retaining cellulose in a state that is suitable for CNC production (solid residue recovery of ≥80%, cellulose content ≥70% and Crl ≥55%) (Bello 2022). The objectives of optimizing the HSHO step are twofold, increasing the lignin yields and purity and reducing hemicellulose content (retaining ≤10%) in the solid residues, therefore increasing the crystallinity of the solid residue. The effectiveness of the HSHO in fragmenting and dissolving the lignin depends on the ethanol concentration, temperature, and duration of high shear homogenization (Bello and Chimphango 2021). The HSHO-optimized conditions, which are a concentration of ethanol of 60%, homogenization duration of 15 min at a temperature setting of 48 °C, can lead to the dissolution of >70% of lignin with purity levels as high as 96% (Bello and Chimphango 2021), which is comparable to the lignin purity (93%) obtained in other studies (Nitsos et al. 2016) and is deemed suitable for phenol-formaldehyde resin production compared to other technical lignins because of its reduced sulfur and ash contents (Zhang 2008; Espinoza-Acosta et al. 2014; Chio et al. 2019).

The cellulose-rich solid residues obtained at the optimal HSHO conditions contain a cellulose content >77%. In addition, the lignin and hemicellulose contents in the residue reduce to below 12% (Bello and Chimphango 2021). The low hemicellulose and lignin contents retained in the solid residue obtainable from

HSHO (Fig. 12.5) are within acceptable levels of 0.5–26% and 0.1–16% for CNC production (de Morais Teixeira et al. 2010; Sánchez et al. 2016; Wang et al. 2020). The recovery of the solid residue is higher than recoveries (69–72%) reported in the literature (Nitsos et al. 2016; Matsakas et al. 2019), attributed to the severe temperatures (183–200 °C) used in the cited studies. At the end of the sequential AP and HSHO processes, the MSH cellulose content falls within the 60–92% range reported for CNP production (de Morais Teixeira et al. 2010; Santos et al. 2013; Li et al. 2015; Sánchez et al. 2016).

The integration of homogenization process with the organosolv treatment has the potential to reduce temperature and chemical requirements for lignin extraction while increasing the yields and purity. The non-assisted organosolv treatments are often operated at temperatures as high as 200 °C and ethanol concentrations of about 65%. Despite these severe conditions, the yield is far much less (43%) than the yield that can be obtained through the HSHO (Table 12.6). Therefore, the synergetic effects between the mechanical and organosolv treatments make the proposed biorefinery scheme more effective than the conventional processes. Furthermore, the pre-extraction of the hemicellulose at the AP stage conditions favored the MSH for selective and effective lignin extraction by reducing the biomass resistance to solvent penetration for fragmentation, thus increasing the dissolution of the lignin. Therefore, the HSHO process can enhance valorization of mango seed waste into products of high economic value.

The cellulose-rich solid residue's CrI increases at the AP stage (44% (untreated) to 58% (AP)) (Bello 2022). The CrI for the residues at this stage is higher than the minimum CrI (57%) recommended for CNC production (Oun and Rhim 2016). The CrI (59%) is also maintained at the HSHO stage (Fig. 12.5).

12.3.3 Cellulose Nanocrystals from Mango Seed Husk

The CrI (>55%) of the cellulose-rich solids enables the CNC to be produced from the MSH under milder organic acid conditions. The solid product from the HSHO is subjected to organic acids (formic acid or acetic acid) hydrolysis without any catalyst to produce the CNC. Organic acid hydrolysis is a preferred method for producing the CNC to the conventional sulfuric acid-based process because of environmental concerns. However, organic acids do not convert the high crystalline cellulose into CNC without the aid of a catalyst (Liu et al. 2016a; Du et al. 2016, 2017). Therefore, adding inorganic acids (HCl, H_2SO_4) or salts ($FeCl_3$) (Liu et al. 2016a; Du et al. 2017) improves the process. The addition of the catalyst can further add to the production costs. In this proposed biorefinery, the synergetic effects of the multiple treatment steps render the cellulose-rich residue amenable to non-catalyzed organic acid treatment. Therefore, it is possible to produce CNC in yields higher than yields obtained from the conventional sulfuric acid process and catalyzed organic acid processes. Optimizing the conditions can give CNC yields that fall within the 42–80% range for a catalyzed formic acid process (Li et al. 2015; Du et al. 2017). Among the organic acids, formic acid is relatively the best performing acid (CNC

Table 12.7 Effect of multi-step fractionation of mango seed husk HSHO residue into nanocellulose crystals

Cellulose nanocrystals (CNC)	Yield (%)	Purity (%)	Crystallinity index (%)	$T_{\max}$ (°C)	Surface morphology
Formic acid	64	–	66	~360	Sphere-shaped
Acetic acid	18	–	62	~350	Sphere-shaped
Sulfuric acid	28	–	71	~310	Rod-shaped
Homogenized acetic acid	78	–	47	~330	Sphere-shaped

Note: Cellulose content of the raw material is 78%

Crl crystallinity index, T_{max} maximum degradation temperature

yields, >60% with increased thermal stability >300 °C) compared to CNC yields (<30%) obtained from the conventional sulfuric acid hydrolysis at 290 °C (Table 12.7).

The organic acid-based methods are sustainable routes for producing CNCs from the solid residue with inherent hydrophobicity and tuned for spherical morphology (Bello 2022). Sphericity is a characteristic that can diversify CNC applications and allow CNC to be applied in highly sensitive applications in the biomedical field. In addition, there is a potential to generate multiple bioproducts (hemicellulose-, lignin-, and the cellulose-rich pulp) in the upper streams. Thus, there is a potential to increase the green credentials and economic viability of the sequential multi-step process to produce the CNC by minimizing the environmental impacts associated with effluent treatments and production costs through recycling and reusing the spent organic acids. The optimization of each step in the sequential fractionation process for multiple products is a relatively more sustainable and highly efficient low-cost method for CNC production than the prevailing production methods. However, the economic, social, and environmental impact assessments for the described process can enhance investment decision-making and implementation at a large scale.

12.4 Challenges of Establishing a Mango Waste-Based Biorefinery

Similar to many fruits waste-based biorefineries (Manhongo et al. 2021), there are many factors that can affect the economic viability and sustainability of a multiproduct mango waste-based integrated biorefinery. In addition to the specific technical challenges already discussed in the chapter, a mango waste-based biorefinery is in general, likely to face some practical, economic, technological, and energy-related problems.

12.4.1 Practical Challenges

There are several practical issues that can hinder the successful implementation of a mango waste biorefinery. Some of the key practical issues include seasonality, storability, moisture content, and location.

12.4.1.1 Seasonality

Mango fruits are seasonal, which would affect the availability of waste as a raw material for the biorefinery. The problem of seasonality can be solved by accessing mango varieties that mature at different times during the year (Manhongo et al. 2021). In addition, the biorefinery, can be developed to be both multi-feedstock and multiproduct, which has implications on the selection of technology-feedstock product combinations. A detailed discussion on multi-feedstock-multiproduct fruit waste-based biorefineries is presented by Manhongo et al. (2021).

12.4.1.2 Storability

The waste that is generated from the processing of the mango fruits is highly perishable, requiring special handling procedures, even for short-term handling (Dzigbor and Chimphango 2019) before conversion into bioproducts. The waste may require special drying or cooling techniques before storage to minimize microbial attacks and the degradation of the heat or freezing labile components of the waste. Consequently, the acquisition of special handling equipment for the biorefinery would likely increase the capital and operational costs.

12.4.1.3 Moisture Content

The short shelf life of the mango waste is attributed to the high moisture content of up to 80% (Gurumeenakshi et al. 2019). The handling of waste with such high moisture content contributes toward high handling costs. In addition to high storage costs, the transportation of the mango waste with a high moisture content from locations where it is generated to where is going to be used as feedstock for the biorefinery can be costly. The alternative is to dry and densify the waste, which has environmental and economic consequences if the source of the energy for these unit operations is fossil-based.

12.4.1.4 Location

The problems associated with the mobilization of the waste and its handling limit the locations where the biorefinery should be established. In view of these challenges, Manhongo et al. (2021) recommended the best location of a fruit waste biorefinery is annex to the waste generating plant. Such location will reduce the cost of mobilizing, storage, and transportation of the waste but might require the reconfiguration of the plant and its management as well as the acquisition of human resources with specialized skills.

12.4.2 Economic

The mango waste is considered a cheap feedstock for the biorefinery. However, the establishment of a biorefinery based on the mango waste as a feedstock requires additional infrastructure and services. The cost of acquiring the infrastructure and the services should be balanced with the market value of the products being produced, hence the use of the MCDA when selecting product combinations for the biorefinery is inevitable. However, the possibility of the fruit processing plants to self-finance the establishment of the integrated biorefinery is low. Therefore, external financial support (e.g., from banks and government) is unavoidable. However, acquiring the financial support from banks can be a challenge because of the increased uncertainty related to the seasonality of the operations, which affect the payback period on the investment and the overall sustainability of the operations.

12.4.3 Technology

In general, the technology for the valorization of biomass to high-value products and their combinations is currently limited to laboratory scale. In addition, the prevailing potential multi-feedstock-multiproduct integrated biorefineries are characterized by several steps that require sophisticated separation techniques to obtain the desired products in high yields and purity. The more the processing steps, the higher the cost, and the lower the efficiency of the process. Therefore, there is need for more research and development to minimize the steps and increase yields before full commercialization.

12.4.4 Energy

The demand for energy in a mango waste biorefinery is distributed across the value chain. Energy is required for mobilization of feedstock, drying, storing, preparation, and actual treatment of the feedstock. Furthermore, energy is required for recovery, purification, storage, and transportation of the products to the point of sale. Other energy requirements emanate from the auxiliary services to the biorefinery. The reliance on energy from the grid, which is fossil-based and unreliable in many developing countries, will make the biorefinery economically unviable and environmentally unsustainable. Therefore, it is imperative that the biorefinery be self-sufficient in energy. The liquid and solid residues generated from the process can be converted to various energy products (heat, power, and fuel) as demanded by the biorefinery, which should offset the use of the fossil-based energy from the grid.

12.5 Conclusions

This chapter has demonstrated the potential of valorizing mango seed waste in integrated biorefineries. Selecting and optimizing individual pretreatment methods, as well as strategically sequencing them in the multi-step biorefinery process, is the key to its success. The integrated biorefineries offer multiple benefits, including reducing environmental pollution, mitigating environmental impacts, and increasing the product spectrum (both food and nonfood) with novel properties for high-value applications within the mango processing industry and beyond. Hence, valorizing the mango seed in an integrated biorefinery embraces the concept of material circularity that is a key driver for circular economy. The multi-step biorefinery schemes can generate multiple products from the MSK (polyphenols, starch, bioactive hemicellulose, and solid residues containing over 80% cellulose and lignin) and from the MSH (hemicellulose-, lignin-, and cellulose-rich solid residue, which is valorized into CNC). The unique choice of process conditions and sequencing of the multiple steps lead to the almost complete valorization of the mango seed waste, which adds value. The sequential treatment of the MSK and thus the OE, EH, and AP can be done to obtain bioproducts of high quality. The sequential AP and HSHO process enables the recovery of two bioproducts (hemicellulose and lignin) and a suitable raw material for CNC production. Manipulating and optimizing the AP process conditions facilitate the extraction of unique product combinations such as mixed hemicellulose containing different ratios of XGN and XLN, uronic acids, and a cellu-lignin residue from the MSH. Additionally, the HSHO process yields lignin with high purity that is less modified from the AP MSH residue. Overall multiple products can be recovered with improved yields and quality than single extraction processes and conventional processes. Thus, the described integrated biorefinery can be implemented as a strategic mango waste management for getting additional revenue while mitigating environmental impacts associated with the conventional disposal of mango waste in the mango processing industry. Implementation at pilot and industrial scales requires techno-economic, and life cycle and social assessments because of some of the additional inputs, equipment, and utilities that might be required.

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13 Applications of Life Cycle Assessment in Biorefinery: Case Study on Mango Peel Waste Biorefinery

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13.1 Introduction

Our heavy reliance on fossil fuels stems from our extensive usage and consumption of petroleum derivatives, which, in combination with depletion oil supplies, raises environmental concerns. Plant photosynthesis, i.e., biomass, is currently the only economically viable way to sequester carbon atoms from the atmosphere for use in materials and energy carriers. The prospect of more efficient and multifunctional use of biogenic feedstock, potentially resulting in reduced climate impact and fossil resource dependency, has piqued interest in biorefineries in recent years (Sandin et al. 2015). A biorefinery is a plant that integrates biomass conversion processes and equipment to produce fuels, electricity, and chemicals (Sandén and Pettersson 2014). Biorefineries help in maximizing the energy potential of organic wastes and also resolve waste management and greenhouse gases (GHG) emissions issues. The biorefinery concept is similar to today's petroleum refinery, which uses petroleum to produce a variety of fuels and products. The biorefinery can be considered of as a process, a facility, or a group of facilities that process biobased feedstocks upstream-midstream-downstream. Biomass production, transportation, and pre-treatment are some of the examples of upstream processes, biomass conversion to desired products is an example of a midstream process, and product distribution is an example of a downstream process. The biorefinery idea integrates technology from several sectors

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(such as agriculture, engineering, chemistry, and microbiology) to separate biomass into its constituent parts, which are subsequently turned into biofuels and biomaterials. Various processes such as mechanical pre-treatment, chemical processes (hydrolysis, transesterification, hydrogenation, and oxidation to change the biomass chemical structure), thermochemical (pyrolysis), and biochemical processes (enzymatic conversion, anaerobic digestion, and fermentation) are applied in biorefinery. Recent literature explores the microalgal biomass as a feedstock for a biorefinery for the production of biofuels and high value products (Li et al. 2022).

Biorefineries will be crucial in the development of sustainable bio economies, although estimates of their environmental impact vary widely (Shi and Guest 2020). In terms of GHG emissions, energy performance, and other environmental consequences, the environmental factor of biorefineries would be validated by a systematic approach. LCA (life cycle assessment) is a method of calculating the environmental effect of systems and products at various phases of their life cycle (Liu et al. 2021). The GHG balance of a biorefinery is heavily influenced by the many life cycle stages based on the waste-derived feedstock and the technology used. Many research on biorefineries have lately used LCA to investigate the environmental consequences of the whole life cycle of biorefinery systems and products (Liu et al. 2021). The LCA results could serve as the foundation for decision support in the development of new technologies, processes, or products for industrial applications, as well as policies for climate change mitigation and fossil resource reliance. Based on the biorefinery system, the evaluation of factors related to its implementation potentials (e.g., feedstock availability), practicality (e.g., technical), and stability (e.g., durability, yield stability) add significant characteristics of new products and production technology. This book chapter discusses about case study of life cycle impacts of mango peel waste biorefinery with three processes.

13.2 LCA in Biorefinery: Need and State of Art

Biomass is the main feedstock for any biorefinery. Biomass has found multiple low-value applications such as cattle feed, landfill, combustion, compost, etc.; with biorefinery we are adding value to the feedstock along with addressing the solid management issue. However, biomass remains to be biodegradable in nature. Literature cites use of bio-culture to expedite the degradation process (Mankhair and Borkar 2020). The use of different chemicals and unit operations and processes to extract value-added product from waste biomass can result in significant amount of environmental impact. Such an environmental impact significantly affects the overall sustainability of the biorefining scheme. Hence evaluation of environmental impacts at the design phase of biorefinery scheme is necessary. Along with the evaluation of gate-to-gate emissions of the biorefinery scheme, it is also necessary to include cradle-to-gate and gate-to-grave system boundary for a holistic evaluation of environmental impacts of biomass and its processing. The products thus extracted/

manufactured from biomass can then be used to compare with conventional process and products.

Evaluation of environmental impacts of biorefinery scheme has gained importance in recent past. Waste-targeted biorefineries are attempting to create account of environmental technology solutions that will enforce the circular economy. Table 13.1 shows literature on incorporation of LCA for environmental impact evaluation pertaining to biorefinery. Li et al. (2022) conducted LCA of microalgae biorefinery where wastewater was used as a cultivation medium to produce microalgae (Li et al. 2022). This research found that adjusting wastewater can help increase the quality of microalgal biofuel production while reducing environmental concerns. Overall lowered environmental impact was found to be 838.52 mPE_{T2000} due to the lower optimal temperature of pyrolysis induced. The LCA of vine shoot biorefinery were performed by Sirohi et al. (2020). Vine shoot LCA shows 3.26 kg of CO2 eq. climate change impact compared to 4.67 kg of CO2 eq. for the reference system for the production of 1 kg lactic acid. The electricity and fuel consumed for the various process phases, including the lime manufacturing process, had the greatest contribution to the lactic acid scenario’s climate change impact (Pachón et al. 2020). Joglekar et al. (2020) conducted LCA of pomegranate biorefinery. Products obtained from extraction were ellagic acid (EA), lignin, and pectin. Based on the weight of pomegranate peels (PP) processed, the yields of the products EA, lignin, and pectin are 10%, 13%, and 19%, respectively. The GWP of the PP biorefinery is 4505.8 kg CO_2 eq/tonne of PP processed. The intensive hydrolysis stage played a significant role in the total GWP index (Shinde et al. 2020). Patrizi et al. (2020) compared two biofuel biorefineries with feedstocks cassava peel and corn stove using energy assessment and LCA. The cassava peel biorefinery was found to be more sustainable from both the user and donor viewpoints. LCA results showed that compared to corn stover biorefinery, the effect categories GWP and AP for cassava exhibited lower values (Patrizi et al. 2020). Joglekar et al. (2019) studied gate-to-gate LCA of citrus waste biorefinery extracting ethanol, limonene, and methane as major products. The entire GWP of the CW biorefinery was determined to be 937.3 kg CO_2 eq, with “hydrolysis and flashing” accounting for around 60% of midpoint indications. It was established that by utilizing modern sophisticated technology, it is possible to achieve a significant order of magnitude reduction in environmental indicator values (Joglekar et al. 2019).

13.3 LCA Framework

Phases included in LCA methodology as per ISO 14044 are (1) goal and scope, (2) life cycle inventory (LCI), (3) impact assessment method, and (4) interpretation (ISO 14044:2006 2006).

Table 13.1 LCA performed on various biorefineries feedstock

Biorefinery feedstock	Product	Environmental impact key observation	Reference
Microalgae	Biofuel	Adjusting wastewater can help enhance the quality of microalgal biofuel production while lowering environmental impacts	Li et al. (2022)
Vine shoots	Lactic acid and furfural	CO_2 emissions were reduced by 30.1–38.6%, while fossil fuels depletion was reduced by 60%	Pachón et al. (2020)
Pomegranate peel	Ellagic acid, pectin, lignin	The GWP was determined to be 4505.8 kg CO_2 eq/tonne of PP treated, with the intensive hydrolysis stage playing a significant role in the total GWP estimate	Shinde et al. (2020)
Corn stover, cassava peel	Ethanol	Environmental impact values found to be lower for cassava compared to corn stover biorefinery	Patrizi et al. (2020)
Municipal solid waste	Bioenergy, microbial protein, lactic acid, succinic acid	In the climate change category, microbial protein synthesis saved −58 to −147 kg CO_2 eq/tonne biopulp, whereas succinic acid and lactic acid-based biorefinery saved −73 and −173 kg CO_2 eq/tonne biopulp, respectively	Khoshnevisan et al. (2020)
Citrus waste	Ethanol, limonene, methane	The overall GWP was determined to be 937.3 kg CO_2 eq, with "hydrolysis and flashing" accounting for almost 60% of the midpoint indication	Joglekar et al. (2019)
Residual lipids (waste cooking oil)	Biofuel	GWP found to be 243 kg CO_2 eq/m^3, co-processing residual biomass with petroleum fractions takes advantage of existing infrastructure to generate lasting fuels	Chrysikou et al. (2019)
Brewery waste	Bioethanol and xylooligosaccharides	The generation of steam necessary to attain the high autohydrolysis temperature and the synthesis of enzymes required in simultaneous saccharification and fermentation were identified as two environmental hotspots across the biorefinery chain	González-García et al. (2018)
Oil palm fronds	Bioethanol	GWP found to be 2.26 kg CO_2 eq/kg, green biomass conversion for feed, and energy generation may give environmental benefits over conventional feed production	Corona et al. (2018)

(continued)

Table 13.1 (continued)

Biorefinery feedstock	Product	Environmental impact key observation	Reference
Sugarcane residue	Ethanol, lactic acid	Due to increased use of processing chemicals, environmental impacts were slightly greater	Mandegari et al. (2017)
Castor	Biodiesel, ethanol, biogas	GHG emissions are reduced by 16% without taking into account the improved effect of soil organic carbon or resource damage. 50 percent less than neat diesel combustion	Khoshnevisan et al. (2018)
Microalgae	Biomethane	The investigated algal biorefinery offers clear benefits in terms of climate protection, fossil resource protection, and ozone depletion when compared to typical waste water treatment and the use of biomethane instead of compressed natural gas as automotive fuel	Maga (2017)
Sugarcane residue	Ethanol	Climate change, acidification, photo-oxidant production, and particulate matter production are all reduced by about 40%, 60%, 90%, and 63%, respectively	Silalertruksa et al. (2017)

13.3.1 Goal and Scope

The determination of the study's goal and scope is the first stage in performing LCA. The aim and scope specification identifies the study's purpose as well as critical aspects such as the system boundary and functional unit. The study's objectives could include identifying environmental hotspots and evaluating items' environmental impact (Shinde et al. 2020). The study's scope also comprises a functional unit-level description of the examined process, with inputs and outputs assigned correspondingly. Because waste biomass is used as a feedstock, the environmental impact of waste manufacturing is not taken into account in any biorefinery. Their transportation, on the other hand, is critical. The biomass production chain and its subsequent conversion to the desired products, as well as the valorization of byproducts and energy supply to the system, are all defined by the system boundaries (Bernstad Saraiva 2017). All of the stages encountered in the system boundaries are used to obtain inventory or data points. Any LCA relies heavily on functional unit. The functional unit is used to determine the LCI and its effects. It's a numerical representation of the underlying function under investigation, and it should be related to the biorefinery's desired outputs. LCA studies for biorefinery functional units are often conducted on a feedstock mass or energy basis, with high added value chemicals and biofuels as final products.

Table 13.2 Different approaches used for LCA of biorefinery

Sr. no.	Approach	Stage
1.	Cradle to gate	Biomass production, harvesting, transportation (Smith and Durham 2016)
2.	Gate to gate	Manufacturing activity (Kim and Overcash 2000)
3.	Gate to grave	Distribution, storage, use, and end of life
4.	Cradle to grave	Entire life cycle of product (Bhatt et al. 2019)
5.	Cradle to cradle	Reuse, recovery, recycle (Bjørn and Hauschild 2013)
6.	Grave to cradle	Recycling (Valero 2013)

A study system encloses a product's manufacturing route and allows for the quantification of its environmental impacts following any of the approach shown in Table 13.2. A "cradle-to-cradle" life cycle implies a system boundary only until product's production stage; a "gate-to-gate" approach accounts only for emissions related to the manufacturing of the product; a "cradle-to-cradle" life cycle includes reuse, recovery, or recycling of a product or its coproducts; and a "gate-to-gate" approach accounts only for emissions related to the manufacturing of the product (Shi and Guest 2020). The accompanying energy and resource utilization and also emissions for the overall system, are quantified in all techniques. "Cradle-to-grave" covers the whole life cycle of a product. It is a comprehensive analysis of a product from its raw materials until its disposal. For both energy-driven and product-driven biorefineries, "cradle-to-gate" is the most popular choice for comparing alternative process topologies and when comparing a principal product to another with the same function (Righi 2019). The cradle-to-gate system has been designed to integrate biomass supply, which includes biomass production, harvesting or collecting, and transportation to the refinery.

13.3.2 Life Cycle Inventory

The life cycle inventory (LCI) is the foundation of an LCA. The purpose of the inventory is to create a model of the product or activity that was identified during goal and scope definition. LCI comprises investigating the material balance, energy flows, and environmental emissions associated with the functional unit's product manufacturing. Inventory data includes process input (electricity, steam, cooling fluid, etc.). Commercial software tools (e.g., SimaPro, Global Emission Model for Integrated Systems (GEMIS), sphera's GaBi, and others) may help to ease the process of assessing the environmental impacts of biorefinery systems because a lack of available inventory data is a significant barrier to LCA practice. General inventory data that can be considered for environmental impact assessment through LCA for a biorefinery is given in Table 13.3.

Table 13.3 Generalized inventory datasheet for gate-to-gate LCA of biorefinery

Sr. no.	Process	Input	Output
1.	Biomass cleaning and sorting	Biomass, water, electricity, steam	Clean biomass for pre-treatment
2.	Pre-treatment	Clean biomass, solvent	Pre-treated biomass
3.	Enzymatic/acid hydrolysis/ treatment/solvent extraction	Treated biomass, water, acid, electricity	Hydrolysate
4.	Separation of solid and liquid product	Hydrolysate, electricity	Solid, liquid hydrolysate
5.	Product precipitation and purification	Liquid hydrolysate, ethanol	Product solution, mixture of solvent
6.	Solvent recovery	Mixture of solvent	Ethanol
7.	Drying	Product solution	Dry product

13.3.3 Impact Assessment Method

The goal of life cycle impact assessment (LCIA) is to transform LCI results into possible contributions to environmental consequences so that we may better comprehend their environmental relevance. The LCIA converts inventory data into prospective contributions to a variety of impact categories, which are then modelled into the LCIA's "areas of protection." It includes determining the impact factors for emissions, energy, and resource consumption. GHG emissions, resource depletion, land-use ecological impacts, human health impacts, regional environmental impacts, and untreated toxic environmental impacts are among the LCA impact categories. Climate change and acidification are two examples of midpoint indicators that focus on specific environmental challenges. Human health, biodiversity, and resource depletion are examples of endpoint indicators that show the environmental impact at three higher levels of aggregation (Finnveden and Potting 2014). Converting midpoints to endpoints makes LCIA data easier to read.

The environmental impacts notably considered during LCA study of biorefinery are (1) global warming potential (GWP) kg CO_2 eq, (2) acidification potential (AP) kg SO_2 eq, (3) eutrophication potential (EP) kg phosphate eq, (4) ozone depletion potential (ODP) kg R11 eq, and (5) photochemical ozone creation potential (POCP) kg ethene eq.

13.3.4 Interpretation

The interpretation of the outcome of a LCA research is a required part of the LCA process and a critical component in reaching solid conclusions and suggestions. The following parts are included in the interpretation:

1. Identification of key issues derived from the results of the LCI and LCIA stages of the LCA
2. Evaluation that takes into account completeness and consistency checks
3. Suggestions, limits, and recommendations

The goal of interpretation is to evaluate and arrange the data of the LCA study's previous phases in order to pinpoint the most important concerns. There are two interconnected components to major issues: (1) the primary contributors to the LCA results which are the most significant life cycle phases, processes and elemental flows, and most essential impact categories and (2) the most important decisions that might affect the accuracy of the final LCA results. Methodological decisions, assumptions, foreground, and background data used to derive process inventories are examples of these. Completeness checks are carried out on the inventory to evaluate how complete it is and whether the cut-off criteria have been satisfied. The consistency check determines if the assumptions, procedures, and data were consistently applied throughout the LCA analysis. By combining the results of the other elements of the interpretation phase and marking on the main findings from the earlier phases of the LCA, the final element of the interpretation phase is to draw a conclusion and recognize the limitations of the LCA, as well as develop recommendations for the intended users in accordance with the goal definition and intentional applications of the results (Zampori et al. 2016).

13.4 Mango Peel Waste Biorefinery: LCA Approach

Arora et al. (2018) assessed the cost and profitability of mango processing waste biorefinery with three pathways that are (1) only pectin extraction (PEP), (2) pectin and seed oil extraction (PSEP), and (3) whole biorefinery with multiple products recovery (WMB).

Dried mango peel powder is refluxed with ethanol and transferred to distillation unit to concentrate polyphenol. Polyphenol extract powder is obtained using spray drier. Dried residue is hydrolyzed with hot acidified water followed by precipitation of pectin, and then pectin extract is dried. Steeping is done to fractionate mango kernel components. Swollen kernels are separated and ground to increase the surface area of kernel. Furthermore, membrane separation is performed for the separation of oil and fiber. Fiber is washed and dried to obtain pure fiber, and de-emulsification process was used to recover pure oil. Liquid stream obtained after oil and fiber extraction is further concentrated to recover protein through centrifuge and belt filtration unit followed by drying. The leftover stream is processed via a series of hydro cyclones to remove solubles from starch and other contaminants after the protein-rich meal is recovered. A steam turbine burns mango seed coat to create combination heat and power. The complete flow diagram of mango processing waste is illustrated in Arora et al. (2018).

LCA was performed in accordance with ISO 14040:2006 (2006). The phases of the LCA technique are as follows: purpose and scope, life cycle inventory, impact assessment method, and interpretation. LCA is a tool for determining numerous environmental issues associated with the manufacturing process. GWP, AP, EP, ODP, and POCP are the environmental indicators studied during LCA. This tool is used to calculate the quantitative impact of numerous potential environmental factors over the lifetime of a product.

13.4.1 Goal and Scope

The specifications of the goal and scope of the study establish the study's objective as well as basic features such as the system boundary and functional unit.

13.4.1.1 System Boundaries

The system boundaries usually define the biomass production chain and its chemical transformation to the required products and also byproduct valorization and energy supplied to the system. LCA data is obtained using all of the stages observed in the system boundaries. Here we considered the gate-to-gate and cradle-to-gate strategy, which specifies emissions from raw material manufacturing, raw material transportation, and product manufacturing. Figure 13.1 shows the general schematic diagram of system boundaries of mango peels. Only environmental effect considerations are considered in the research of sustainability analysis. The raw material (RM) transit distance is estimated to be 30 km.

13.4.1.2 Functional Unit

The functional unit for this study is 12,960 MT of mango peels and 30,240 MT of mango seeds (Table 13.4).

13.4.2 Impact Assessment Method

The CML 2001 impact assessment approach is used to investigate the environmental effects of the mango peel waste biorefinery (Cherubini and Jungmeier 2010). To reduce uncertainty, this strategy confines quantitative modelling to the early phases of the cause-effect chain. The results have been presented in five distinct midpoint indicators mentioned as mentioned early.

13.4.3 Interpretation

Table 13.5 shows how each step contributes to the overall environmental indicators. The GWP of the mango peel waste biorefinery has been determined to be 3,230,000 kg CO_2 eq for PEP. High value is attributed to the use of electricity. The AP for the biorefinery of mango peel waste is found to be 35,900 kg SO_2 eq for PEP. The consumption of electricity is credited with a high value in AP, EP, ODP, and POCP.

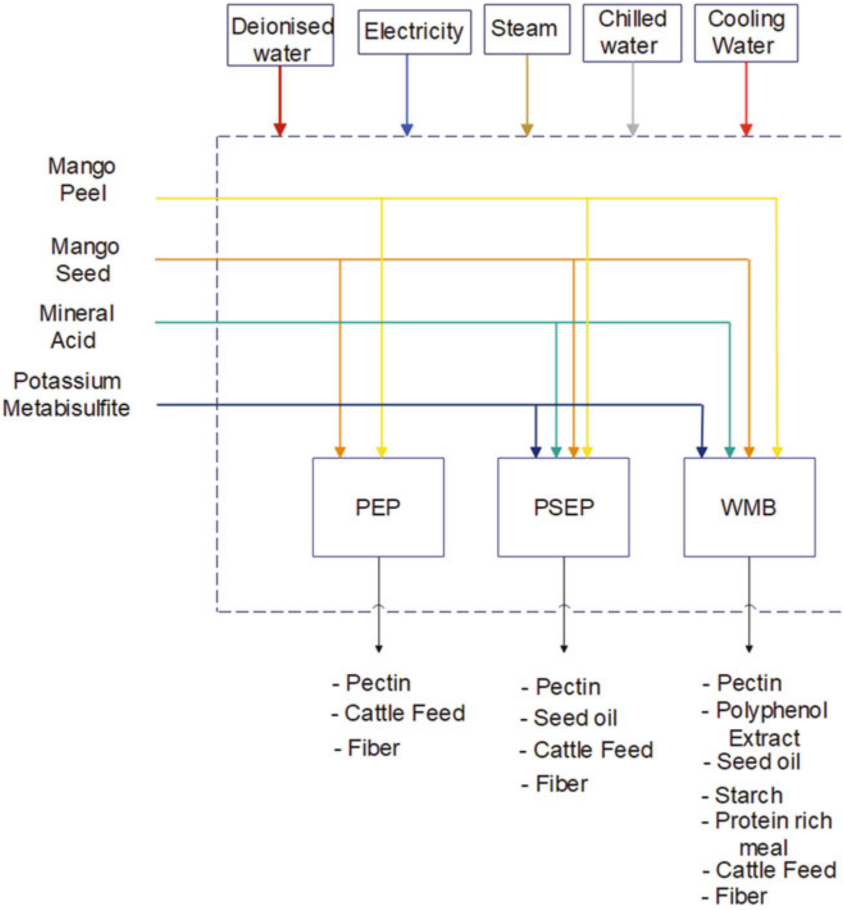

Fig. 13.1 Schematic diagram of system boundaries for mango peel waste biorefinery

Figure 13.2 depicts each process's % contribution to the process's overall midway indicators. The percentage contribution of all the three process was greater due to the electricity used in the process like centrifugation, cooling water chilling water, hydrolysis, etc. It is observed that as the number of products increases, contribution to the environmental impact also increases. If we recover only pectin, contribution to environmental impacts is very low due to less number of processing steps. For multiple product biorefinery, environmental impact gets allocated among themselves. Table 13.5 shows the environmental indicators' related values resulted for the three processes per kg of product from mango peel biorefinery.

After performing mass allocations and cost allocations, similar results were obtained. When comparing the PEP and WMB processes in terms of mass and cost allocation, the WMB process produces more emissions, but it also generates

Table 13.4 Inventory analysis of mango peel biorefinery (based on calculation made by Arora et al. (2018))

Sr. no.	Materials	PEP	PSEP	WMB
Raw material				
1	Mango peel (MT)	12,960	12,960	12,960
2	Mango seed (MT)	30,240	30,240	30,240
3	Mineral acid (HCl) (kg)	0	432	432
4	Potassium metabisulfite (kg)	0	23,528.66	23,528.66
5	Water (MT)	45,870	69,375.71	68,892.857
6	RO water	0	0	11,986
Electricity				
1	Std power	21,010,826.67 kWh	24,097,840 kWh	25,685,880
Utilities				
1	Steam	205,812.639 kWh	216,331.1314 kWh	111,632.529
2	Cooling water (MT)	2,796,340	2,867,540	6,341,860
3	Chilled water (MT)	1,242,370	1,023,987.5	1,434,962.5
Product				
1	Pectin (kg)	1,146,955.7	1,146,955.7	114,0150.9
2	Polyphenol extract (kg)	0	0	95,749.46667
3	Seed oil (kg)	0	1,253,994.625	1,253,994.625
4	Starch (kg)	0	0	6,450,130
5	Protein-rich meal (kg)	0	0	848,512
6	Cattle feed (kg)	2,655,100	2,655,100	2,638,600
7	Fiber (kg)	252,000	5345.833	5345.833

Table 13.5 Environmental indicators for mango peel waste biorefinery

Sr. no.	Process	GWP	AP	EP	ODP	POCP
1	PEP	3.23E+06	3.59E+04	1.78E+03	1.65E−08	1.51E+03
2	PSEP	2.67E+07	3.10E+05	1.43E+04	1.36E−07	1.44E+04
3	WMB	2.91E+07	3.39E+05	1.55E+04	1.49E−07	1.59E+04

more revenue since the number of products form in the WMB process is larger than the PEP and PSEP processes. Following equations are used for calculating mass and cost allocation, respectively.

$$\mathrm{GWP}_{\mathrm{PEP}}^{\mathrm{Pectin}} = \frac{\text{Mass of pectin} * \mathrm{GWP}_{\mathrm{PEP}}}{\sum \text{Mass of Products}}$$

$$\mathrm{GWP}_{\mathrm{PEP}}^{\mathrm{Pectin}} = \frac{\text{Cost of pectin} * \mathrm{GWP}_{\mathrm{PEP}}}{\sum \text{Cost of Products}}$$

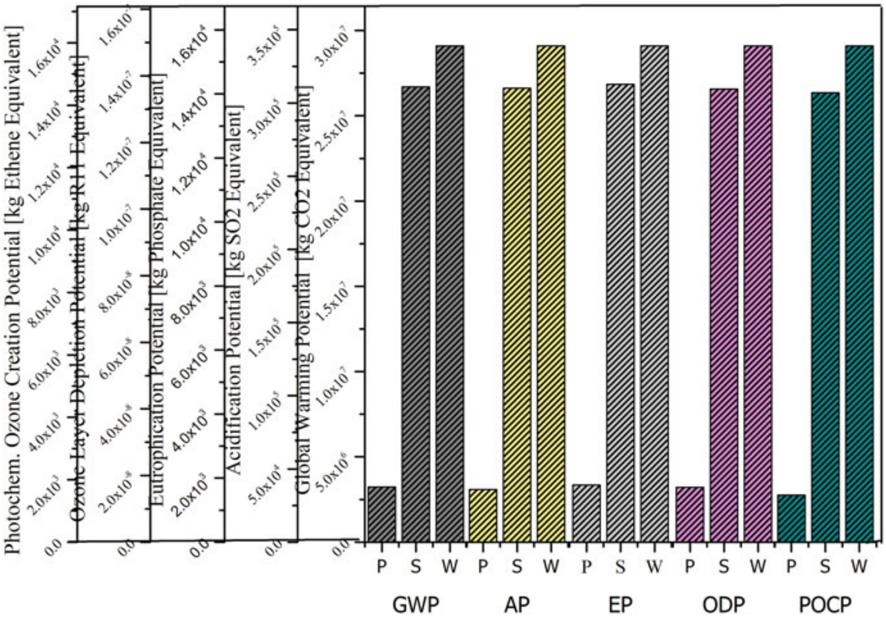

Fig. 13.2 Percent contribution of process in overall environmental impacts

Similar equations are used for calculating mass and cost allocation of other environmental impacts for three of the processes. Tables 13.6 and 13.7 show the mass and cost allocation of the three different biorefineries with respect to the environmental impacts. The case study showed multiple environmental impacts that can be allocated among various products, and hence it is always advisable to extract maximum possible products so that individual attribution/allocation of the product will be cutless.

13.4.4 Limitations of the Study

Following are the certain limitations considered during LCA approach:

1. No environmental impact of waste considered in the LCA study.
2. Generation/cultivation of biomass needs to be included in the study.
3. Packaging of product is not as a part of LCA database.
4. Construction and demolition phase is not included in system boundaries.
5. Other processes on which processing of waste is dependent have to be studied in detail.

Table 13.6 Mass allocation

				GWP allocated			AP allocated			EP allocated			ODP allocated			POCP allocated		
Products	PEP	PSEP	WMB	PEP	PSEP	WMB	PEP	PSEP	WMB	PEP	PSEP	WMB	PEP	PSEP	WMB	PEP	PSEP	WMB
Pectin	1,146,955.7	1,146,956	1,140,151	9.14E+05	6.05E+06	2.67E+06	1.02E+04	7.02E+04	3.11E+04	5.04E+02	3.24E+03	1.42E+03	4.67E−09	3.08E−08	1.37E−08	4.27E+02	3.26E+03	1.46E+03
Polyphenol extract	0	0	95,749.47	0	0	2.24E+05	0	0	2.61E+03	0	0	1.19E+02	0	0	1.15E−09	0	0	1.22E+02
Seed oil	0	1,253,995	1,253,995	0	6.62E+06	2.94E+06	0	7.68E+04	3.42E+04	0	3.54E+03	1.56E+03	0	3.37E−08	1.50E−08	0	3.57E+03	1.60E+03
Starch	0	0	6,450,130	0	0	1.51E+07	0	0	1.76E+05	0	0	8.04E+03	0	0	7.73E−08	0	0	8.25E+03
Protein-rich meal	0	0	848,512	0	0	1.99E+06	0	0	2.31E+04	0	0	1.06E+03	0	0	1.02E−08	0	0	1.09E+03
Cattle feed	2,655,100	2,655,100	2,638,600	2.12E+06	1.40E+07	6.18E+06	2.35E+04	1.63E+05	7.19E+04	1.17E+03	7.50E+03	3.29E+03	1.08E−08	7.13E−08	3.16E−08	9.89E+02	7.55E+03	3.37E+03
Fiber	252,000	5345.833	5345.833	2.01E+05	2.82E+04	1.25E+04	2.23E+03	3.27E+02	1.46E+02	1.11E+02	15.1	6.66	1.03E−09	1.44E−10	6.41E−11	93.9	15.2	6.84

Table 13.7 Cost allocation

					GWP allocated			AP allocated			EP allocated			ODP allocated			POCP allocated		
Products	PEP	PSEP		WMB	PEP	PSEP	WMB	PEP	PSEP	WMB	PEP	PSEP	WMB	PEP	PSEP	WMB	PEP	PSEP	WMB
Pectin	11,469,557	11,469,557		11,401,509	3.18E+06	1.42E+07	1.29E+07	3.53E+04	1.65E+05	1.50E+05	1.75E+03	7.59E+03	6.86E+03	1.62E–08	7.22E–08	6.59E–08	1.49E+03	7.64E+03	7.04E+03
Polyphenol extract	0	0		1,436,242	0	0	1.62E+06	0	0	1.89E+04	0	0	8.64E+02	0	0	8.31E–09	0	0	8.86E+02
Seed oil	0	10,031,957		10,031,957	0	1.24E+07	1.13E+07	0	1.44E+05	1.32E+05	0	6.64E+03	6.04E+03	0	6.31E–08	5.80E–08	0	6.69E+03	6.19E+03
Starch	0	0		1,935,039	0	0	2.19E+06	0	0	2.55E+04	0	0	1.16E+03	0	0	1.12E–08	0	0	1.19E+03
Protein-rich meal	0	0		848,512	0	0	9.59E+05	0	0	1.12E+04	0	0	5.11E+02	0	0	4.91E–09	0	0	5.24E+02
Cattle feed	106,204	106,204		105,544	2.94E+04	1.31E+05	1.19E+05	3.27E+02	1.52E+03	1.39E+03	16.2	70.3	63.5	1.50E–10	6.68E–10	6.10E–10	13.8	70.8	65.1
Fiber	75,600	1603.75		1603.75	2.10E+04	1.98E+03	1.81E+03	2.33E+02	23.0	21.1	11.5	1.06	0.965	1.07E–10	1.01E–11	9.28E–12	9.80	1.07	0.990

13.5 Conclusion

Traditional solutions on waste management (landfilling, composting, cattle feeding) are not economically as well as environmentally attractive. Landfilling and composting of biomass lead to the CH_4 and N_2O emissions. So conversion of biomass into useful products is environmentally sustainable. Biorefinery also have environmental impacts but can be reduced up to some extent using life cycle assessment method. To assess environmental impacts and identify environmental hotspots, a representative mango peel waste biorefinery was chosen. It is more important to do gate to gate LCA of different biorefinery schemes in order to have a more sustainable biorefinery strategy. The GWP was found to be 3.23E+3 tonnes CO_2 eq for PEP. As overall GWP, AP, EP, ODP, and POCP are higher for WMB, it gets allocated among themselves. As a result, it is always preferable to extract as many products as possible so that individual attribution of the product is as simple as achievable. Similar approach can be used to perform LCA of other biorefineries. Thus, LCA work has been extrapolated.

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Sustainable Fruit Peel Waste Biorefinery: Challenges and Future Perspectives

14

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14.1 Introduction

Fruit peel waste accounts for between 15% and 60% of all fruit waste that is generated and is typically thrown away. There is a significant amount of solid waste generated by the processing of fruits into dried and canned/frozen slices or powders, wine, or juice. Because of the moisture and microbial levels present in these fruit wastes, they are a direct source of pollution for the environment. Also, because of their high biodegradability and fermentability, these fruit wastes can pose a significant environmental and human health concern if not adequately managed. Additionally, there is a considerable risk of pollution of both the surface water and the groundwater. When compared to the disposal of other kinds of solid waste, the high moisture content of fruit waste suggests that incineration may not be an effective or practical choice. The landfill is the technique of trash disposal that is used the most frequently, but it is also the method that costs the most expense. The most significant sources of these emissions occur in developing countries, Asia,

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Europe, and North America. Anaerobic biological breakdown of organic matter is the third largest human source of atmospheric methane emissions, with 2010 global emissions exceeding 32 million tonnes, equivalent to 800 million tonnes of carbon dioxide (Jiménez-Moreno et al. 2019; Leong and Chang 2022; Manhongo et al. 2022; Banerjee et al. 2017; Satari and Karimi 2018; Rivas-Cantu et al. 2013).

The waste generated mainly includes fruit and vegetable peels and their seeds. In some instances, the volume of waste generated exceeds that of the product itself (Ayala-Zavala et al. 2011; García et al. 2015). Different fruits such as banana, citrus (e.g., orange, lemon, grapefruit), mango, pineapple, pomegranate, and grapes are mostly used in their natural form or as preserved pulps (or derivatives such as juices) with very high demand (Schieber et al. 2001; Ayala-Zavala et al. 2011). The majority of fruit waste is disposed of in landfills, incinerated, or burned openly, although some of the fruit waste can be used as an animal feed supplement (Leong and Chang 2022). Fruit peels can also be used to produce biochemicals, biofertilizers, renewable energy (biogas or methane), industrial enzymes, and functional ingredients and dietary fiber in baked products, in addition to being used as animal feed (Pathak et al. 2021). Different compositional studies of the FPW suggest that different residual fractions contain a wide range of bioactive compounds. Most of these bioactive compounds come from plants. They are called primary and secondary metabolites. Some examples of secondary metabolites are alkaloids, gums, phenolics, volatile oils, glycosides, mucilage, and oleoresins (Banerjee et al. 2017). Some FPW are exceptionally abundant in bioactive chemicals and nutraceuticals, including dietary fiber, carotenoids, saponins, phenolic compounds, fatty acids, lipids, isoprenoids, proteins, and phytoestrogens (Jiménez-Moreno et al. 2019). When it comes to waste disposal, processing firms, particularly in developing nations, are limited by finances, space, and in some cases, rigorous government laws. In comparison to processed fruit, processing waste is thought to be of low value because the majority of these industries are small and informal (Banerjee et al. 2017).

Sustainable management must be created in order to address this issue. There are numerous advantages to managing agricultural waste, including the creation of value-added products and the prevention of environmental pollution and other issues. There are four main categories of agricultural waste management: reduction or minimization, conversion, segregation, and usage (Yaashikaa et al. 2022). Reusing FPW and exploring its use as raw material for value-added goods are critical from an environmental standpoint. Ecosystems would benefit and the global economy would benefit as a result (Pathak et al. 2016). The production of usable chemicals and fuels from FPW has been proposed using a system called a “biorefinery” that is comparable to a petroleum refinery. A facility known as a biorefinery incorporates conversion techniques and tools to create fuels, electricity, and chemicals from FPW (Fernando et al. 2006). If waste biorefineries were built in developing nations, they could generate electricity, save land, create new businesses and jobs as a result, reduce the cost of landfills, reduce greenhouse gas emissions, and conserve groundwater, soil, and other natural resources. The difficulties in successfully implementing the biorefinery concept in poor nations (Nizami et al. 2017).

Several biorefineries are now operational, particularly in Germany, Italy, Finland, and France; however, their competitiveness is limited in comparison to their fossil counterparts, limiting their economic exploitation. Some significant technologies are still in the research and development, pilot scale, or demonstration stages with inadequate technical readiness. Industries and policies are becoming increasingly conscious of the need to shift from energy-only systems to bioenergy and biomaterial applications for better economic viability and total biomass resource use (Manhongo et al. 2022). In addition, making a contribution toward the environmentally responsible expansion of the livestock business will turn "waste into chances for development" (Tartrakoon et al. 1999; Wadhwa and Bakshi 2013). As a result, it is necessary to find a strategy or procedure that will enable us to recycle FPW in order to make products that are both beneficial and profitable thus, making "wealth from waste" (Pathak et al. 2019).

14.2 The Concept of Biorefinery

The concept of biorefinery emerged in the late 1990s as a result of the shortage of fossil fuels and the growing usage of biomass as a sustainable feedstock for the production of nonfood goods (Maity 2015). Biorefinery is a concept that focuses on increasing the economic potential of bioproduct manufacturing by reusing by-products through the combination of multiple conversion methods (Ubando et al. 2021). To extract valuable chemicals and fuels from biomass, a system replicating a petroleum refinery labeled a "biorefinery" has been proposed (Fig. 14.1). A biorefinery is a facility that combines conversion processes and equipment in order to produce biomaterials, fuels, and chemicals from biomass (Pathak et al. 2017; Fernando et al. 2006). The biorefinery is aimed to produce an ecosystem that includes humans utilizing solar energy. The biorefinery helps the ecology and economy. The biorefinery could tackle environmental concerns, the food crisis, and supply futuristic technologies (Ohara 2003). Waste biorefineries in underdeveloped nations might provide electricity, save land, create new businesses and jobs, reduce GHG emissions, and save land, soil, and groundwater (Nizami et al. 2017). Biomass is composed of carbohydrates, proteins, lignin, lipids, and, to a lesser extent, other components such as pigments, vitamins, and flavors. The goal of a biorefinery is to transform such plentiful biological feedstock into useful products through the use of a mix of technologies and techniques. The primary goal of a biorefinery is to produce high-value low-volume and low-value high-volume products through a series of unit operations (Fernando et al. 2006). To be genuinely effective, the method's wastes must be environmentally compatible in a short timeframe. Even though manufacturing processes have become more efficient in terms of using resources and reducing waste, the industry needs to keep track of its methods by keeping detailed inventories of all inputs and outputs (Clark and Deswarte 2008).

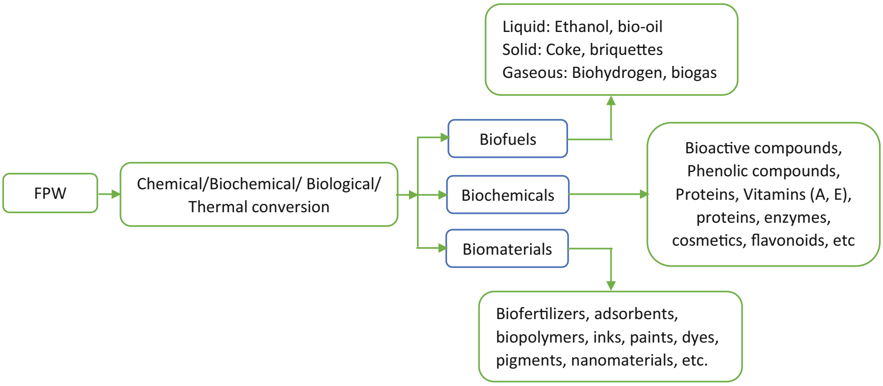

Fig. 14.1 Biorefinery scheme

14.3 Challenges and Future Prospectives

There are several problems with turning agricultural waste into bioproducts and biomaterials in order to lower the cost of production. These problems include the use of energy, differences in the composition of waste feedstock, feedstock production, feedstock system, development of energy-efficient technologies, and societal insight. Focusing on these problems is important if the biorefinery is to be good for the economy and the environment (Ginni et al. 2021). Despite the great significance of bio-based products for numerous industries, experts still see many technical, strategic, and commercial challenges that essential to be dazed before any large-scale commercialization of the biorefinery can succeed. The challenges which restrict for making the FPW as a great source for a sustainable biorefinery are discussed here.

14.3.1 FPW Variety

The origin, seasonal fluctuations, cultivars, ripening stages, and geographical location all affect the physical, chemical, and mechanical qualities of PFW. Thus, this has an impact on how these materials are designed, handled, and processed as well as the cost of operations. These parameters contribute to variation in outcomes of the desired products. Work on characterization of FPW should be done with these and other comparable factors in mind. This database will assist in the analysis of experimental data consistency and repeatability. Also, the diversity makes it challenging to develop replicable biomass supply systems and particular biocontrol or biofuel transformation procedures for various types of lignocellulosic feedstock. Thus, standardization of raw material quality offers a big barrier for BP's biorefinery, which is difficult to resolve (Pathak et al. 2015, 2017; Senthil Kumar and Yaashikaa 2020).

14.3.2 Storage, Handling, Transportation, and Cost

Collection, storage, handling, and transportation are all affected by the high moisture content of FPW. Intense biodegradability can be caused by BP's high organic matter content and moisture level. As a result, FPW must be dried before it may be used again. For this objective, an inexpensive and easy-to-use drier must be developed. Any accessible heating source such as solar energy, waste heat, or a combination of these should be explored as an alternative option for drying materials on-site. Also, the use of FPW as a feedstock during energy production is solely dependent on the energy content or heating value of the material. Despite this, it has a low energy efficiency because to its high moisture content (Pathak et al. 2016). Likewise, native plants in agricultural areas regulate biorefinery operations, making them infrequent. Long-term biomass storage solves this problem. The biorefinery, which needs a lot of biomass, must be far from the source (Senthil Kumar and Yaashikaa 2020).

Production costs are still high because of FPW's limited supply, logistical concerns due to scattered generation, and complicated, difficult-to-process composition. Because of this, this industry appears to be better positioned to take advantage of economies of scale. FPW valorization is possible only if retailers and households separate FPWs at the point of origination and collect them. It is suggested that biorefineries be centralized or annex to existing fruit processing facilities to decrease transportation costs and logistical difficulties, issues with handling and storage, and disruptions in feedstock supply. Additionally, direct collection from processing facilities may lessen the need for segregation during processing, saving a sizable monetary amount (Jiménez-Moreno et al. 2019; Banerjee et al. 2017; Manhongo et al. 2022).

The supply chain for turning fruit waste into viable commercial products may be impacted by the fluctuating supply of fruits (especially seasonal fruits) due to growth seasons, weather patterns, regional differences, perishability, and other reasons. Some solutions include prioritizing fruit wastes from non-seasonal fruits as feedstock, using fruit wastes from alternate fruits as feedstock during off-seasons, storing food waste in significant amounts under suitable conditions (drying and ensilage) during harvest season, and using more adaptable integrated multifeedstock biorefinery approaches (Leong and Chang 2022).

14.3.3 Effect of Preservatives and Pesticides

More research is needed on the effects of chemical additions, preservatives, and pesticides on the valorization of fruit wastes (Leong and Chang 2022).

14.3.4 Use of Land

It takes a lot of space to completely replace biomass with chemicals, fuels generated from petroleum, polymers, etc. The main objective is to reduce waste biorefinery's land use (Senthil Kumar and Yaashikaa 2020).

14.3.5 Predictable R&D Ventures

FPW has a lot of potential for producing a variety of products with added value. However, the reviewed data do not include any in vivo investigations; they are only based on in vitro trials. Despite the fact that in vitro technologies for extracting value-added products are widely developed, finding ways to implement these on an industrial scale is still difficult. However, many of innovative products are still in the early stages of development. Consistent assistance is essential for logical understanding and innovative developments in biorefinery yield-producing approaches. Government, academia, and business made significant improvements in feedstock and biorefinery development (Senthil Kumar and Yaashikaa 2020).

14.3.6 Pretreatment

The pretreatment operation is the most expensive yet critical for improving enzyme accessibility during saccharification, exposing cellulose, breaking down lignin structure, modifying structural and chemical characteristics, and breaking down cellulose crystallinity. To facilitate enzymatic hydrolysis and other downstream operations, the sugar-based biorefinery platform requires pretreatment of refractory lignocellulosic materials. Pretreatments for lignocellulosic biomass can be physicochemical, physical, chemical, or biological. Most pretreatment methods have features that make them appealing for scale-up applications, but one method cannot be used for all feedstocks, and there is limited literature on "green" processes. Interest in more recent pretreatment methods, such as ionic liquids and deep eutectic solvents, is growing; however, the large number of studies on steam explosion, organosolv, and other methods indicates that they will continue to play an important role in the planning of future full-scale biorefineries (Capolupo and Faraco 2016; Galbe and Wallberg 2019; Ruiza et al. 2020).

14.3.7 Multiple Products

The use of FPW as a feedstock for the extraction of valuable components is currently restricted. Benefits could be achieved from utilizing biomass in its entirety in the creation of bioenergy and high-value, low-volume products. It is important to look at the value-added chemicals that are made by the integrated biorefinery. These chemicals help the refineries make fuel and electricity, both economically and technically. FPW can be utilized as a single starting material in an integrated biorefinery model to recover and produce coproducts. Sustainable use of all resources can be achieved by more effective and comprehensive usage of biomass in food production. Fertilizers, water, soil health, efficient land management, and power are among these resources. Future biorefineries using FPW have the potential to produce bioenergy and biologically active molecules at the same time (Fernando et al. 2006; Banerjee et al. 2017; Manhongo et al. 2022).

14.3.8 Standardization of Biorefinery

The concept of a biorefinery is still in its early stages. If standards aren't already in place, they need to be made for the products made by biorefineries as soon as possible, so that the intermediate products vary as little as possible and can be used with other technologies. One thing that needs to be thought about carefully is whether modern biorefineries should be set up to make a whole new line of chemicals or products, like platform chemicals that are the building blocks for high-value chemicals, or whether they should be set up to make raw materials that could be used as starting feedstock for refineries or chemical plants that already exist. Standardizing biorefinery product quality requirements earlier on minimizes variability. Standardization will focus future research on quality products and helps in identifying these minimum features is a difficulty due to the subject's multidisciplinary nature. It should be done in close coordination with petroleum engineers, bioenergy engineers, chemists, and biologists (Fernando et al. 2006).

14.3.9 Use of Technologies

Currently, fruit waste valorization strategies are underutilized and not widely acknowledged due to doubts about their efficiency and economic viability. The production, quality, sustainability, and economic viability of fruit waste value-added products can be enhanced by technological advances such as big data analytics, AI-assisted technologies, advances in biotechnologies, and bioreactor engineering (Leong and Chang 2022). A reliable, cost-effective, and hassle-free supply of FPW is required for its use in both animal feed and industrial-scale manufacturing of value-added products. Because of a lack of expertise in handling, processing, and transportation, long-term storage is impossible. The development of real-time data on the availability of BP and the mapping of sources using GIS is therefore necessary (Pathak et al. 2016).

Use of Tools: Process simulation and economic analysis tools can help evaluate biorefinery setups; it enables research and development to increase economic viability. Biorefineries must be sustainable so economic gains don't trump environmental and/or social harms and sustainability assessments followed by standard assessment procedure should be followed, accordingly (Senthil Kumar and Yaashikaa 2020; Manhongo et al. 2022). It is evident that the Sustainable Development Goals (SDGs) as stated by the United Nations cannot be achieved by merely working on the economic viability of any product or process. Factors such as environmental and social need to be considered particularly for development of biorefineries. Development of a sustainable biorefinery schemes has put forth several cross-domain challenges such as energy savings, supply chain, environmental emissions, and social impacts. The overall sustainability of the biorefinery can be based on economic, environmental, and social parameters. There are significant number of tools and correlations available for evaluation of techno-economic evaluations. Many researchers have developed biorefinery-specific techno-economic assessment models used for different biorefinery schemes (Klein-Marcuschamer et al. 2011; Vlysidis et al. 2011; Wang et al. 2015). Use of proprietary softwares such SuperPro Designer® a simulation software for techno-economic analysis of chemicals processes is used for many bioprocesses (Flora et al. 1998; Thomsen et al. 2011; Harun et al. 2019; Canizales et al. 2020).

The feedstock of biorefinery being degradable in nature and emissions caused in processing of such feedstocks for value-added chemicals needs to be evaluated and compared with conventional production schemes. Life cycle assessment is a tool that quantifies such environmental emissions over the entire life cycle of the product (Lindeijer and Guinée 2002). Proper life cycle monitoring and modelling are needed to understand the social, environmental, and economic implications of biorefineries. Life cycle assessments should be done from biomass assets through the product's end. Biorefineries vary in feedstocks, methods, and output. Most biorefinery ecological maintainability assessments include economic factors like greenhouse gases release and energy demand. Eutrophication, water shortage, fermentation, and biodiversity effects should be added to the manageability assessment for a more complete picture of ecological sustainability. Environmental impact assessment, process design, and simulation can be used to minimize risk early on. Techno-economic, socio-economic, life cycle, exergoeconomic, and exergoenvironmental analyses can be used to analyze biorefinery sustainability (Manhongo et al. 2022; Senthil Kumar and Yaashikaa 2020).

LCA pertaining to biorefineries have been gaining research interest across different domains of engineering. Few recent literatures cites use of LCA for evaluation of environmental emissions of chemical processes including biorefinery (Joglekar et al. 2019a, b).

Social life cycle assessment is one such tool that can be employed to evaluate the social/socio-economic impacts of a biorefinery. Since the publication of guidelines for social life cycle assessment of products in 2009, a significant number of SLCAs have been performed in different domains such as supply chain, recycling, tourism, biorefinery, etc. (Petti et al. 2018; Souza et al. 2018). One of the limitations of SLCA is the lack of reliable stakeholder data or social impact assessment data especially during the design phase of biorefinery. However, the implementation of such tool is recommended in the early stages of biorefinery development (Souza et al. 2021).

Authors have developed a methodology that integrates economic, environmental, and social indicators in a scale of 0–1 (0, least desired; 1, most desired). The methodology is based on both multicriteria decision-making and multi-attribute theory. Various biorefinery schemes can be compared on common platform with the help of such methodologies (Joglekar et al. 2022). Other multicriteria decision methods which include PROMETHEE, AHP, MAUT, and ELECTRE can also be employed for environmental decision-making (Kiker et al. 2005).

14.3.10 Pilot Plant Study

Pilot-scale investigations are needed to bridge the gap between lab-scale and commercial-scale applications. Government, academia, and private enterprises may need to spend heavily in cutting-edge research and technology at the lab, pilot, and industrial production stages. Consistent R&D is needed, especially for evaluating and validating new technologies. Mathematical modelling; process simulation; life cycle, techno-economic, and socio-economic analyses; and feasibility studies can be used to evaluate and optimize fruit waste valorization's economic feasibility and eco-friendliness (Saini et al. 2019; Leong and Chang 2022).

14.3.11 Scale Up

Although the extraction procedures were successful in the lab, they will need to be modified significantly before they can be used on an industrial scale. Thermodynamic properties of raw and pretreated FPW, the impact of pretreatment on physicochemical properties such as surface area, particle size, and surface morphology, sustainable techniques for recovering value-added products, key process data for small-to-medium biorefinery facilities related to the real waste generating capacity, and other fundamental engineering factors are all important for scaling up and optimizing processes. Concerns over the uninterrupted supply of raw material and the careful separation of desired components are among the most significant obstacles associated with this challenge (Rivas-Cantu et al. 2013; Pathak et al. 2016).

14.3.12 Biorefinery Size

People have many different ideas about the size of biorefineries that should be in the future. However, scientists predict that biorefineries will be a mix of huge facilities, which can fully capitalize on economies of scale and have more purchasing power when acquiring feedstocks and little plants, which can do the same while utilizing all existing process integration technology. Their optimal size will depend on the feedstock/(s) they process, the location of the facility, and the technologies they employ, which vary depending on the size of the biorefinery. Their best size will be a balance between the cost of transporting pretreated biomass and the cost of processing, which goes down as the size of the biorefinery goes up. Before commercial-scale biorefineries of any size can be built, they need to be based on full-scale technologies that have been tested and shown to work (Clark and Deswarte 2008).

14.3.13 Waste Disposal

After extraction or conversion of value-added goods, a thorough research must be conducted on the disposal of FPW. After extraction of conversion of single products, the research should be carried out to extract multiple products from the residue so that the biorefinery must generate zero solid waste. In addition, FPW has some calorific value and can be utilized in the biomass gasification of residues created after product extraction. This step is very important toward the green biorefinery approach and minimizing the pollution.

14.3.14 Policies for Farmers

The Common Agricultural Policy has been updated for the implementation of bioeconomy to further the objective of boosting the value of biomass through the provision of financial aid to farmers and the encouragement of the more efficient use of existing resources. In addition to this, policies, rules, benefits, and subsidies for not burning agricultural waste should be implemented. There should also be better availability and leasing of agricultural implements like tools, machines, and equipment. Programs for technology development, improvement, and demonstration should also be supported (Ginni et al. 2021).

14.3.15 Integration Between Policies

In order to accurately predict the future of biorefineries, numerous policies, such as those pertaining to forests, energy, research and development, and chemicals, need to be properly integrated. It would appear that policy domains that are pertinent to the bioeconomy are riddled with an excessive number of conflicts and contradictions. There are two distinct steps that need to be made in order to advance in terms of both infrastructure and capabilities. To begin, create and put into effect financial incentives that are capable of increasing the demand for all kinds of products and services that are based on biomaterials (Palgan and McCormick 2016).

14.3.16 Awareness About FPW

There is already a lot of interest in working with this type of trash because of the emphasis on green chemistry and greener procedures. However, with the support of academic and commercial collaborations, the lack of FPW awareness in underdeveloped nations can be overcome. For the most efficient use of biomass, these enterprises must also consider how they might return valuable nutrients and organic matter to soil once all other usable products have been recovered (Banerjee et al. 2017).

14.3.17 Use of Edible Biomass

A food crisis, a rise in food costs, and an economic imbalance are all real dangers posed by the biorefineries' extensive use of pricey edible biomass. Biorefinery that employs the most abundant and inexpensive nonedible biomass on Earth, lignocellulosic, is the best option. The primary barriers to its wide-scale deployment are the availability of significant volumes of biomass with consistent quality and cost-competitive processing methods (Maity 2015).

14.4 Conclusion

Biorefineries have the potential to play a significant role in combating climate change by increasing demand for sustainable energy, materials, and chemicals. Furthermore, it may contribute in the development of new opportunities, particularly in rural areas where incomes and economic prospects are currently inadequate and may promote the expansion of bio-based enterprises. By drying, size reduction, solvent extraction, fermentation, and pyrolysis, FPWs can be converted into a variety of economically viable compounds with improved nutritional, medicinal, and antioxidant qualities. Although the extraction procedures worked well in the lab, they must be scaled up to the industrial level. Major impediments to solving this problem include issues with ongoing raw material availability and selective separation of needed components. These materials' energy efficiency is low due to their high moisture content. As a result, newer and more advanced methods for conversion should be created. It is observed that FPW serves as a valuable bioresource for biofuel, biochemicals, and biomaterials. For optimized and economical utilization of these bioresources, an integrated biorefinery approach is proposed. However, there are significant challenges ahead for conversion of FPW into value-added products in full extent. To overcome these challenges, a proper scheme and technologies should be established. Therefore, reuse FPWs has potential to produce useful and profitable products thus, generating "wealth from waste."

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Tomato Utilization: Techno—Economic and Social Aspects

15

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15.1 Introduction

Tomato (*Lycopersicon esculentum*) belongs to family Solanaceae, which is the most important warm season fruit vegetable grown all over the world. Tomato is the second largest fruit vegetable produced in the globe. In 2020, the worldwide production of tomato was 186,821,216 tonnes harvested on the 5,051,983 ha land (FAOSTAT 2020). Tomato fruits are consumed fresh or cooked on a daily basis, while in the food processing industry, they are used to make products such as pickles, sauces, puree, syrup, paste, ketchup, powder, juice and so on. Because of the presence of different types of polyphenols (antioxidants) such as carotenoids (lycopene and carotene), polyphenolics (phenolic acid—caffeic, chlorogenic, ferulic, and *p*-coumaric acids; flavonoids—quercetin, kaempferol and naringenin) and vitamins, both fresh and processed tomatoes have high nutritional value (C and E) (Savatović et al. 2012; Roja et al. 2017; Dominguez et al. 2020).

From the total produced tomatoes, more than 33% are used in processing industries, which makes them world's leading fruit vegetable for the processing. Once tomatoes are processed in factories, a large amount of waste is made. This waste, called tomato pomace, is made up of the seeds, peel and some of the pulp. It

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makes up about 10–40% of the total amount of processed tomatoes. The wet pomace is made up of 33% seeds, 27% peel and 40% pulp. The dried pomace, on the other hand, is made up of 44% seeds and 56% pulp and peel. These by-products have valuable nutritional compounds like fibres (59.03%), proteins (19.27%), total fats (5.85%), minerals (3.92%), total sugars (25.73%), pectins (7.55%) and antioxidants [on dry weight basis]. Also, there are many valuable compounds in tomato pomace, such as lycopene, which is a strong antioxidant, cutin, which can be used to start making biopolymers, and pectin. Due to the high water content of these by-products, their storage period is very limited. Traditionally, this generated waste is utilized for animal feed, fertilizer or in some cases landfilled (Kaur et al. 2008; Savatović et al. 2012; Luengo et al. 2014; Roja et al. 2017; Casa et al. 2021). According to Silva et al. (2019), dietary fibre had the most nutrients (50.74 g/100 g dw), followed by proteins (20.91 g/100 g dw) and fat (14.14 g/100 g dw). While measured with the TEAC assay (224.81 mol Trolox equivalent/100 g dw), the pomace has a high in vitro antioxidation capacity. This waste product has a lot of potential as a source of high-value nutrients, especially dietary fibre and lycopene (Silva et al. 2019).

Tomato seeds have higher bioactive compounds (polyphenols, carotenoids, proteins, minerals, fibres and oil), while peels are rich in lycopene. Flavonol glycosides (quercetin and kaempferol) are in a concentrated form in tomato peel (Chérif et al. 2010; Savatović et al. 2012; Noura et al. 2018; Lu et al. 2019). Also, the compounds like lycopene, β-carotene, lutein and other phenolic substances are present in tomato peels (Szabo et al. 2019).

The industrial processing of tomatoes results in the generation of a significant quantity of pomace, the vast majority of which is not converted to the best available use. This not only results in the loss of important resources but also increases the strain that is imposed on the environment (Lu et al. 2019). According to literature some other products can be obtained from tomato and its wastes which have higher value than the traditional products and include carotenoids (lycopene and β-carotene), seed oil, pectin and products by fermentation. This chapter gives general overview of tomato valorization, back-of-the-envelope calculations for equipment costing and research challenges.

15.2 Valuable Products by Tomato Food Processing

Processed tomato food products available in the market are of following categories: canned, paste form, powder form, additives, ready to cook, ready to consume, personal care and ready to eat. Processing enhances the value of tomato by about three orders of magnitude 1000. Table 15.1 lists various products produced by processing tomato. The real challenge lies in consistency in quality, shapes and sizes of tomato to be used for food processing sector.

Because of defined product specifications, approximately 68.6–86.7% of undamaged, edible, harvested tomatoes are rejected as outgrades and discarded. Sometimes these are rejected on the basis of their shapes (odd shaped, too large or too small), or if they have some marked. 71.2–84.1% of tomatoes were not harvested because the

Table 15.1 Various products produced by processing tomato

Tomato form	Uses
Canned/dried	Whole peeled, stew tomato (cooked and canned), crushed, fire roasted, dehydrated flakes, sun-dried, freeze dried
Paste form	Curries, gravies, puree, sauce, ketchup, chutney, dips, pickle, pesto
Powdered form	Dehydrated tomato powder, ready masalas, soup powder, seasonings/ sprinklers
Additives	As preserves, food colour, food flavour
Ready to cook	Sambhar, powder paneer gravy, tuna chunks in sun-dried tomatoes
Ready to consume	Dips, juice/health drink, soup powder, tomato ice cream, flavoured cheese, tomato spread for pizza, pasta sauce, tomato glaze
Personal care	Face pack, whitening/age cream, sunburn mask, lipstick
Ready to eat	Crunchy fried green tomatoes, flavoured chips, flavoured sev, puree for infants, tomato bread

costs of harvesting and delivering them to market exceeded any profit. With only 44.1% and 59.7% of harvestable tomatoes reaching customers in the two supply chains analysed, a food 'waste' chain may be more appropriate than a food 'supply' chain (McKenzie et al. 2017). Hence there is a need to find alternate valorization options for tomatoes which are 'not-so-good' for food processing and even waste of tomato processing industry. Following section deals with extracting valuable derivatives from tomato which include biochemicals, bioenergy, biofertilizer and animal feed.

15.3 Valorization of Tomato Processing Unit (TPU) Waste

The waste obtained from TPU (seeds, peel and pomace) contains various bioactive compounds which can be converted into high-value products. Figure 15.1 demonstrates all possible utilization of TPU waste. The following section explains the new products that can be obtained from tomato.

Advanced valorization strategies that are based on green chemical technologies and use both bio- and chemo-technological protocols are better from an economic and a sustainability point of view (Driouich et al. 2016).

15.3.1 Production of Carotenoids

Carotenoids are found in high amounts in tomatoes (90–180 mg/kg), mostly in the form of lycopene (80–90% of all carotenoids) and β-carotene (2–3% of all carotenoids). There are also small amounts of other carotenoids like α-, γ- and ϵ-carotenes, phytofluene, phytoene, neurosporene and lutein. Lycopene and beta-carotene are natural colourants that can be added to processed foods to make them look better. These colourants are used in butter, popcorn, salad dressings and beverages and are available in wide range of colours (from yellow to red). Lycopene

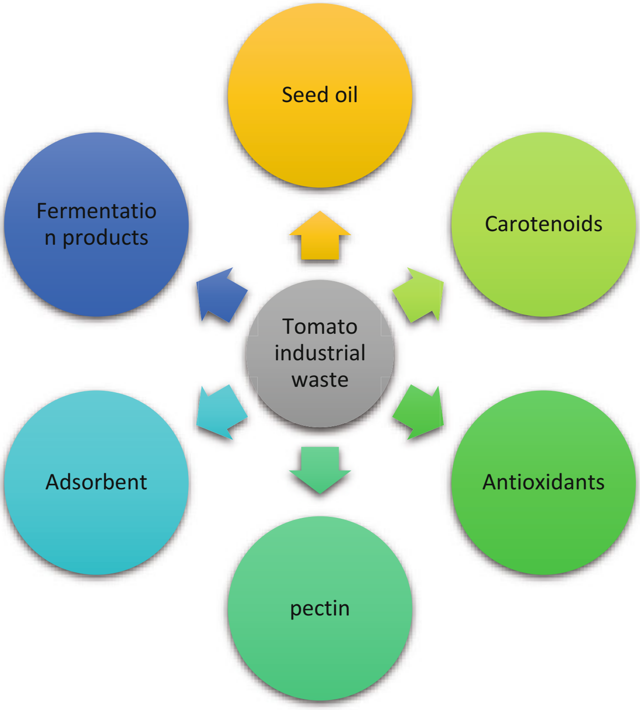

Fig. 15.1 Valorization of tomato TPU waste

has colour intensity six to eight times greater than that of β-carotene (Sabio et al. 2003, Strati and Oreopoulou 2011a, b, Luengo et al. 2014). The colour comes from conjugated double bonds, which also give carotenoids their ability to fight free radicals. Carotenoids also have some health benefits, such as the possibility that they could prevent chronic diseases such as skin cancer, prostate cancer and atherosclerosis, modulate the immune system, have provitamin A activity and reduce in cardiovascular disease (Chiu et al. 2007; Strati and Oreopoulou 2011a, b; Luengo et al. 2014). So, if TPU waste could be used to make carotenoids (lycopene) powder, it would be very helpful for the food and health industries (Chiu et al. 2007). But large amount of carotenoids are lost at the time of industrial processing of tomatoes (Kaur et al. 2008). The usage of natural colour compounds in the cosmetic, food and pharmaceutical industries has raised the importance of these carotenoids (Sabio et al. 2003; Trombino et al. 2021).

The lycopene content in the tomato varies with variety (generally genetic factors), season, environmental conditions, age and maturity. The water-insoluble component in the peel accounts for 72–92% of the lycopene. Hence, lycopene content is higher in tomato peel than the other parts. For extraction of lycopene from peel, which is the part of pomace, is firstly separated by the techniques of floatation-cum-sedimentation from other constituents like seed and fibrous matter for better colour pigment extraction. The high water content in the fresh peel helps in microbial proliferation and spoilage; hence, for extraction of lycopene, dried peels are preferred (Kaur et al. 2008).

In recent studies for better extraction of lycopene from tomatoes, advanced methodologies such as CO_2 supercritical extraction, microwave extraction, ultrasonic, homogenizer heating and enzymatic extractions were applied. In a flow apparatus, Nobre et al. (2009) used supercritical CO_2 to get trans-lycopene from TPU wastes (skins and seeds). At 60 °C, 300 bar, 0.59 g/min solvent flow rate, 0.36 mm particle size and 4.6% feed moisture content, 93% of the trans-lycopene was extracted (Nobre et al. 2009). At 300 bar and 80 °C, using about 130 g of CO_2 per gramme of matrix at the lower CO_2 flow rate, Sabio et al. (2003) extracted 80% of the lycopene and 88% of the β-carotene (Sabio et al. 2003).

Driouich et al. (2016) used three solid-phase extraction methods: ultrasonic, microwave and moderate-temperature homogenizer heating. The research explored the effects of solvent polarity, solid-to-liquid ratio, temperature and time on lycopene extraction. It was observed that at 50 °C, 1 bar pressure, 30 min of time using food grade ethanol the extraction was maximum. Lycopene remains stable if mixed with olive oil (as a natural antioxidant) while gets 80% degraded if exposed to day light at 25 °C for 1 month (Driouich et al. 2016).

Lazzarini et al. (2022) extracted carotenoids, especially lycopene and β-carotene from TPU composed of skin and seeds. To reduce volume, weight and water activity of tomato pomace, three distinct drying procedures were used: heat drying, freeze-drying and non-thermal air-drying. Three solvent mixes like ethyl acetate/ethyl lactate, *n*-hexane/acetone and menthol/lactic acid with distinct drying techniques. Overall, non-thermal air-drying produced the greatest levels of lycopene (75.86 g/g dried sample) and β-carotene (3950.08 g/kg dried sample) of all the extraction methods (Lazzarini et al. 2022).

According to Choudhari and Ananthanarayan (2007), the enzyme-assisted extraction of lycopene under optimized condition enhances the yield. The enzymes cellulase yielded 132 lg/g of lycopene with the enhancement of 198% yield while with the enzyme pectinase it was 108 lg/g with increase of 224% from whole tomato (Choudhari and Ananthanarayan 2007).

Nour et al. (2015) found that the dry TPU waste can be used to supplement wheat flour at 6% and 10% levels (w/w flour basis) in bread making. Addition of dry TPU waste in bread (not more than 10%) shows good sensory characteristics and overall acceptability (Nour et al. 2015).

In addition, because lycopene is fat-soluble and water-insoluble, it is more easily extracted using organic solvents such as hexane, ethanol, benzene petroleum ether, acetone and chloroform. Because alternative components, such as tetrahydrofuran and diethyl ether, may contain peroxides and can react with carotenoids, a mixture of hexane with ethanol/methanol/acetone is typically recommended. Similarly, lycopene is more stable in extracts obtained with hexane/acetone or hexane/ethanol than in extracts obtained with other organic solvents (chloroform, methanol or dichloromethane) (Kaur et al. 2008).

15.3.2 Seed Oil

The tomato seeds are another valuable product obtained from TPU waste. The seeds contain crude fat (2.1%), crude fibre (28.3%), ash (5.8%), carbohydrates (4.1%) and crude protein (29.8%); the detail composition is given in Table 15.2. These seeds are good source of edible oil (about 20%) and can be extracted by simple extraction methods. The extracted oil contains high amount of unsaturated fatty acids and can be used for cooking. Also, tomato seed oil is a bioactive-rich edible oil with added health benefits that can be used in functional foods as well as for nutritional or industrial purposes (Lazos et al. 1998; Botineștean et al. 2012; Botinestean et al. 2014; Szabo et al. 2021).

Szabo et al. (2021) found Linoleic acid was the most abundant fatty acid in tomato seed oil (61.73%), while syringic acid looked to be one of two major

Table 15.2 Characteristics of tomato seed oil (Zuorro et al. 2012)

Fatty acid composition		Total sterols and sterol composition (wt%)			
Myristic (C14:0)	0.14 ± 0.02	Cholesterol	7.5 ± 0.4	β-Sitosterol	58.4 ± 1.8
Palmitic (C16:0)	15.13 ± 0.23	Δ7-Cholesterol	1.0 ± 0.1	Sitostanol	1.2 ± 0.2
Palmitoleic (*cis*-9 C16:1)	0.38 ± 0.05	24-Methylene cholesterol	0.3 ± 0.1	Δ5-Avenasterol	9.5 ± 0.4
Stearic (C18:0)	5.82 ± 0.16	Campesterol	5.7 ± 0.3	Δ5,24-Stigmastadienol	0.9 ± 0.3
Oleic (*cis*-9 C18:1)	21.19 ± 0.45	Campestanol	0.4 ± 0.1	Δ7-Stigmastenol	0.2 ± 0.0
Linoleic (*cis*, *cis*-9,12 C18:2)	54.82 ± 1.51	Stigmasterol	11.3 ± 0.5	Δ7-Avenasterol	0.2 ± 0.0
Linolenic (*cis*, *cis*,*cis*-9,12,15 C18:3)	1.98 ± 0.06	Δ7-Campesterol	0.8 ± 0.1	Total (mg/kg)	3979 ± 10
Arachidic (C20:0)	0.45 ± 0.03	Clerosterol	0.9 ± 0.2		
Eicosenoic (*cis*-10 C20:1)	10 ± 0.02				
Physicochemical properties and tocopherol content					
Acidity (as oleic acid) (wt%)	1.6 ± 0.1	α-Tocopherol (mg/kg)	25.7 ± 0.3		
Peroxide value (mEq/kg)	2.0 ± 0.1	γ-Tocopherol (mg/kg)	1244.6 ± 6.0		
Refractive index	1.4728 ± 0.0001	δ-Tocopherol (mg/kg)	6.4 ± 0.2		
Total tocopherols (mg/kg)	1276.7 ± 5.9				

phenolic acids detected in the cold break process (Szabo et al. 2021). According to Zuorro et al. (2012), the seed cake obtained after oil extraction is rich in protein (38.4 wt%) and crude fibre (17 wt%) with low ash content (1.9 wt%), and it also contains amino acids (Glu, Asp and Arg were major amino acids while Met was the less abundant). The oil content of the cake was found to be 17.9 ± 0.2 wt%.; this value suggests the use of this de-oiled cake for food fortification or other nutritional applications (Zuorro et al. 2012).

15.3.3 Antioxidants

TPU waste consists of considerable amount of polyphenol (151.60 mg/100 g). The extracts of tomato waste have significant amount of phenolic antioxidants and showed good antioxidant properties. Because of the substantial antioxidant and antiproliferative activity, TPU waste is considered as potential nutritive resource which is capable of providing significant low-cost, nutritional dietary supplements (Ćetković et al. 2012). Solvent extraction, ultrasonic and microwave-assisted extraction methods with various hydrophilic and lipophilic solvents like distilled water, ethanol, isopropanal, ethyl lactate, ethyl acetate and *n*-hexane can be employed to extract different antioxidant compounds (El-Malah et al. 2015). The real challenge lies in selective extraction of an individual polyphenol. According to Gomes et al. (2022), ultrasound showed promise for extracting total phenolic components from TPU, permitting the synthesis of antioxidant-rich extracts with reduced extraction time makes ultrasound more efficient (Gomes et al. 2022). The tomato waste has a less antiradical activity as compared to tomato concentrate but also higher than that of the juices (Chérif et al. 2010; Savatović et al. 2012; Noura et al. 2018). The higher the microwave power, the higher the extraction temperature, which increased the solubility of bioactive chemicals, as determined by Lasunon et al. (2021). However, increasing the microwave power may degrade the purpose chemicals, rendering them less active. Also, the more time is spent extracting, the more bioactive compounds are taken out. However, if the microwave power goes up or the extraction time goes up, the bioactive compound could be damaged. In terms of the antioxidant, the conditions of extraction made it less effective as an antioxidant. The microwave condition that produced the bioactive molecule had less antioxidant activity. Bioactive chemical type determines optimal conditions. A 300 W extraction for 60 s offered the best quality for both hydrophobic and hydrophilic fractions, according to the overall performance index (Lasunon et al. 2021). Grassino et al. (2020) used high-hydrostatic pressure extraction as an alternative to standard thermal treatment for the extraction of polyphenols from TPU generated from canning industry. Due to its high recovery and low time investment, high-hydrostatic pressure extraction is judged suited for the recovery of polyphenols from thermoplastic polyurethane (TPU) (5 min). Combining 50% and 70% methanol with 45 and 55 °C yields the most effective extraction. Despite this, its application is hindered by its lack of food grade quality (Grassino et al. 2020).

According to Szabo et al. (2021), carotenoids, phenolic compounds and fatty acids were impacted by industrial pretreatments in TPU, particularly cold break (at 65–75 °C) and hot break (85–95 °C) operations (Szabo et al. 2021). Additionally, Szabo et al. (2019) evaluated ten tomato varieties based on their carotenoids concentration, phenolic composition and antioxidant and antibacterial activity. Despite the fact that each variety was grown and processed under identical conditions, the results reveal substantial variances. The results demonstrate that variety has a significant impact on the bioactive component of tomato peels. Tomato peel methanolic extracts exhibited antibacterial efficacy against *S. aureus* and *B. subtilis* strains, and some kinds were also efficient against *E. coli* (Szabo et al. 2019).

15.3.4 Fermentation Products

TPU waste can be converted into value-added products via fermentation route. The valorization via this route is economically beneficial to enhance the industrial and farmers economy.

The production of lactic acid via fermentation route is one of the important applications. Carillo et al. (2018) provided the material balance for the production of lactic acid from TPU waste (mainly tomato pomace) and evaluated that about 0.07–0.14 kg of lactic acid can be produced per kg of pomace. That is about 152 kilotonnes (kt) of dried pomace can produce 10.6 kt to 21.2 kt of lactic acid (Carillo et al. 2018).

TPU waste was used as a co-substrate to increase the feasibility of the process. Belhadj et al. (2014) examined the methane production from a mixture of 95:5 (wet weight) sewage sludge to tomato waste. The methane yield coefficient was 159 L/kg VS at 0 °C, 1 atm, and the mixture displayed a high anaerobic biodegradability of 95% (in VS) (Belhadj et al. 2014). Hills and Nakano (1984) studied the effect of particle size (1.3, 2.4, 3.2, 12.7 and 20 mm) on methane gas production in laboratory digesters (4 L operating volume) for 18 days. The highest gas production was obtained with the particle size of 1.3 mm. In this case, the substrate makes 0.81 volume of methane per volume of digester per day, and there is a 60.3% reduction in volatile solids. The amount of methane gas made is inversely related to the average size of substrate particles and their shape (sphericity) (Hills and Nakano 1984). Sarada and Joseph (1994) studied the effects of HRT, loading rate and temperature on methane production from TPU waste during anaerobic digestion. Total gas yield (0.7 ms) and methane yield (0.42 m^3/kg) were highest during 24 days HRT, 4.5 kg/m^3 loading rate, at 35 °C. The stable digitation was obtained up to 40 °C, while higher temperature 45 °C was unfavourable for methanogenesis (Sarada and Joseph 1994). According to Szilagyi et al. (2021), the biomethane potential of corn stover, tomato waste and their combination were similar, around 280 mL methane/g volatile solid. In a continuous mesophilic anaerobic digestion system, corn stover, tomato waste and their mixture produced 860 ± 80, 290 ± 50 and 570 ± 70 mL biogas/g volatile solid/day, respectively, having 46–48% methane. Also, tomato waste may suppress the growth of microbes as it contains antibacterial and antifungal compounds such flavonoids and glycoalkaloids (like tomatine and tomatidine). In batch fermentation trials, tomatine reduced biogas yield. Metagenomic study showed that tomato plant waste rearranged microbial populations in continuous reactors. For continuous anaerobic fermentations, tomato waste was shown to be a good co-substrate with corn stover at a 2:1 ratio (Szilagyi et al. 2021). Girotto et al. (2020) studied the effect of ultrasound pretreatment on tomato pomace prior to anaerobic digestion. After 4 and 22 days of anaerobic digestion, the substrate pretreated for 15 min with an ultrasonic wave amplitude of 152 m (0.9 W/mL) produced methane yields that were 18.9% and 5% higher, respectively. The highest theoretical maximum methane production rate (224.4 m^3CH_4/tVS/day) determined using the modified Gompertz model with 15-min ultrasonic pretreatment at 152 m amplitude was 89.7% quicker than the control (118.3 m^3CH_4/tVS/day). The energy evaluation, on the other hand, showed that the energy needed for ultrasound pretreatment was more than the extra energy made by the higher methane output (Girotto et al. 2020).

To improve the nutritional value of tomato pomace from TPU, solid state fermentation (SSF) was conducted with various lactic acid bacteria, including *Lactobacillus plantarum*, *L. acidophilus* and isolate *Lactobacillus* spp. and yeast strains, including *Saccharomyces cerevisiae*, *S. boulardii* and isolate *Saccharomyces* spp. Tomato pomace fermented with lactic acid bacteria strain (*L. plantarum*) and yeast strain (*S. boulardii*) was more successful in reducing total soluble solids (TSS) (1.37% and 1.50%) and pH (4.54% and 4.31%) and enhancement in protein (16.15% and 17.89%), titrable acidity (1.16% and 1.78%), fat (9.54% and 9.77%) and energy (223.31 and 230.16 kcal) along with minerals Mg (342.67 mg and 342.33 mg/100 g), P (95.33 mg and 91.67 mg/100 g), Ca (413.33 mg and 422.33 mg/100 g), and Fe (15.00 mg/100 g and 13.67 mg/100 g), respectively, in the tomato pomace. The results confirm that the fermentation of tomato pomace by lactic acid bacteria and yeast enhances the nutritional properties and reduces fibre content and is a good source for animal feed supplement (Roja et al. 2017).

15.3.5 Pectin Production

Pectin is the material having lot of industrial applications. These are mainly used in food industry as stabilizers and thickener in jellies, jams, fruit juices, confectionery products and medicine. The tomato peel is the potential source of pectin with a yield of 15.0% by solvent extraction. Changing the processing parameters (appropriate extraction duration, pH, origin of extracted material, temperature, material-to-solvent ratio and number of extractions) of pectin extraction processes can improve pectin quality and yield (Grassino et al. 2016). Also the ultrasound-assisted extraction of pectins shows less time of extraction as compared with conventional solvent extraction for the similar pectin yield (Grassinoa et al. 2016).

Pectin extraction from industrial tomato waste was explored by Lasunon and Sengkhamparn (2022) using ultrasound-assisted, microwave-assisted, and ultrasound-microwave-assisted methods. The result showed the optimum conditions for ultrasound-assisted extraction of pectin were pH (1.5) and solid-liquid ratio (1: 30) at 80 °C and 20 min for high pectin yield and high total carboxyl group and lycopene content. In order to extract the most galacturonic acid and lycopene from the pectin, a power of 300 W and a period of 10 min were used. Ultrasound-microwave-assisted pectin extraction considerably synergizes pectin yield and galacturonic acid content, yet lowers harshness while enhancing pectin production (Lasunon and Sengkhamparn 2022). Sengar et al. (2020) also studied five different extraction methods which were used to get the pectin extraction from TPU waste. In order to better understand the kinetics of extraction and degradation, a variety of extraction methods, including ultrasound-assisted microwave extraction, ultrasound-assisted ohmic heating extraction, and ultrasound-assisted microwave extraction, are being tested at various power levels. Both quantity and quality were improved by using lower-energy ultrasound and microwave extraction, according to the results. As a food additive, pectin produced from TPU meets all of the standards. The amount of pectin that could be extracted ranged from 9.30% with ohmic heating to 25.42% with a microwave. Also, there wasn't much difference between the yields of pectin extracted by microwave-assisted extraction and ultrasound-assisted extraction, but the degrees of esterification were 59.76 ± 0.70% and 73.33 ± 1.76%, respectively. Also, all of the pectin that was extracted under optimal conditions was clean enough to use. The amount of galacturonic acid in the pectin ranged from 675.8 ± 11.31 to 913.3 ± 20.50 g/kg (Sengar et al. 2020).

Halambek et al. (2020) found that pectin extracted from inexpensive tomato peel waste from the canning industry might be used as an environmentally friendly corrosion inhibitor for tin. This is in line with sustainability trends in the food processing industry of recycling and reusing compounds with added value. As the concentration of the pectins (0.1–20 g/L) goes up, their ability to stop tin from corroding goes up. After 24 h of tin immersion in apple pectin and tomato peel waste, the highest values of 75.9% and 73.9% are found, respectively. In the end, the similar values found for apple pectin and tomato peel waste, as well as the good agreement between the methods used, showed that pectin isolated from tomato peel waste can stop tin from rusting in a harsh, acidic food-like solution (Halambek et al. 2020).

15.3.6 Water Treatment Agent

TPU waste is a potential adsorbent for wastewater treatment containing heavy metal and dyes.

Yargıç et al. (2015) studied the removal of copper (II) ion from aqueous solutions with HCl treated TPU waste. At pH 8 the maximum metal removal was achieved as 92.08% (Yargıç et al. 2015). Also NaOH-treated tomato waste was showed good efficient in removal of Pb(II) (152 mg/g) (Heraldy et al. 2018). In addition with this Saygılı and Güzel (2016) evaluated the $ZnCl_2$-activated TPU waste for the treatment of removal of cationic and anionic dyes containing waste water. The carbon obtained has surface area of 1093 (m^2/g), total pore volume of 1.569 (cm^3/g), mesoporosity (91.78%) and average pore diameter (5.92 nm). The maximum adsorption capacity was obtained as 400 mg/g and 385 mg/g for methylene blue and metanil yellow, respectively (Saygılı and Güzel 2016). Mutavdžić Pavlović et al. (2021) used tomato waste for removal of five pharmaceuticals like praziquantel, dexamethasone, febantel, tylosin tartrate and procaine from water and obtained the removal efficiency of 449 μg, 461 μg, 524 μg, 677 μg and 1230 μg, respectively, with 1 g of tomato waste (Mutavdžić Pavlović et al. 2021).

Thus, TPU waste can be a low-cost biosorbent for removal of contaminants from wastewater.

15.3.7 Biofilter

Pereira et al. (2021) used a biofilter media made of tomato waste to reduce NH_3, N_2O, CO_2 and CH_4 losses from pig slurry. The results showed that adding oxalic acid to biofilter media mixes raised the amount of NH_3 that was retained from 51–77% to 72–79%. Also, biofilter media combinations with and without oxalic acid showed that they could keep CH_4 (29–69%) but not N_2O, which had no effect on the chance of global warming. Tomato-based biofilters help reduce slurry gas emissions (Pereira et al. 2021).

15.3.8 Compost

Kakabouki et al. (2021) used waste from making tomato sauce mixed with organic fertilizers to make a fertilizer. Overall, the results of study showed that mixing processing tomatoes with organic fertilizers made a big difference in soil quality, plant growth, yield and processing tomato quality. It was said that putting down a mixture of manure and compost helped total porosity the most. Arbuscular mycorrhizal fungi went up a lot when organic blends were used. Glomalin, an important part of soil organic matter, was made by a lot of arbuscular mycorrhizal fungi, so the quality of the soil is getting better. According to results, the nitrogen source and nitrogen fertilization rates both had a big effect on the plant growth and total yield of TPU. By using organic blends, the soil's physical properties, like how porous it is and how hard it is to dig into, were improved. Also, the amount of nitrogen in the soil ranged from 0.10% (control and NPK) to 0.13% (Tomato pomace and Farmyard manure). The yield improved a lot because of the amount of nitrogen in the soil and the number of roots. Overall, the amount of soil N improved, and so did the amount of total soluble solids. Thus, using tomato pomace with organic fertilizers enhanced soil quality and increased yield (Kakabouki et al. 2021).

15.3.9 Biofilms

Poly(vinyl alcohol) was mixed with itaconic acid, chitosan and TPU extract to make active films to make new bioactive formulations for food packaging films. The TPU-enhanced poly(vinyl alcohol) (3% wt/v) and chitosan (1% wt/v) films exhibited excellent antibacterial activity against *S. aureus* and *P. aeruginosa*, with a minimum inhibitory concentration (MIC) of <0.078 mg dw/mL and significant antimicrobial effects against all tested strains. By making the poly(vinyl alcohol) films brittle, itaconic acid and chitosan rendered them less transparent and more rigid. The addition of TPU rendered the films slightly stretchy. In addition, the total phenolic content of TPU-enhanced poly(vinyl alcohol) and chitosan film-forming solutions may exhibit significant antioxidant activity. Because of this, the films made can be used to package a wide range of foods (Szabo et al. 2020).

15.3.10 Nanofluids

Hardian et al. (2021) investigated the performance of $Al(OH)_3$ nanoparticles in nanofluids after using tomato waste extract as a chelating agent in the sol gel process to create them. The crystallite diameters of $Al(OH)_3$ nanoparticles vary by 45 nm, 48 nm and 60 nm throughout the course of 1 h, 3 h and 5 h of calcination, respectively. By reducing the $Al(OH)_3$ concentration in tomato waste extract, it is possible to make nanofluids with improved properties (Hardian et al. 2021).

15.3.11 Dietary Fibre

The large amount of insoluble fibre in tomato peels makes it hard for the body to use the lycopene in them. The amount of lycopene and soluble fibre that can be extracted from tomato peels could be greatly increased by changing the enzymes. Gu et al. (2020) modified the peels by adding 5% (w/v) Viscozyme L solution at pH 6 and a solids-to-liquids ratio of 1:10 (w/v) for 35 min. By using enzymes to treat the tomato peels, they were able to get 72.3% more dietary fibre out of the peels than they did before. Both the original dietary fibre and the enzyme-treated version had the same thermal properties, but the enzyme-treated soluble dietary fibre was better at absorbing water and absorbing glucose. Also, after enzymatic treatment, the tomato peels had 170.67 mg of lycopene per 100 g. This was a 23.8% increase from the original tomato peels. These results show that enzymatic treatment is a possible way to change the way tomato products are made so that peel waste can be used to make functional food materials. As a new food additive, peels that have been treated with enzymes could improve health because they are high in lycopene and dietary fibres (Gu et al. 2020).

15.4 Waste/Rotten Tomato Utilization

According to McKenzie et al. (2017) postharvest losses of tomatoes are found to be in between 40.3% and 55.9% of the total harvestable tomatoes. These waste tomatoes reduce the economy of farmers. The only way to avoid this is to utilize these waste tomatoes to produce some alternative profitable products (McKenzie et al. 2017).

The teams of researchers have found that the waste, damaged, rotten tomatoes can be the good source of electricity (ACS 2016). The researchers at The Ohio State University in the USA have developed a new technique for converting tomato peels into practical replacements for carbon black which is petroleum-based filler (The Economic Times 2017). Another way to use this waste tomato is to convert them into the compost. The rotten or waste tomatoes can also be used to extract extracellular fungal pectinases along with appreciable amount of pectin (Bali 2003).

15.5 Biorefinery Approach

Literature confirms that tomato or their residues are used to make arrays of products which include bio fuel, biochemicals, biomaterials and biofertilizers. Instead of utilizing tomato for a single use, it would be advantageous to build an integrated strategy for numerous applications that ensures economic viability. This integrated strategy is referred to as ‘biorefinery’. Thus, biorefinery has emerged as a concept for the sequential exploitation of biomass that promotes the conversion of all biomass into various biofuels and chemicals.

Tomato biorefinery is technically possible, but for making the process economically feasible, there is a need to extract products which have high market price and market demand. To make tomato biorefinery techno-economically viable product range should be of two types: high volume with low value and high value with low volume.

Figure 15.2 gives the schematic of tomato biorefinery. Based on the schematic of proposed biorefinery, an approximate cost analysis of the equipment required for processing 1000 kg of tomato is listed in Table 15.3.

15.6 Tomato Biorefinery: Technical, Economic and Social Perspective

The variance in tomato pricing in the Indian market is quite surprising and disturbing. Tomatoes are sold 2 Rs at one time of the year, while the same is sold for 50 Rs per kg in retail market. Tomato being an integral part of Indian daily dishes, bouncing of tomato prices between these two extremes is worrisome for tomato producers as well as consumers. This makes tomato prices a very sensitive social-political issue. The country has witnessed agitation by farmers for

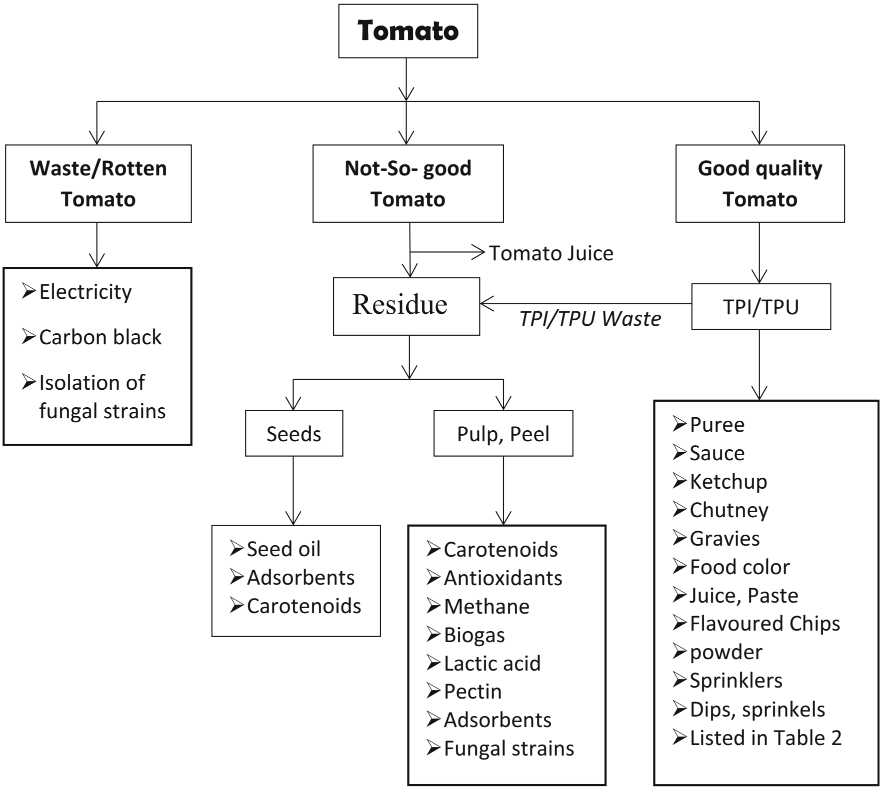

Fig. 15.2 Proposed tomato biorefinery

underpricing while protest by consumers for over pricing during different period of the year countrywide.

The possible solution to this wicked problem is to bracket tomato prices within an acceptable limit. The decision of upper and lower limit of the bracket is a critical multi-criteria decision analysis problem which involves parameters like social, environmental and economic aspects. Tomato has three routes for reaching the market; first is direct sell, and second is as value-added edible products (ketchup, sauce, juice, etc.) and its pomace and third is valuable bio-components (lycopene, etc.). In any agro-based system, raw material is the limiting factor, and in this case also out of the total available tomato at any point of time, the decision of distributing them among the said three routes is a complex multi-objective optimization problem which needs a solution. The optimization problem involves parameters like market demand of tomato and its valuable derivative, manufacturing cost (fixed and operating cost), raw material availability, environmental impacts and man hours of processing. The authors' group has undertaken this study.

Table 15.3 Cost analysis of equipment required for tomato biorefinery

Sr. no.	Equipment name	Sizing	Material of construction	Approx. cost (Rs.)
1	Hydrolyser	Volume 1.77 cu.m	SS-316	265,539
2	Stirrer for hydrolysis	Power load 3 kW	SS-316	50,000
3	Expansion chamber	Volume: 35.44 cu. m	SS-316	1,956,515
4	Mixing vessel	Volume 1.77 cu.m	SS-316	265,539
5	Decanter	Volume: 1.42 cu. m	MS	130,000
6	Fermentor	Volume: 88.60 cu. m	MS	2,042,228
7	Stirrer for fermentor	Power: 110.02 kW	MS	200,000
8	Settler	Volume: 13.29 cu. m	MS	576,543
9	Anaerobic digester	Volume: 80 cu.m	MS	2,861,827
10	Utility section	Piping and pump, boiler, compressor, distillation setup and DCS control and automations and other downstream		

15.7 Proposed Model

A set of unit operations and unit processes involved in sequential extraction of valuable derivative from tomato or as a matter of fact from any fruit/vegetable is almost same. Following is the list of general equipment required for extracting valuable products from tomato.

Table of equipment:

Model 1: A centralized facility, tomato processing unit (TPU) can be created at Tehsil Mandi premises with the support of government and private industry(ies). Land and other logistics support can be provided by the government, while the industrial partner will invest in fixed and operating cost. The local youth can be trained for executing supply chain management and running the plant. A new trait in Tehsil ITI titled 'TOP (tomato-onion-potato) food processing' can be designed and started to develop skilled manpower. The equipment cost and operating cost of a TPU of capacity 1 tonne is around 1.5 Crore.

The TPU can have following products: tomato juice—from tomato pomace—lycopene, carotene and seed oil, by fermentation lactic acid and bioethanol.

Model 2: It's a distributed manufacturing approach based on AMUL cooperative model where either of the products listed under TPU will be produced by a farmer or a group of farmers. Unit operations like solvent extraction, fermentation, oil extraction and pulverization could be handled by village youth trained in the Tehsil ITI. The equipment listed above can be designed and fabricated by frugal approach using resources available locally. The equipment cost of a cottage industry can be limited to 5 lakhs for 50 kg capacity batch.

15.8 Conclusion

Based on the extensive literature survey, it was observed that value-added products can be obtained from tomato by various food processing techniques. With growing urban consumers' food demand, new and value-added products are finding place on the shelves. Tomato through modern processing and distribution network can fetch and enhance value by three orders of magnitude. The tomatoes which are not-so-good quality, instead of food processing, can be used for deriving the products like, carotenoids (lycopene and β-carotene), antioxidants, fermentative products (methane, lactic acid, etc.), seed oil and electricity. The waste of the tomato processing industry can also be valorized by different routes. Back of the envelop calculations suggests that the equipment and the operating cost of tomato processing unit of capacity 1 tonne is about 1.5 crores, while that for cottage industry of capacity 50 kg would be 5 lakhs. The optimum distribution of tomatoes between direct sell through *Mandi* and to food processing unit will stabilize the tomato market.

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