Clean Energy Production Technologies

Series Editors: Neha Srivastava · P. K. Mishra

Pradeep Verma *Editor*

Thermochemical and Catalytic Conversion Technologies for Future Biorefineries

Volume 1

Springer

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Series Editors

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The consumption of fossil fuels has been continuously increasing around the globe and simultaneously becoming the primary cause of global warming as well as environmental pollution. Due to limited life span of fossil fuels and limited alternate energy options, energy crises is important concern faced by the world. Amidst these complex environmental and economic scenarios, renewable energy alternates such as biodiesel, hydrogen, wind, solar and bioenergy sources, which can produce energy with zero carbon residue are emerging as excellent clean energy source. For maximizing the efficiency and productivity of clean fuels via green & renewable methods, it's crucial to understand the configuration, sustainability and techno-economic feasibility of these promising energy alternates. The book series presents a comprehensive coverage combining the domains of exploring clean sources of energy and ensuring its production in an economical as well as ecologically feasible fashion. Series involves renowned experts and academicians as volume-editors and authors, from all the regions of the world. Series brings forth latest research, approaches and perspectives on clean energy production from both developed and developing parts of world under one umbrella. It is curated and developed by authoritative institutions and experts to serves global readership on this theme.

Pradeep Verma
Editor

Thermochemical and Catalytic Conversion Technologies for Future Biorefineries

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ISSN 2662-6861 ISSN 2662-687X (electronic)
Clean Energy Production Technologies
ISBN 978-981-19-4311-9 ISBN 978-981-19-4312-6 (eBook)
https://doi.org/10.1007/978-981-19-4312-6

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Dedicated to my beloved mother

Preface

The rise in global energy needs and fast depletion of the existing conventional fossil fuels force the stakeholders to search for alternatives. Biomass such as food crops, lignocellulosic, algal, and hybrid energy crops can be converted to biofuel and different value-added chemicals, thus acting as a potential substitute for petroleum-based biorefineries. Also, this strategy helps to overcome the pollution caused by the management of this waste generated worldwide. The widespread availability and structural composition of biomass motivated the scientific community to look at it as a potential substrate for the oil and chemical industry. Thus, leading to the development of biomass-based biorefinery. However, the conversion of biomass to high-value products is not as easy as it seems. It involves several stages such as pretreatment, hydrolysis, fermentation, and recovery. The pretreatment and hydrolysis of biomass involve several thermochemical and advanced catalytic technologies. This book will attempt to provide an account of knowledge on biomass available for biomass-based biorefineries. It focuses on understanding the recalcitrance of biomass and how it limits the overall conversion efficiency. It also gives an insight into different conventional approaches available for pretreatment and hydrolysis of the biomass. The chapter deals with highlights on how enzymes can be a powerhouse and play pioneering roles in biomass valorization. The book will also throw light on technical aspects of thermochemical conversion strategies such as pyrolysis, gasification, and organosolv methods. Further the generation of value-added materials such as high-quality bio-oil, biochars, and biobased chemicals are also included in the book. These high-value compounds can be put to widespread application in biofuel, biocatalyst, waste bioremediation (heavy metal removal), air purification, and effluent treatment applications. The book will also provide literature on the limitations of already existing technologies and prospects of each technology. This book is of interest to teachers, researchers, bioenergy scientists, capacity builders, and policymakers. Also, the book serves as an additional reading material for undergraduate and graduate students of energy studies, chemical engineering, biotechnology, and environmental sciences. National and international energy scientists and policymakers will also find this book to be a useful read.

Ajmer, Kishangarh, Rajasthan, India Pradeep Verma

Acknowledgment

First, I would like to convey my gratitude to the series editor Dr. Neha Srivastava and Prof. P.K. Mishra considering the submission of this book entitled *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries-Vol I* under the book series *Clean Energy Production Technologies*. I am thankful to Springer Nature for accepting my proposal to act as editor for this book volume. This volume of the book series is only possible because of the support from all the researchers and academicians who contributed to the book; therefore, the editor is thankful for their contribution. I would also like to thank my Ph.D. scholar, Dr. Bikash Kumar, currently working as a Post-doctoral Researcher at IIT Guwahati for providing me with all the necessary technical support and editorial assistance during the entire stage of book development. I am also thankful to the Central University of Rajasthan (CURAJ), Ajmer, India, for providing infrastructural support and a suitable teaching and research environment. The teaching and research experience at CURAJ has provided the necessary understanding of the needs of academicians, students, and researchers in a book that was greatly helpful during the development of the book.

I am always thankful to God and my parents for their blessings. I also express my deep sense of gratitude to my wife Savita and my son Mohak and daughter Netra for their support during the development of the book and in life.

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Chapter 1
Scope and Characteristics of the Biomass Sources Suitable for Biorefinery Applications

**Azeem Asghar, Muhammad Afzal, Rizwan Haider,
Muhammad Sajjad Ahmad, and Muhammad Aamer Mehmood**

Abstract Biomass-derived biorefineries seem a promising approach for the complete valorization of biomass into bioenergy and a range of bioproducts. However, the product quality and bioprocessing strategy highly depend on the nature, composition, and quality of the biomass feedstock. The source and cultivation conditions do not only affect the quality and composition of the biomass but also affect the cost of biomass. Therefore, the choice of cultivation conditions and selection of biomass suitable for its subsequent use is critically important. Accordingly, residual biomass from agricultural or industrial activities or biomass production on marginal lands using wastewater offers an opportunity to produce low-cost biomass without creating any competition with food or land for food. However, it is important to consider that how these conditions affect the nature and composition of biomass with reference to its downstream processing. This book chapter covers the desired characteristics of the biomass to consider it as a potential feedstock for biorefinery while achieving environmental and economic sustainability.

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
https://doi.org/10.1007/978-981-19-4312-6_1

Keywords Feedstock characteristics · Environmental sustainability · Bioenergy · Biorefinery

Abbreviation

GHG	Greenhouse gases emissions

1.1 Introduction

Urbanization, industrialization, and transportation depend on fossil resources to meet their energy needs (Tey et al. 2021), but their depletion and negative impacts on the environment face challenges in terms of both social and economic impacts (Liu et al. 2021). A strong global dependence and huge consumption of petroleum derivatives are causing political and environmental concerns due to greenhouse gases emissions (GHG) like nitrogen oxides, methane, and carbon dioxide (NO_X, CH_4, CO_2). Accordingly, there has been a rush towards finding alternative resources to fuel the current and rising future needs of liquid fuels. It is believed that biomass is one of the most promising sources, due to its renewable and sustainable nature and is considered a third fuel source used to generate bioenergy, chemical, and industrial products.

Lignocellulosic biomass (the second-generation feedstock) has shown maximum accessibility in subtropical, and tropical macroclimates worldwide with an annual production of 1.3 billion tons, whereas only 3% of it is being used to produce biofuels, bioenergy, and biochemicals (Baruah et al. 2018). Biomass-derived biorefineries are believed to be an encouraging path to develop a new bio-industry by using the plants' biomass for gaining the food, non-toxic and pure feed, and materials for the chemical industries, energy, and other valuable products (Sanna et al. 2016). The selection of the raw material for biorefinery primarily is influenced by the origin and nature of the feedstock. Cultivation conditions affect the composition of biomass which subsequently determines the process parameters for the downstream processing of the biomass. Instead of using freshwater and agricultural lands, biomass for biorefineries can be produced using non-arable lands and urban wastewater. Likewise, integration of the biomass production landscapes with the phytoremediation using floating gardens or constructed wetlands could be a promising green approach to produce biomass as a feedstock for the biorefinery (Zhang et al. 2020). This chapter is focused on the impact of biomass source, its composition, and nature for its utilization as a biorefinery feedstock.

Biorefinery is a multidisciplinary approach that involves the transformation of biomass through sustainable processing to produce biofuels and value-added chemicals with a zero or minimum waste generation, where each by-product of the process is believed to be recycled to ensure environmental sustainability and cost-effectiveness. The biorefinery approach is a range of combined techniques targeting to complete suitable conversion of biomass into their value-added products such as hydrogen, carbohydrates, and proteins, with the simultaneous production of biofuel, bioenergy, and biochemical (Bhardwaj et al. 2021; Carvalho et al. 2014; Kumar and Verma 2021; Verma 2020). Biorefineries need prime conversion efficiency of lignocellulosic biomass, within efficient production of energy (Hirani et al. 2018). The European vision of biorefinery 2030 document entitled supply of the tools and data to enable policymakers to draw a framework for the development of sustainable research based, with a network of refinery playing a vital role (Płaza and Wandzich 2016). Several biorefinery systems are believed to be developed in the future by taking the advantage of modern flexible technologies for efficient biotransformation of biomass into myriads of green products (Panwar et al. 2011). With respect to the technology employed, biorefineries can be categorized as: (i) pyrolysis-based refinery, (ii) fermentation-based refinery, (iii) hydrothermal-based refinery, and (iv) bio syngas-based refinery. All of these are used to produce materials, biofuels, and chemicals from the biomass.

1.2 Low-Cost Sources of Biomass

Production of biomass on agricultural land in huge quantities is a big challenge at present due to scarcity of the fertile soils so marginal lands can be employed for this purpose and instead of freshwater, the bioenergy crops can be cultivated using urban wastewater (Asghar et al. 2021) which offers additional benefits of phytoremediation and mitigating atmospheric carbon (Kurade et al. 2021). Wastewater is often rich in nutrients, where no additional sources (e.g., fertilizers) are needed to achieve higher biomass productivity. Besides, it does not only reduce the cost of cultivation but also does not cause any competition with the freshwater sources and agricultural lands. Another possibility is the integration of biomass production facilities with the wastewater treatment plants. For instance, para grass was cultivated on industrial and urban wastewater using a floating garden system, and it was found that overall biomass productivity was better when compared to the para grass biomass produced on the soil (Asghar et al. 2021; Singh et al. 2022; Agrawal and Verma 2021). Similarly, salt-affected soil was used to produce biomass in huge quantities without any fertilizers, fungicides, or pesticides with low cost and ensure environmental sustainability. The biomass of *Brachiaria mutica* (Asghar et al. 2021), *Typha domingensis*, *Phragmites australis,* and *Leptochloa fusca* (Afzal et al. 2019b) has been cultivated on wastewater and *Parthenium hysterophorus, Pennesetum benthiumo* (Ahmad et al. 2019), *Calotropis procera* (Ahmad et al. 2021), *Urochloa mutica* (Ahmad et al. 2017), and *Cymbopogon schoenanthus* (Mehmood et al. 2017b) have been cultivated on salt-affected soils. The biomass productivities of these grasses on poor soils have shown a promising potential of these soils to produce low-cost biomass (Fig. 1.1).

Fig. 1.1 Global sources of biomass sources for bioenergy production

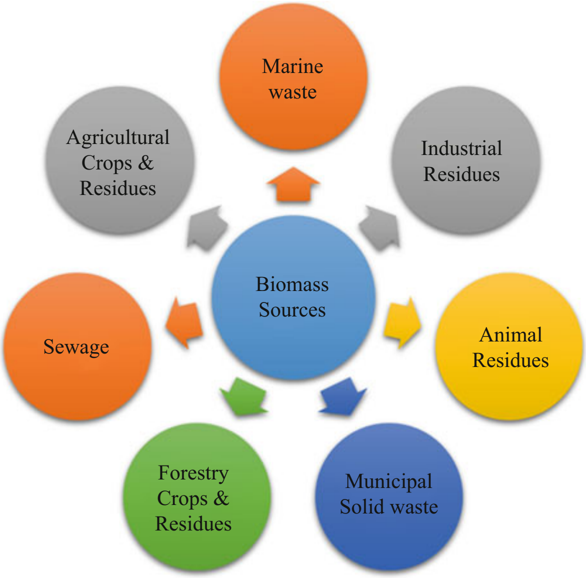

Table 1.1 Different lignocellulosic biomass and their composition

Biomass	Extractives (%)	Hemicellulose (%)	Lignin (%)	Cellulose (%)	References
Pearl millet	4.26	23.16	15.75	48.93	Laouge and Merdun (2020)
Calotropis procera	32.5	33	17.91	16.57	Ahmad et al. (2021)
Ricinus communis	16.40	22.40	20.20	38.42	Kaur et al. (2018)
Sagwan sawdust	11.3	12.9	24.7	51.1	Gupta and Mondal (2019)
Rice husk		17.16	26.26	33.10	Ashraf et al. (2019)
Sunflower disc		14.12	27.87	31.46	Ashraf et al. (2019)

Biomass is either classified according to its composition/characteristics (Table 1.1) or the source (Table 1.2). Low-cost biomass can be obtained through agricultural practices, residues from forestry, industrial wastes, aquaculture, or municipal waste (Poveda-Giraldo et al. 2021). It is estimated that global plant biomass production is around 200×10^9 metric tons where 90% of the biomass is lignocellulosic in nature (Saini et al. 2015). Lignocellulosic biomass mainly comprises three components including cellulose (35–50%), hemicellulose (20–35%), and lignin (14–26%) with a small percentage of extractives. Macromolecules gather to form 3-D polymorphic structures which represent their function to deliver skeleton material with stiffness to the cell wall of plants (Madanayake et al. 2017). The main part of lignocellulosic material is hemicellulose, cellulose converted into

Table 1.2 Sources and products of biomass feedstocks

First generation	Second generation	Third generation	Fourth generation
Rich sugar biomass	Lignocellulosic biomass	Aquatic biomass	Rich solar-efficient aquatic biomass
Sources			
Sugar beet, sugarcane, starch, vegetable oils	Non-food crops wheat straw, maize stovers, corn, wood, solid waste	Algae, microalgae, cyanobacteria	Genetically engineered Plants and algal materials
Products			
Biogases, bio-oils, and biofuels	Biochemicals, electricity, power, heat, biogases, bio-oils, and biofuels	Fertilizers, biochemicals, electricity, power, heat, biogases, bio-oils, and biofuels	Biogases, bio-oils and biofuels, fertilizers, biochemicals, electricity, power, and heat

monosaccharides unit by a process of depolymerization such as xylose, glucose along mannose, galactose, sugar acids (galacturonic and glucuronic acid), and arabinose. In biomass, the matrix of hydrogen and covalent bond connect the lignin and hemicellulose with cellulose and also observed that lignin due to its strong chemical bonding nature also plays a role as binding agent (Kassaye et al. 2017).

1.3 Cost-Effective Cultivation Practices and Impact of Cultivation Condition on the Biomass Characteristics

Wastewater and marginal lands have a great economic impact in terms of cost used to produce biomass because these both resources it does not use agricultural land and have no negative effect but in addition, it makes more profitable because the use of non-agriculture land and eliminate the toxic, heavy metal from wastewater which directly improve the bioenergy production. Biomass cultivation in wastewater bodies used a novel approach with a very low cost called a floating wetland system (Afzal et al. 2019a; Asghar et al. 2021; Goswami et al. 2021a). Marginal lands and wastewater which are not used for agriculture purposes can be used to produce cost-effective biomass without posing any negative impact on the environment. Municipal wastewater and industrial wastewater are serious global environmental problems, so a new phytoremediation treatment of wastewater is employed for the cultivation of biomass using a floating gardening system. So, this approach is a *three-in-one* approach offering wastewater treatment, fixation of atmospheric carbon, and carbon-neutral biomass production. The potential of poor soils for the cost-effective production of biomass is shown in Table 1.3.

Table 1.3 Low-cost biomass sources for bioenergy

Crop	Nature, adapted climate	Biomass Yield (Tons ha^{-1} y^{-1})	Potential characteristics	Energy potential	References
Eichhornia crassipes	Perennial aquatic plant native to tropical desert to the subtropical or warm temperate desert to rainforest zones	28,000	Fast-growing, perennial, aquatic weed	124–127	Ruan et al. (2016)
Phalaris arundinacea	*P. arundinacea* now has a world-wide distribution. It is regarded as native to both North America and Eurasia	35–45	Extensive single species stands along the margins of lakes and streams and in wet open areas		Alhumade et al. (2019)
Bamboo (*Bambusa balcooa*)	Perennial, adapted to moderately acidic loamy soils, warm humid environment	40–50	One of the fastest-growing plants, alcoholic and phenolic compounds	41.85 GJ ha^{-1}	Mehmood et al. (2017a)
Cardoon (Cynara *cardunculus)*	Perennial, adapted to high temperature and low rainfall	7.4–14.6	Artichoke oil, feedstock for the first biorefinery and biodiesel	138 GJ ha^{-1}	Francaviglia et al. (2016)
Eucalyptus (*Eucalyptus obliqua*)	Perennial, adapted to temperate, tropical, and subtropical poor soils	20	Source of essential oils, phenolic compounds, medicinal compounds, fast growing	233–245 GJ ha^{-1}	Wadhwani et al. (2017)
Giant reed (*Arundo donax* L.)	Perennial, adapted to Mediterranean environment	36	Resistant to drought, used in dissolving pulp, durable yields, impressive bioenergy feedstock	2281 CH_4 kg^{-1}	Nassi o Di Nasso et al. (2013)
Poplar (*Populus tremula*)	Circumpolar subarctic and cool temperate	6–15.8	Biofuels, carbon mitigation potential, and fast growing	92 TW h^{-1}	Saha and Eckelman (2015)
Reed canary grass (*Phalaris arundinacea* L.)	Perennial, adapted to temperate regions, wet-soils, colder climatic, flood plains	15	Drought-tolerant, phytoremediation, sources of drugs	97 GJ ha^{-1}	Lord (2015)

Switchgrass (*Panicum virgatum* L.)	Perennial, adaptive to versatile growth conditions, C4-pathway	1–22	Ethanol, butanol, biogas production, thermal energy, phytoremediation, drought, and flooding tolerant	60 GJ ha^{-1}	Nassi o Di Nasso et al. (2015)
Virginia mallow (*Sida hermaphrodita*)	Perennial, native to sandy or rocky river shores, temperate	9–20	Source of food and nectar for honeybee rearing, the potential for bioenergy production	219.5 GJ ha^{-1}	Țîței (2017)
Wolffia arrhiza	Smallest vascular plant on earth rich in water-loving species		*Wolffia arrhiza* is a species of flowering plant	171 kJ ha^{-1}	Ahmad et al. (2018)

1.4 Correlation of the Biomass Characteristics with the Biomass Valorization Techniques

Nature and biomass composition affects the down-streaming processing which offers various benefits along with the challenges. Valorization analysis of hemicellulose and cellulose shows that it has a high capacity to produce biochemicals, biofuels, paper, pulp, and animal feed. For example, to achieve the attractive target agro-industrial residues such as rice husk (Singh et al. 2014), pruning waste (Martín et al. 2010), sugarcane bagasse (de Araujo Guilherme et al. 2019), fruit peels (Gordon et al. 2011), coffee cut-stem (Aristizábal-Marulanda et al. 2020), and wood materials have been excessively employed for the production of biofuels (Poveda-Giraldo et al. 2021). Various biomasses including para grass (Asghar et al. 2021), *Wolffia arrhiza* (Ahmad et al. 2018), *Calotropis procera* (Ahmad et al. 2021), Chinese liquor-industry waste (Ye et al. 2018), and microalgae biomass (Agrawal et al. 2020; Goswami et al. 2021b, c, 2022; Mehariya et al. 2021; Shahid et al. 2019) have been produced using industrial wastewater and/or municipal wastewater. While the modification in the biochemical composition in response to wastewater cultivation showed positive impact on the biomass with respect to its usage as a bioenergy feedstock.

The basic conversion processes include pyrolysis, gasification, torrefaction, and fermentation where either biochemical or thermal reactions are to progress (Akhtar et al. 2018). There are other less common, and more experimentally or exclusive thermal processes that may lead to cost-effectiveness, such as the hydrothermal upgrading process (Smith et al. 2018). The biomass with higher lignin content may be more suitable to produce biochar, while biomass with higher moisture and less lignin content may be more suitable for fermentation. Similarly, the biomass which contains some chemicals that have allelopathic impact can be processed using a two-stage biorefinery approach, where residual biomass can be used for bioenergy production through pyrolysis or fermentation after extracting the high-value biochemicals for applications such as medicine, preservatives, fragrance, cosmetics, and nutraceuticals.

1.5 Conclusion and Recommendations

Biorefinery is an environmentally friendly approach for the biotransformation of biomass with minimum waste and efficient resource recovery. The fate of biomass feedstock depends on its biochemical composition, source, cost-effectiveness, ease of transportation, and mechanism of processing. While cultivation conditions and seasons sometimes can be easily employed to modify the biochemical composition of the biomass for biorefinery applications. In the future, integration of the biorefinery with the urban wastewater treatment and phytoremediation systems could be cost-effective and could result in multifaceted opportunities. However, the impact of cultivation conditions, involvement of machine learning, modeling, and simulation-based studies should be conducted to refine the methodologies for achieving commercial robustness.

Competing Interests All the authors declare that they have no competing interests.

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Chapter 2
Recalcitrance of Lignocellulosic Biomass and Pretreatment Technologies: A Comprehensive Insight

Rohit Rai, Vikash Kumar, and Prodyut Dhar

Abstract Plant biomass is an excellent lignocellulosic source that can produce renewable and environment-friendly biofuels. However, the natural physiochemical structure of plant lignocellulose has strong recalcitrance and heterogeneity, which results in low yields of biofuels, limiting its effective valorization in biorefineries. This rigidity of lignocellulose presents economic and technical challenges in biomass conversion processes. Various pretreatment methods are used separately and in combination to resolve this. Pretreatment methods change the structure and chemical composition of the plant biomass, which makes it more accessible to the conversion systems for biofuel production. This chapter will discuss the physical and chemical basis of lignocellulose recalcitrance and the biomass components contributing to it. This chapter will also explain the role of pretreatment strategies in biorefineries and their influence on the structure and composition of lignocellulosic biomass. The fundamental understanding of biomass recalcitrance and the role of pretreatment methods can aid in the efficient utilization of lignocellulosic biomass in biorefineries and the development of future pretreatment methodologies.

Keywords Lignocellulose · Recalcitrance · Pretreatment · Biorefinery

Abbreviations

[EMIMAc]	1-Ethyl-3-methylimidazolium acetate
ASA	Accessible surface area
BET	Brunauer-Emmett-Teller

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
https://doi.org/10.1007/978-981-19-4312-6_2

CSC	Cellulose synthase complex
CESA	Cellulose synthase A
CSL	Cellulose synthase-like family
DES	Deep eutectic solvents
DP	Degree of polymerization
G	Guaiacyl
Glu	Glucopyranosyl
GT	Glycosyltransferases
H	*p*-hydroxyphenyl
IPCC	Intergovernmental Panel on Climate Change
LCB	Lignocellulosic biomass
LCC	Lignin-carbohydrate complexes
NMMO	*N*-methylmorpholine *N*-oxide
S	Syringyl
T_g	Glass transition temperature
TSA	Total surface area
UDP	Uridine diphosphate
UTP	Uridine triphosphate
X	Xylopyranosyl

2.1 Introduction

The rapid industrialization and population growth this century have created a high demand for energy and materials, which is essential for the proper functioning of day-to-day life. They hold a huge economic significance and their scarcity can have a high impact on the stability of the global economy, industries, technological advancement, and diplomacy around the world. Conventional fuels and materials are petroleum-based, whose reserves are depleting rapidly in several nations. It also has huge drawbacks due to the environmental harms associated with it such as global warming, water pollution, and climate change (Foston and Ragauskas 2012). According to the Intergovernmental Panel on Climate Change (IPCC) report 2021 (IPCC report 9 Aug 2021), global warming is increasing rapidly and can cross 1.5 °C of global warming in coming decades, if the quick, large-scale reduction in greenhouse gas emissions is not done. Another highlight of the report states that climate change is happening globally and affecting almost every region on the planet severely. The change in the water cycle, rainfall and flooding patterns, and sea-level rise in the recent decades is prominent proof of this. Most of the harmful environmental emissions originate from conventional petroleum-based sources. These limitations have incited the search for alternative fuel and material resources in recent decades that have the potential to replace conventional resources (Foston and Ragauskas 2012). In that context, alternative fuels and materials from plant biomass are becoming an upcoming choice as it is the most abundant biomass source in the world. It also has exciting features such as renewability, low cost, sustainability, and environment-friendliness that suggest its potential in becoming the leading source of fuels and materials in the coming future. However, utilization of plant biomass to obtain bioproducts is not as simple as it contains an inherent resistance to various types of treatments (chemical, physical, and biological) which is called biomass recalcitrance. The biorefinery approach has been utilized in recent years to solve this complication by using plant biomass to obtain products like biogas, biofuels, pulp and paper, building block chemicals, adhesives, and surfactants. Biorefineries are facilities that have a role in changing biomass into several value-added products and are usually characterized by the feedstock used; for example, forest-based biorefineries, corn-based biorefineries, and algae-based biorefineries. Some challenges that are present in using the biorefinery approach are variation in biomass composition, production of fermentation inhibitors, and quality control. In addition, the effective performance of pretreatment and conversion strategies available during industrial scale-up are for a wide variety of biomass are the major hurdles (Agrawal et al. 2020; Goswami et al. 2021; Kamm 2014; Ng et al. 2017).

This chapter discusses the structure, properties, and synthesis of various chemical components of plant biomass (lignocellulosic) and its recalcitrance concerning the contribution of various physical and chemical components present. It also highlights the role of pretreatment in biorefineries and the change in physical properties and chemical composition of lignocellulosic biomass on the application of various pretreatment processes.

2.2 Lignocellulosic Biomass (LCB)

The plant biomass is composed of lignocellulose that has lignin (5–30%), hemicellulose (20–35%), and cellulose (35–50%) as its components. The collective term for cellulose and hemicellulose is holocellulose which are polysaccharides with high molecular weight (325–490 kDa) (Bjurhager et al. 2012) whereas, lignin is made up of polymerized phenylpropanoic acids into a three-dimensional (3D) structure. Lignocellulose components are present in the form of a heteromatrix in which the individual components are linked extensively. The complex arrangement of cellulose, hemicellulose, and lignin in the cell wall is unique. Cellulose arranges itself in a fibrous crystalline structure and is present in the core of the lignocellulosic complex as presented in Fig. 2.1(a). Hemicellulose is present between both macro- and microfibrils of cellulose whereas lignin is present in the outer part of the complex and has a structural and protective role (Bajpai 2016). The other constituents present in the LCB are extractives (11.4%), pectin (10–35%), ash (8.52%), and proteins (10%) (Alvarez-Barreto et al. n.d.; Hernández-Beltrán et al. 2019).

The ratio of lignocellulosic components (cellulose, hemicellulose, lignin) in plants varies across different species, and even in the same plant, it may vary depending on the stage of growth and age. The various forms of LCB present are herbaceous (lettuce, ferns), agricultural (rice, wheat), softwoods (balsa, spruce), and

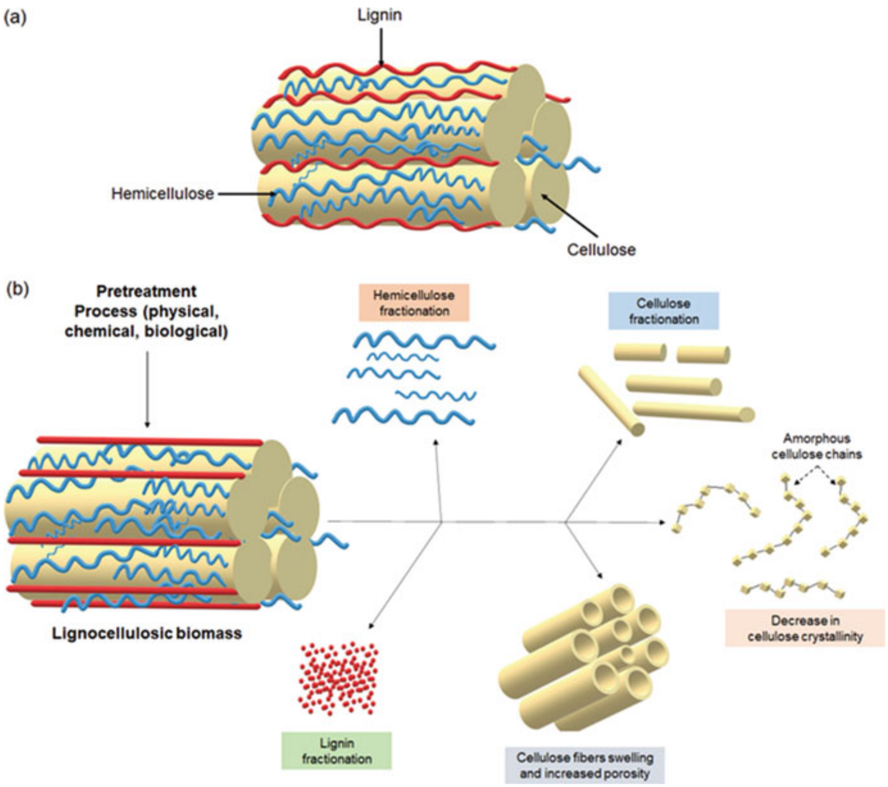

Fig. 2.1 (**a**) Schematic representation of lignocellulose complex containing cellulose, hemicellulose, and lignin (**b**) schematic representation of changes induced after pretreatment of lignocellulosic biomass

hardwoods (birch, hibiscus) (Bajpai 2016). The woody biomass of hardwoods and softwoods has a different lignocellulosic composition. Hardwoods have a higher amount of cellulose and hemicellulose with fewer amounts of lignin (18–25%) whereas softwood has a comparatively higher amount of lignin (25–35%). The lignin in softwood is mainly composed of coniferyl alcohol and is termed "guaiacyl lignin." In contrast, hardwood lignin consists of coniferyl and sinapyl alcohols which is termed as "syringyl-guaiacyl lignin." The ratio of these two lignin types of lignin mentioned varies in different lignin in a ratio of 4:1–1:2 (Demirbaş 2005; Rowell et al. 2005). A significant difference in non-woody (e.g., agricultural) and woody biomass (softwood and hardwood) is their chemical composition and physical properties. Woody biomass is structurally stronger, denser, and physically larger than the non-woody plants. Woody plants also have higher lignin contents than other groups. Generally, LCB biorefineries utilize agricultural biomass and their by-products because it is a cheap waste substrate that could be used in biorefineries for yielding high value-added products (Kumar et al. 2020; Kumar and Verma 2021; Zhu and Pan 2010). The diversity in the lignocellulosic components in biomass and their interactions significantly affects the selection and optimization of appropriate pretreatment methods which in turn affects the cost and economical aspects of the bioproducts made out of it (Demirbaş 2005; McMillan 1994).

2.2.1 Chemical Interactions in Lignocellulosic Biomass

The components of lignocellulose are bound to each other with several linkages which helps in designing the complex structure of LCB. There are five types of bonds found in the lignocellulose structure that are (i) hydrogen (*–H*) bonds, (ii) carbon-carbon (*C–C*) bonds, (iii) ester bonds, (iv) ether bonds, and (v) acetal bonds. These linkages have a major role in forming two types of bonding interactions, i.e., bonding within a component (intramolecular bonding) and bonding between the components (intermolecular bonding). The intermolecular bonds formed during lignin biosynthesis between the lignin and the carbohydrates (cellulose and hemicellulose) and the combined structure of lignin and carbohydrates are called lignin-carbohydrate complexes (LCC). During its formation, lignin substitutes most of the water in the cell wall and results in making a tough solid matrix by forming covalent interactions with the carbohydrates present. To obtain value-added products from LCB, its components need to be separated so that the individual components of biomass become more accessible to treatments. The LCC makes biomass processing in biorefineries challenging as it inhibits the fractionation and isolation of individual components (Harmsen et al. 2010; Tarasov et al. 2018). The type of linkages that are present in LCC are (a) benzyl ether bonds, (b) glycosidic or phenyl glycosidic bonds, (c) benzyl ester bonds, and (d) acetal or hemiacetal bonds. Benzyl ether bonds α-carbon of mannosyl or glucosyl residues of the carbohydrates with the arylpropane unit in lignin whereas glycosidic bonds have a function to link side-chain hydroxyl moieties of the lignin with the carbohydrates. In the case of phenyl glycoside, the lignin which is linked by glycosidic bonds has a phenolic hydroxyl group. Benzyl ester bonds link carbohydrates (mostly xylan) with lignin by utilizing uronic acid of sugar and hydroxyl ($-$OH) group (at α or γ carbon) of lignin. Acetal bonds are formed by the hydroxyl group of carbohydrates and the carbonyl group of phenylpropane of lignin molecules. These linkages in LCC almost combine all the lignin present in the wood with cellulose and hemicellulose and are important for valorization aspects (Tarasov et al. 2018; Zhao et al. 2020). The intramolecular bonding between individual components of lignocellulose will be discussed later in the chapter.

2.3 Components of LCB: Cellulose, Hemicellulose, and Lignin Derivatives

2.3.1 Cellulose: Structure, Synthesis, and Properties

Cellulose holds its position as the most abundant natural polymer worldwide and has an annual global production of approximately 1.5×10^{12} tons (Klemm et al. 2005). Rapid research in the previous decades in the field of cellulose has enabled its utilization at a large scale in industries. The properties of cellulose such as biodegradability and renewability are attractive features and its properties can be further modified by physical and chemical modifications. This broadens its potential applications in industries such as textiles, coating materials, optical films, and functional materials (Heinze and Liebert 2012; Mohanty et al. 2000). Cellulose is present abundantly in plant species such as Kapok (*Ceiba pentandra*) (70–75%), Jute (*Corchorus*) (60–65%), Hemp (*Cannabis sativa ssp. sativa*) (70–75%), and Bamboo (*Bambusa vulgaris*) (40–55%). Cotton (*Gossypium*) plants are the most common cellulose source and contains a high amount of cellulose (~90 wt%) (Hon 2017). The structure and properties of cellulose influences its utilization for industrial applications. Since cellulose is the core component of the lignocellulose complex, its structural understanding and property evaluation is important to develop and select appropriate pretreatment techniques for the lignocellulose utilization in biorefineries.

2.3.1.1 Cellulose Structure

Cellulose structure is composed of ᴅ-glucopyranose moieties in a $^4C_1$ chair type configuration which is the minimum energy conformation. The individual glucose rings are joined with *β-(1,4)* glycosidic linkage in which the cellulose chain turns alternatively by 180 degrees as presented in Fig. 2.2(a) (Krässig 1993; Rao et al. 1967). The hydroxyl groups are found at the *C2, C3*, and *C6* position on the glucopyranose ring in the cellulose chain which can participate in various chemical reactions as shown in Fig. 2.2(b). The ends of the cellulose chain are different from each other. One end of the chain is non-reducing in which the anomeric carbon participates in the formation of glycosidic bonds and contains a pendant hydroxyl group whereas the other end is reducing in which the ᴅ-glucopyranose unit contains an aldehyde group (Krässig 1993). The hydrogen bonding in and between the cellulose chains and its pattern plays a significant part in the determination of cellulose chain properties such as reactivity, solubility, and crystallinity (Kondo 1997). Both intramolecular and intermolecular hydrogen bonds are present in cellulose chains that are formed by the interaction of hydroxyl groups and glucose ring oxygen atoms, and glycosidic linkages in the cellulose chain. Intramolecular hydrogen bonds are the reason for cellulose chains rigidity and high viscosity of the solutions formed. On the other hand, the intermolecular hydrogen bonds provide strong linkage among chains of cellulose. The hydrogen bonding results in the

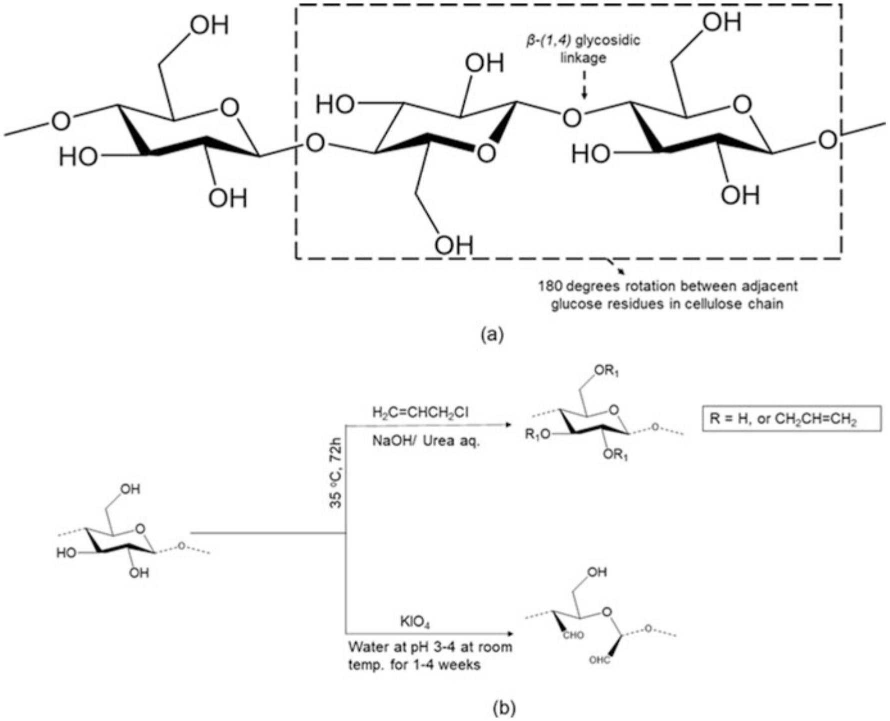

Fig. 2.2 (**a**) Structure of cellulose chain containing glucopyranose units linked with *β-(1,4)* bonds (**b**) participation of hydroxyl groups of at *C2, C3*, and *C6* position of glucose in cellulose chain into various chemical reactions

creation of three-dimensional crystal structures of cellulose chains (Gardner and Blackwell 1974; Krässig 1993). The six different crystalline cellulose types are cellulose I, II, III_I, III_{II}, IV_I, IV_{II}, also called cellulose polymorphs (Gardiner and Sarko 1985; Wada et al. 2001; Zugenmaier 2001). In natural systems, only cellulose I polymorph is present and the other polymorphic forms are derived from it by chemical treatment. The native “cellulose *I*” is further categorized into two different allomorphic forms, namely *Iα* and *Iβ* and their proportions differ from species to species in plants. In LCB, the *Iβ* form is present abundantly. Cellulose *Iα* has a triclinic *P1* unit cell, and each unit cell has a single chain. The dimensions and angles of the unit cell of cellulose *Iα* are $a = 6.72$ Å, $b = 5.96$ Å, $c = 10.40$ Å, $\alpha = 118.08^{\circ}$, $\beta = 114.80^{\circ}$, and $\gamma = 80.38^{\circ}$ (Poma et al. 2016). On the other hand (Moon et al. 2011), I*β* allomorph of cellulose I have a monoclinic $P2_1$ unit cell, and each unit cell has two cellulose chains. The dimensions and angles of the unit cell are $a = 7.78$ Å, $b = 8.20$ Å, $c = 10.38$ Å, $\alpha = \beta = 90^{\circ}$, and $\gamma = 95.5^{\circ}$ (Poma et al. 2016). The average degree of polymerization (DP) of cellulose chains in plants is between 1000 and 30,000 (Gardner and Blackwell 1974; Krässig 1993; Poma et al. 2016).

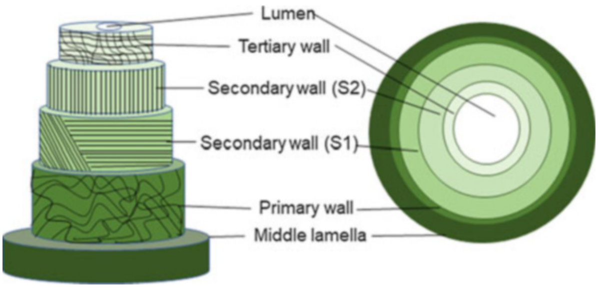

Fig. 2.3 Schematic representation of different layers presents in plant cell wall and arrangement of cellulose fibers in these layers

In crystalline forms of cellulose, the pattern of chain alignment is close and ordered which is linked side by side with hydrogen bonds. Amorphous cellulose is shortly ordered and linked by isotropic intermolecular hydrogen bonding. The amorphous regions of cellulose chains; however, help in forming turns between adjacent chains. The amorphous regions also display random orientations and low density (de Souza Lima and Borsali 2004). The cellulose chains in the cell wall are present as fibrils that have their diameter in the nanometer (nm) range. These fibers arrange themselves in bundles to form microfibrils and microfibrils during which the magnitude of dimensions increase from nm to micrometers (μm) (Krässig 1993). During growth, plant cells first form the primary cell wall which is thinner than secondary and tertiary cell walls. The primary and tertiary walls have a disordered arrangement of cellulose nanofibrils whereas cellulose microfibrils are arranged parallelly in secondary wall sublayers as presented in Fig. 2.3 (Rytioja et al. 2014). The morphologies and dimensions of cellulose in cell walls differ from species to species. For example, spruce cellulose fibers are untwisted and cotton fibers are twisted whereas straight and round fibers are found in bast plants. However, these microfibrils have the same internal structure across the various plant species (Ioelovich 2008).

2.3.1.2 Chemical Properties of Cellulose

Pure cellulose is insoluble in the water because of its crystalline structure, hydrogen bonding, and high molecular weight. Due to this, special procedures and mediums are used to dissolve cellulose. The solvents that are used for the dissolution of cellulose are segregated into two categories, namely (i) derivatizing and (ii) non-derivatizing solutions. Derivatizing solutions (e.g., CF_3COOH, HCOOH) form covalent linkages of low stability with the polymer whereas non-derivatizing solvents (e.g., dimethylsulfoxide, ammonia) only interact physically with the polymers. An important process used for cellulose dissolution at the industrial level is with the mixture of copper hydroxide and aqueous ammonia (Schweizer's reagent), followed by precipitation in dilute sulfuric acid which is the part of fiber production in the viscose process. An alternate strategy for dissolution of cellulose is by dissolving it physically with *N*-methylmorpholine-*N*-oxide monohydrate (derivatizing) which is used in the Lyocell process (Heinze and Liebert 2001). Most of the solvents that are used for cellulose dissolution are developed and processed at the laboratory scale. Some of the semi-industrial scale solvents utilize the applications of ionic liquids such as salts of 1-alkyl-3-methylimidazolium [(1-Ethyl-3-methylimidazolium acetate) (EMIMAc)] (Ebner et al. 2008; Liebert 2008; Swatloski et al. 2002)**.** Ionic liquid for cellulose dissolution came into existence in the year 2002 and are proved to be a good solvent for cellulose because the anions in the ionic liquids are always accompanied by equal numbers of cations to maintain the electroneutrality. Different ionic liquid display difference in solubility and spinning characteristics for cellulose. For example, EMIMAc dissolved cellulose display a poor spinnability whereas *N*-methylmorpholine *N*-oxide (NMMO) cellulose solutions shows high draw ratios during spinning (Hauru et al. 2016).

Even before the nature of cellulose was understood completely, glucan cellulose was utilized as chemical modification precursor for cellulose. The hydroxyl groups of the cellulose participate in the chemical reactions and several industrially important compounds are obtained from cellulose modifications. For example, cellulose in the partially nitrated form is sold commercially with the trade name of "Celluloid" which acts like plastic. Another important chemically modified cellulose product is cellulose acetate which is highly utilized in industries and research. The chemical modifications of cellulose include acylation, sulfation, amino modification, carbonylation, silylation, and oxidation (Gerhartz 1988; Habibi 2014). However, the mechanisms of these chemical modifications are beyond the scope of this chapter and are mentioned to give an idea about varieties of chemical modifications of cellulose available.

2.3.1.3 Mechanism of Cellulose Synthesis in Plants

The synthesis of cellulose in plants is performed by cellulose synthase (CSC) enzymes. It is present as a rosette-like complex in the cell membrane of plants. The catalytic part of the CSCs is called CESA protein (cellulose synthase A) (Chen et al. 2018). CESA subunits arrange themselves to form a rosette-type structure which is composed of 36 CESA subunits. These 36 CESA are organized into six subunits, and each subunit contains six CESA units. CESA is present as a complex in the cell membrane that can synthesize cellulose (Endler and Persson 2011; Turner and Kumar 2018). The *CESA* genes are responsible for the synthesis of cellulose in plants. Some *CESA* genes are necessary for primary cell wall formation (*CESA1, CESA3, CESA6*), whereas some are needed for the construction of secondary cell wall (*CESA4, CESA7, CESA8*). During cellulose synthesis in plants, glucose subunits are polymerized by CESA to form cellulose. The glucose subunits are utilized as uridine diphosphate glucose (UDP-glucose). The enzyme UDP-glucose phosphorylase forms UDP-glucose by utilizing uridine triphosphate (UTP) and glucose-1-phosphate (Guerriero et al. 2010). Sucrose synthase (Susy) enzyme has also been assumed to connect cellulose synthesis by converting sucrose and UTP into UDP-glucose. During the initialization of cellulose synthesis, the enzyme has two

UDP-glucose units in the substrate-binding site, and after that, polymerization begins. During polymerization, glucose subunits are introduced to the non-reducing end of the chain, and the chain is released in the extracellular part simultaneously. This exported cellulose chain then assembles and crystallizes to form cellulose microfibrils (Brown Jr and Saxena 2000). The system for plant cellulose synthesis is based on the mechanism of *Arabidopsis thaliana,* which is used as a model for plant species (McFarlane et al. 2014).

2.3.2 Hemicellulose: Structure, Properties, and Synthesis

Hemicellulose is the most abundant polysaccharide after cellulose in the plant's system. They are also the most abundant heteropolysaccharides found in nature. The hemicellulose family is diverse in context to their origin and relative proportion to cellulose in the plant cell wall. On a molecular level, hemicellulose displays a high variation in the degree of branching and molecular weight. However, their DP is comparatively less than cellulose (Timell 1967). In-plant species, the composition of hemicellulose differs in terms of the types of sugar and their respective amounts. Even in the same plant, several forms and amounts of hemicellulose may exist in different macroscopic structures (root, core, branches). The difference in hemicellulose composition and the amount is also observed in different cell wall layers and within the wood structure (heartwood, latewood, and earlywood). Hemicellulose composition in the hardwoods is quite similar in species such as birch and aspen and is composed mainly of xylan (high amount) and mannan (low amount). In the case of softwood, the major monomer is glucomannan, and arabinogalactans and xylans are present in the smaller amounts. In recent decades, there has been a huge development towards complete characterization of the hemicellulose, providing a comprehensive understanding of hemicellulose structure which was a great challenge in the last century (Albertsson et al. 2011).

2.3.2.1 Structure of Hemicellulose

The hemicellulose is a complex heteropolysaccharide composed of a single or combination of pentoses and hexoses. The pentoses involve monosaccharides such as xylose and arabinose whereas hexoses include D-galactose, D-glucose, D-mannose, D-glucuronic acid, etc. (Aspinall 1959; Aspinall 1962). Fucose and rhamnose sugars are also found in some hemicelluloses. The composition of sugars varies in plant species based on the tissue of origin and geographical location. The representative structure of hemicellulose is considered as β-(1,4) linked xylopyranose subunits that are present in various plant parts including stem, root, and leaves. The complexity of the hemicellulose structure is enhanced further by branching in the form of side groups at the *C2* and *C3* positions of the sugar. Examples of these side groups are

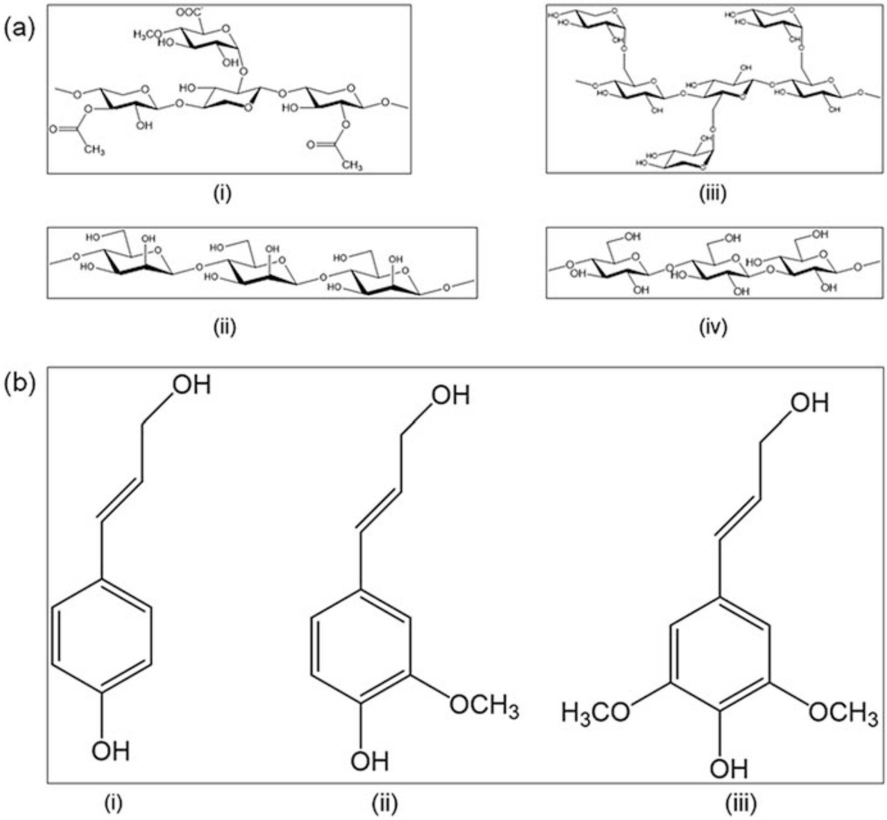

Fig. 2.4 (**a**) Structure of different types of hemicellulose present in plant cell wall (i) xylan, (ii) mannan, (iii) xyloglucan, (iv) *β*-glucans (**b**) structure of lignin monomers (i) *p*-coumaryl alcohol, (ii) coniferyl alcohol, (iii) sinapyl alcohol

glucuronic acid, rhamnose, arabinofuranose, and phenolic acids. The phenolics like coumaric acids have antimicrobial, antioxidant, and anti-inflammatory properties (Adams and Castagne 1951; Aspinall 1962; Ghali et al. 1974).

Due to the different kinds of sugars involved in the hemicellulose structure, they are categorized into four types that are (i) xylans (ii) mannoglycans or mannans, (iii) xyloglucans, (iv) *β*-glucans (Scheller and Ulvskov 2010) as shown in Fig. 2.4(a). The first group, xylans are the most common and abundant form of hemicellulose. It is composed of xylopyranosyl subunits linked with *β-(1,4)* bonds. It is substituted by branches containing arabinosyl, glucuronosyl, and acetyl residues based on the extraction method and biomass source (Hauru et al. 2016). The xylan found in straw has l-arabinofuranose in its side chains. Some plants also contain the acidic xylans in which the acidic group is provided by the *4-O*-methyl-d-glucoronic acid. The complex forms of xylans contain xylopyranose, galactopyranose, furanose, and uronic acids as their side groups. The xylans that contain simple chains of xylopyranosyl subunits linked with *β-(1,3)* and *β-(1,4)* or both the bonding are called homoxylans whereas the xylans that contain a large variety of sugars are called heteroxylans (Ebringerová and Heinze 2000; Scheller and Ulvskov 2010; Teleman et al. 2000).

Mannans are the second group of hemicellulose and are abundantly present in the softwood hemicellulose. The mannans are of four types: (a) mannan, (b) galactomannans, (c) glucomannan, (d) (galacto)glucomannans. Mannans are composed of mannose sugar linked with *β-(1,4)* bonding whereas the galactomannans are composed of ᴅ-mannopyranosyl subunits with *β-(1,4)* bonding. At *C6* position, the ᴅ-galactopyranosyl with short branching are linked to mannan units in galactomannans. The glucomannans contain a ᴅ-mannopyranosyl subunit liked with *β-(1,4)* linkages. Some glucomannans have ᴅ-galactopyranosyl components as their side groups and therefore and are called (galacto)glucomannans. In softwoods, the mannans are usually acetylated at *C2* and *C3* positions. Mannans are utilized commercially in food industries as thickeners and emulsifiers (González 1978; Scheller and Ulvskov 2010).

The third group, xyloglucans are formed of ᴅ-glucopyranose subunits linked with *β-(1,4)* linkages and are present within primary cell walls of angiosperms, grasses, and fruit plants (Fry 1989; Yapo and Koffi 2008). The xylopyranosyl (X) subunits combine with glucopyranosyl (Glu) at *C6* position with *α*-linkages, based on which xyloglucans are further categorized into two groups: (a) XXXGlu group and (b) XXGluGlu group. XXXGlu groups have four glucopyranosyl repetitive subunits, of which three contain xylopyranosyl units. In the case of XXGluGlu, two of the four repetitive glucopyranosyl subunits are xylosylated followed by two non-substituted units (Cui and Wang 2009).

The last group of hemicellulose is *β*-glucans which are linear hemicelluloses containing *β-D*-glycopyranosyl subunits similar to the structure of cellulose. The main difference between cellulose and *β* -glucans is that the cellulose only contains *β-(1,4)* linkages whereas *β*-glucans contains both *β-(1,3)* and *β-(1,4)* bonds. Two types of building blocks are found in the *β*-glucans: (a) cellotriosyl and (b) cellotetraosyl. The cellotrisyl units are composed of two continuous *β-(1,4)* bonds and a *β-(1,3)* linkage is present in between them. On the other hand, the cellotetraosyl has three repetitive *β-(1,4)* bonds followed by a *β-(1,3)* bond. The relative abundance of cellotriosyl and cellotetraosyl varies from one plant to another and depends on the growing environment. For example, barley is found to be rich in *β*-glucans whereas wheat hemicellulose is majorly composed of arabinoxylan (Cui and Wang 2009; Izydorczyk et al. 1998). The structural aspects of hemicellulose are crucial to understanding as it has a significant effect on the properties of this polysaccharide which eventually affects the properties of LCB.

2.3.2.2 Properties of Hemicellulose

The physical, chemical, and functional properties of hemicellulose depend on the DP, molecular mass, macroscopic structure, and branching (Belgacem and Gandini

2011). The hemicellulose is different from cellulose as it contains both pentose and hexose sugars and displays a lower DP. Hemicellulose is non-crystalline and is more accessible to utilization compared to cellulose (Dumitriu 2004). However, like cellulose, hemicellulose is also insoluble in water and there are several methods used for their solubilization and recovery. Arabinoxylan or *β-(1,4)* xylan (unsubstituted) forms insoluble complexes by aggregation which is stabilized with intermolecular hydrogen bonding. It forms a left-handed helix having three folds which appear as an extended twisted ribbon-like structure in solid-state. The formation of aggregated complexes could be the most probable reason for their low solubility in water (Belgacem and Gandini 2011). Xylans from hardwoods can also be solubilized in alkaline solutions which is a high yield method. The products obtained out of this solubilization are similar to native hemicellulose, except all the acetyl side chains, *p*-coumaryl, and feruloyl moieties are saponified (Puls 1997). Similar to cellulose, hemicellulose could also be extracted using ionic liquids which is an upcoming strategy for dissolving individual components of the lignocellulosic components. Ionic liquids such as 1-butyl-3-methylimidazolium chloride (BmimCl), and 1-butyl-3-methylimidazolium bromide (BmimBr) can be used to dissolve hemicellulose (Yuan et al. 2019).

In hardwood, xylans are present abundantly whereas in softwood mannans are most common. Both these groups contain hydroxyl groups with them which allows them to participate in several chemical reactions with multiple chemical agents. These reactions are performed for the enhancement of the properties such as hydrophobicity, thermal stability, and water resistance. The chemical reactions and modifications such as acetylation, esterification, etherification, fluorination, benzylation, and cross-linking could be done with hemicellulose which widens its scope of application as a polymer. For example, hemicellulose has the ability to react with acids, chlorides, and acid anhydrides. The substitution of the hydroxyl group in this reaction will affect the properties of hemicellulose such as thermoplastic behavior and waterproofing. The degree of substitution with reaction with acyl chlorides is affected by reaction conditions such as reaction temperature, time, and the molar ratio of the substrate. Another example of hemicellulose participating in reaction would be esterification which is generally performed with a fatty acid chloride. This modification has shown an increase in the water-resistance properties due to the presence of long-chain fatty acids on the surface and can be used for coating applications (Hu et al. 2020).

2.3.2.3 Hemicellulose Synthesis in Plants

From the previous sections, we know that hemicelluloses are composed of a variety of sugars. The biosynthesis of these individual sugar constituents varies depending on the type of sugars which is being synthesized. In the hemicellulose, the mannans, xylans, xyloglucans, and mixed-linkage glucan biosynthesis are generally considered. Similar to all the polysaccharides that are present in the plant cell wall, hemicelluloses are also synthesized by the activated nucleotide sugars such as guanosine diphosphate (GDP)-glucose, uridine diphosphate (UDP)-galactose, and GDP-mannose. The enzyme cellulose synthase-like family (CSL) are glycosyltransferases that majorly participate in hemicellulose synthesis. The proteins from this family such as CSLA, CSLC, and CSLH are found in the Golgi of the plant cell and have a huge role in the synthesis of mannan, xyloglucan, and mixed-linkage glucans, respectively. They synthesize the hemicellulose components in Golgi and export them to the cytoplasmic side for deposition into the cell wall. The enzyme β-mannan synthase (ManS) is an example of a CSL enzyme that is responsible for the heteromannan synthesis and uses GDP-mannose as a substrate (Pauly et al. 2013). Although CSL proteins have a huge role in hemicellulose synthesis in plants. For backbone synthesis in xylan, these proteins do not participate. The proteins belonging to glycosyltransferases (GT) GT43 and GT47 (present in Golgi) are responsible for xylan backbone synthesis. These proteins are type II membrane proteins with a single membrane anchor at *N*-terminal which is different from CSL family multiple transmembrane segments. The processes involved in hemicellulose biosynthesis are backbone formation, modifications by hydrolases, acetylation, reducing end modification, and formation of side chains of the participating constituents (Scheller and Ulvskov 2010).

2.3.3 Lignin: Structure, Properties, and Synthesis

Lignin comes after cellulose and hemicellulose polysaccharides in terms of polymer abundance in nature. Lignin is a complex aromatic phenylpropanoid polymer that is associated with the cellulose and hemicellulose in the plant cell wall (Boerjan et al. 2003). It helps in cementing these polysaccharides in the cell wall chemically and physically. Lignin has a structural and protective role in the plants which makes them rigid and inaccessible to biotic and abiotic stress conditions (Kirk 2018). It also aids in plant growth and development by enhancing water conduction through xylem vessels. In the industrial valorization of the LCB, lignin has been always considered a non-desired product such as Klason lignin. Klason lignin is an insoluble residue that is obtained after the acid hydrolysis of plant biomass. However, the lignin wasted in the biorefineries can be utilized which will strengthen the economic value of lignocellulosic biomass-based industries. Lignin has been utilized as emulsifying agents, binding agents, reinforcing materials, and composites. The recent research in the direction of lignin extraction, depolymerization, and subsequent valorization has shown excellent results which suggests that it contains a huge potential from an industrial and commercial perspective and is yet to be unleashed (Ponnusamy et al. 2019; Whetten and Sederoff 1995).

2.3.3.1 Structure of Lignin

The phenylpropane units that are involved in the lignin formation are called monolignols. The three types of monolignols that constitute lignin are (i) *p*-hydroxyphenyl (*H*) (ii) guaiacyl (*G*), and (iii) syringyl (*S*) structures. These monolignols combine through radical-based polymerization to produce a three-dimensional lignin structure. The building blocks of lignin are *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol as presented in Fig. 2.4(b). Lignin is a heterogeneous material and does not have a regular structure like cellulose and the exact chemical structure of lignin is not completely defined (Hatakeyama and Hatakeyama 2009). The monolignols in lignin are bonded with carbon-carbon *(C-C)* and ether linkages. Trifunctionally linked adjacent units present branching sites that generate the network structure of lignin. The types of linkages that are present between the monolignols in the lignin are aryl glycerol-*β*–aryl ether *(β–O–4)*, non-ring benzyl-*O*-aryl ether *(α–O–4)*, coumaran *(β–5)*, 1,2-diaryl propane *(β–1)*, diaryl ether *(4–O–5)*, and *β*–*β* (Lebo Jr et al. 2002). In gymnosperms, the lignin majorly consists of the *G* subunits with a small number of *H* units whereas in angiosperms dicot lignin majorly consists of *G* and *S* units. Softwood contains a high amount of *H* units which are abundant in grasses. The variation in lignin composition not only varies with taxa, species, growth conditions, and environment but also differs from cell to cell. It can be dissimilar even at the level of cell wall layers which was revealed by infrared, Raman, and ultraviolet spectroscopy. The concentration of lignin in the plant cell is uniform in the secondary cell wall; however, a high rise in the concentration of lignin is seen at the primary cell wall area and middle lamella periphery. In typical wood cells, the pattern of lignin distribution is like this with a high amount in the interfiber area and low concentration in the bulk of the cell wall. In the primary cell wall and middle lamella, the lignin is present as spherical entities, however, in the secondary cell wall, lamellae formation occurs that is based on microfibril orientation. In the lignocellulose, lignin is the most complex and least characterized component. Comprehensive studies on the structure and distribution of lignin in plant cell walls can potentially unravel the new findings which will further improve the understanding of this complex polymer (Boerjan et al. 2003; Vanholme et al. 2010).

2.3.3.2 Properties of Lignin

The general properties of native lignin are its high thermal stability, high carbon content, biodegradability, stiffness, and antioxidant activity. Lignin in the wood is present in an amorphous form in the cell wall and does not present an absorption peak in the visible light spectrum (Huang et al. 2019; Melro et al. 2018). The color in lignin derived from heartwood is a result of impurities such as flavonoids and tannins. Kraft and sulfite pulps are also brownish because of the presence of chromophoric moieties. Lignin shows UV absorption range which is the reason for the apparent color of lignin (Huang et al. 2019). Using techniques such as light scattering and vapor pressure osmometry, the milled softwood lignin molecular weight is calculated as 20 kDa. However, more variation to this molecular weight can happen depending on the method of estimation and wood source. For the solubility properties of lignin, like cellulose and hemicellulose, lignin is also an insoluble polymer. The lignin is soluble in solvents such as acetone, pyridine, and dioxane (Lebo Jr et al. 2002). The organic solvents are traditionally used for lignin extraction (e.g., methanol, acetic acid); however, it displays low solubility. An alternative to the organic-based solvents could be the use of ionic liquids that have demonstrated intriguing properties such as non-toxicity and high thermal stability. These solvents are also called "green solvents." Some solvents that have been utilized for lignin dissolution are s 1,3-dimethylimidazolium methylsulfate, [Mmim][$MeSO_4$] and 1-butyl-3-methylimidazolium methylsulfate, [Bmim][$MeSO_4$]. Another category of "green solvents" includes deep eutectic solvents (DES) which are formed by mixing a hydrogen bond donor and a hydrogen bond acceptor. Some of the DES that can be used for lignin dissolution is choline chloride and formic acid (2:1) and propionic acid and urea (1:2) (Melro et al. 2018). Lignin acts as a thermoplastic polymer and has a range of glass transition temperatures (T_g) which depends on the isolation method, heat treatment, and sorbed water. For example, the T_g of dioxane lignin was found to be 440 K. The process of delignification is enhanced by the thermal softening of lignin in chemical pulping. It also improves the strength of bonds of fibers in paper-making process (Atack and Mi 1978; Hatakeyama 1972).

Lignin can participate in a variety of chemical reactions such as reduction, oxidation, and hydrolysis. It is also susceptible to enzymes. The hydroxyl, carbonyl, and benzylic hydroxyl groups in the phenolic structure of lignin enable it to participate in chemical reactions. The abundance of these functional groups varies depending on the wood species, morphological location, and isolation methods (Andersson and Samuelson 1985; Schuerch 1975). These chemical reactions result in reactive intermediates formation such as phenoxy anion and phenoxy radical. These radicals are significant in processes such as lignin isolation, enzymatic degradation, and light-induced discoloration. Lignin also demonstrates electrophilic substitution which aids in its modification process. The reactions that generally participate in lignin modification are nitration, ozonation, chlorination, etc. A clear characterization of the lignin properties is an important step towards lignocellulose valorization in biorefineries. The process involved in the treatment and extraction of individual components in lignocellulose can be strategized efficiently for the complete characterization of lignin properties (Melro et al. 2018).

2.3.3.3 Lignin Biosynthesis in Plants

Lignin biosynthesis in the plant systems begins with the formation of monolignols that are synthesized by the general phenylpropanoid pathway. In this, phenylalanine acts as a common precursor of monolignols throughout the plant systems. However, tyrosine also acts as a precursor in grasses. The phenylalanine first deaminates to form cinnamic acid. This reaction is performed by the enzyme ammonia-lyase which is one of the most studied enzymes in plant systems. The cinnamic acid obtained from this is then hydroxylated to *p*-coumaric acid by enzyme cinnamate 4-hydroxylase which is a monooxygenase. After the synthesis of *p*-coumaric acid, the lignin biosynthesis divides into two branches (Whetten and Sederoff 1995). The first branch sequentially forms caffeic acid, ferulic acid, and 5-hydroxyferulic acid that participates in the formation of *G* and *S* monolignols along with the intermediates from the other branch. The synthesis of caffeic acid by *p*-coumaric acid occurs through hydroxylation with the enzyme coumarate 3-hydroxylase. The second branch progresses through the conversion of *p*-coumaric acid to *p*-coumaroyl-CoA by enzyme coumaroyl-coenzyme *A 3*-hydroxylase. After the formation of *p*-coumaroyl-CoA, this pathway branches further in which one leads to the formation of caffeoyl CoA and feruloyl CoA whereas the other leads to the formation of *p*-coumaroyl alcohol. The *p*-coumaroyl alcohol participates in the formation of *H* monolignols whereas caffeoyl CoA and feruloyl CoA help in the formation of *G* and *S* monolignols (Mamedes-Rodrigues et al. 2018). Figure 2.5 shows a schematic representation of *p*-hydroxyphenyl (*H*), guaiacyl (*G*), and syringyl (*S*) subunits biosynthesis pathway in plant cell along with the enzymes involved in each step.

After the formation of monolignols, these are exported to the cell wall, where their oxidation and polymerization occurs. The accumulation of monolignol *4-O-β-D*-glucosides in the cambial tissues in both gymnosperms and angiosperms is the basis of the hypothesis that these are the transport or storage forms of monolignols (Steeves et al. 2001). The completion of monolignols transfer to the cell wall is followed by the process of dehydrogenation and polymerization. The process of dehydrogenation helps in the formation of monolignol radicals and is performed individually and in combination by the enzymes (Kumar and Verma 2020a, b; Bhardwaj et al. 2021) such as laccases (Agrawal et al. 2019; Agrawal and Verma 2020), peroxidases, coniferyl alcohol oxidase, and polyphenol oxidases (Christensen et al. 2000; Onnerud et al. 2002). The formation of monolignol radicals then proceeds into the polymerization process by the radical coupling process. The radicals because of their electron delocalization are relatively stable and present in a coupled form. The extension of three-dimensional lignin polymer occurs by the cross-coupling reaction. However, these reactions quench the radicals; therefore, two coupling molecules require new radicals for every extension. These radicals in the synthesizing lignin polymer are produced with the transfer of radicals from monolignols or their intermediates. For example, in the sinapyl alcohol coupling reactions, *p*-coumarates function as intermediates. Due to their rapid oxidation by peroxidase, they can supply the radicals to sinapyl alcohol which is comparatively stable radical (Hatfield et al. 1997; Takahama and Oniki 1994). Oxidation of *p*-coumarates, therefore, occurs only when all sinapyl alcohols are polymerized. The radical coupling process completes the process of lignification in the cell walls of plants. The lignin is an intriguing component of LCB because of its aromatic nature and complexity. It also has a very significant role in providing LCB a resistant nature

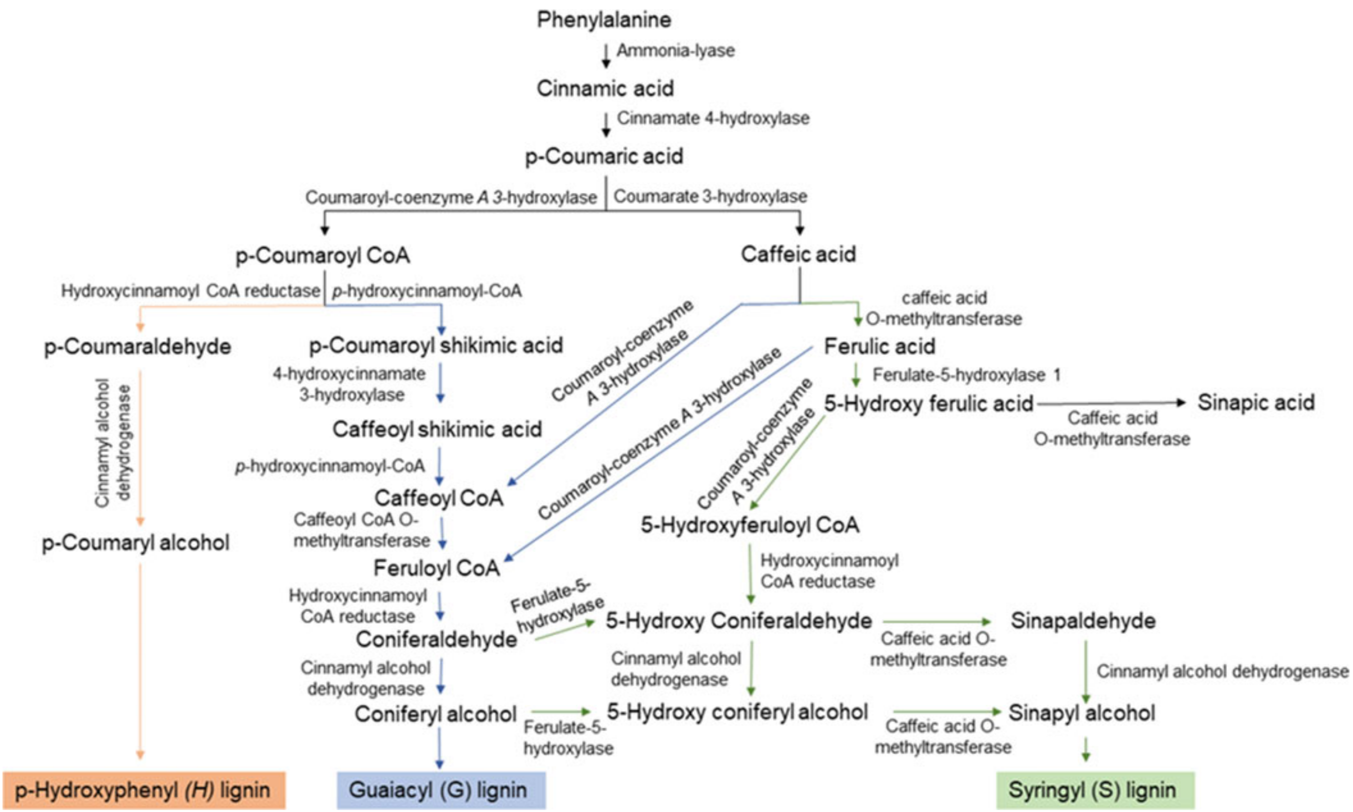

Fig. 2.5 Biosynthetic pathway of *p*-hydroxyphenyl (*H*), guaiacyl (*G*), and syringyl (*S*) subunits of lignin in plants cell

towards the environmental agents (Boerjan et al. 2003). In the further sections, this resistance or recalcitrance of LCB will be discussed in detailed and the contribution of individual components will also be highlighted.

2.4 Recalcitrance of Lignocellulose Biomass (LCB)

Since plants are present in an environment where they interact with a large number of biotic and abiotic agents, they have been evolved to form a complex structure. This structure is difficult to deconstruct by the pathogens and protects the plants. This resistance of plant biomass is called biomass recalcitrance (Himmel et al. 2007; Ritter 2008). Due to this, the processing of LCB in refineries is difficult as it restricts the depolymerization of its components to their respective monomers. The recalcitrance of LCB possesses difficulty in bioproducts production. The components of the plant cell wall that were discussed previously have a huge contribution to the recalcitrance of LCB. LCB is composed of lignin, glycosylated proteins, and cross-linked networks of polysaccharides (Ritter 2008). The main factors that contribute to the lignocellulose recalcitrance are (i) physical properties of the plant cell (ii) chemical composition (iii) and their mixed interactions as displayed in Fig. 2.6 (Zhao et al. 2012a).

2.4.1 Effect of Physical Properties of LCB on Recalcitrance

2.4.1.1 Cellulose Crystallinity

The cellulose in LCB is present as crystalline and amorphous forms. The crystalline portion of cellulose exists in the form of microfibrils and dozens of these microfibrils combine to produce a paracrystalline assembly. This structure has a high number of hydrogen bonds and is more resistant to degradation by enzymes when compared to amorphous portions of cellulose (Laureano-Perez et al. 2005). The crystallinity of cellulose reduces with the enzymatic digestion of the cellulose. Since cellulose

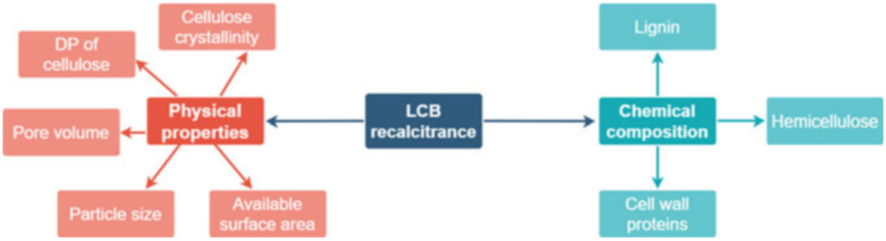

Fig. 2.6 Schematic representation of physical properties and chemical composition-based factors contributing to lignocellulose recalcitrance

crystallinity differs from species to species; therefore, the recalcitrance present by LCB from various biomass sources could be a result of it (Zhao et al. 2012a). However, the conversion of native cellulose to its polymorphic forms can reduce the extent of hydrogen bonding, making it more suitable for digestion (Chundawat et al. 2011). The amorphous portion of cellulose is more suitable for hydrolysis as it is more disordered and has lesser hydrogen bonds than crystalline cellulose (Zhang and Lynd 2004). The quantitative parameter to determine the cellulose crystallinity is called Crystallinity Index (C.I %) which is obtained using X-ray diffraction (Zhao et al. 2008). In LCB, hemicellulose and lignin are present that can interfere with the crystallinity index results of the cellulose and can result in an inaccurate result. To resolve this, biomass crystallinity is measured using methods such as infrared (IR) spectroscopy, Raman spectroscopy, and solid-state 13C NMR (Park et al. 2010). Although crystallinity is considered an important factor towards LCB recalcitrance, some studies also show that cellulose hydrolysis does not depend on the crystallinity of the cellulose in LCB. A possible reason for this could be that the use of pure cellulose for determining the effect of crystallinity on cellulose digestion does not give an idea about the heterogenous biomass (Chandra et al. 2007). The other structural properties that affect the LCB recalcitrance are DP of cellulose, pore volume, particle size, and surface area (Zhao et al. 2012a).

2.4.1.2 Degree of Polymerization (DP)

The number of monomers per unit of a polymer chain is called the degree of polymerization (DP). DP of cellulose defines the number of glucose molecules per unit of the cellulose chain. The process of enzymatic hydrolysis is depolymerization of the cellulose chains by an individual or synergistic action of enzymes such as endo-*1-4-β*-glucanase and *β*-glucosidase. It has been observed that hydrolysis of cellulose with shorter chains is much easier than longer chains (Duff and Murray 1996; Sánchez 2009). Similar to crystallinity, DP is also not an independent factor and affects the overall properties of the LCB. For example, the beating of LCB reduces the fiber DP but increases the swelling behavior. The studies on the effect of DP on biomass recalcitrance have proved that it is contributing factor and its variation can influence the LCB digestion process (Nazhad et al. 1995).

2.4.1.3 Effect of Pore Volume, Particle Size, and Surface Area

The enzyme absorption on the biomass substrate is necessary for its degradation by enzymatic systems. This makes the surface area of biomass which is accessible to the digestion system, an important factor in LCB recalcitrance. The overall accessible surface area (ASA) depends on the physical properties of LCB such as porosity, particle size, and pore volume. For example, an increase in the pore volume or decrease in the particle size can lead to an increase in ASA (Zhao et al. 2012a). Several studies have proven the effect of ASA on LCB recalcitrance; however, there is a limit to reduction in particle size after which the digestion does not improve. This particle size limit was found to be 350–590 μm in LCB (Chang et al. 1997; Moniruzzaman et al. 1997; Wen et al. 2004). The other factors that can influence the ASA and eventually LCB recalcitrance are pore volume and porosity. The total surface area (TSA) of LCB is a function of two components: (i) the external surface area of LCB which depends on the length and width of the section and (ii) internal surface area which is majorly affected by the number of substrate pores, cracks, and the size of the lumen. For cellulose, the internal surface area is higher by one or two orders than the external surface area (Chandra et al. 2007; Chang et al. 1981). It has been proven by several studies (Huang et al. 2010) that the internal surface area is the most important factor towards LCB recalcitrance. For cellulose as a substrate, the enzymatic systems access it mainly through the pores, and about 90% of enzymatic digestion is controlled by the ASA of the pores (Wang et al. 2012). The increase in TSA usually increases the ASA of biomass. However, the increase in the pore areas will increase the TSA but the pore has to be of a size that can entrap the enzyme systems performing hydrolysis (Tanaka et al. 1988; Zhang and Lynd 2004). The untreated biomass samples usually have the micropores and macroporous type of pore structures and no pores less than 100 nm diameter is present in them. However, after pretreatment nanopores between 50 and 100 nm are observed in the biomass (Meng et al. 2015). From multiple studies, the rate-limiting pore size limit for LCB was estimated to be 5.1 nm below which the enzyme systems cannot access the pore's internal surface area (Zhao et al. 2012a). The reason for this is the size of cellulase compositions obtained from an organism such as *Trichoderma reesei* lies in this size range (~5.1 nm). The methods to measure TSA and ASA are based on the quantity of cellulase absorbed on a substrate. BET (Brunauer-Emmett-Teller) is a classical method to measure the TSA by utilizing nitrogen absorption. The shortcomings of BET are changes on biomass surface characteristics due to drying and use of nitrogen for estimation that ring in difference than enzymes used for hydrolysis (Mansfield et al. 1999; Zhang and Lynd 2004). The other methods that can be used to calculate interior surface area of the biomass are mercury porosimetry, X-ray scattering, DSC (differential scanning calorimetry), and NMR (nuclear magnetic resonance) (Beecher et al. 2009).

2.4.2 Contribution of Chemical Components of LCB on Recalcitrance

2.4.2.1 Lignin

Lignin has been widely accepted as the most important factor that is responsible for the recalcitrance of LCB. Conventionally, lignin present in the LCB is removed by applying a variety of methods which has been observed to enhance biomass hydrolysis. From the structural aspect, lignin is present as a physical barrier that restricts the access of enzymes to the cellulose and hemicellulose present in the biomass

(Chang and Holtzapple 2000; Zhao et al. 2012a). The LCC formed by lignin and carbohydrate complexes also limits the accessibility to the LCB components (Chabannes et al. 2001). It is observed that woody biomass due to its high lignin content requires a comparatively harsh treatment process for its valorization than the grass-based biomass. The crucial factors that determine the effect of lignin on LCB recalcitrance are the variety of monolignols present and their abundance, and type and degree of cross-linking among polysaccharides and lignin in the cell wall (Laureano-Perez et al. 2005; Zhu et al. 2010). The structural aspects of lignin have a crucial function in determining the extent of biomass hydrolysis (Chandra et al. 2007). Some studies (Rollin et al. 2011) also suggest that removal of lignin does not necessarily imply that after this LCB would be more accessible to the enzymatic digestion system. Delignification certainly increases the rate of biomass hydrolysis; however, its removal does not ensure enhanced access to the cellulose substrate. An intriguing observation about the lignin in LCB is that it can absorb cellulase enzymes irreversibly. However, this ability to absorb cellulase depends on the biomass source and composition of lignin (Pan 2008; Sutcliffe 1986). Enzyme cellulase binds the lignin with electrostatic and hydrophobic interactions and the binding is spontaneous which was observed from thermodynamic studies. The time required for adsorption of cellulase molecules to lignin was estimated to be 3 h during studies which is much higher than the time required for cellulase adsorption to the pure cellulose (~60 min). The free energy change ($\Delta G°$) of cellulase adsorption on lignin is 29.9 to −37.1 kJ/mol which shows that the binding is a result of physical adsorption. The effect of temperature is not significant in the case of cellulase adsorption to lignin as it is to cellulose; however, the ionic strength of the salts can decrease the cellulase binding to lignin. The adsorption of cellulase enzyme onto the lignin is in the range of 4.87–15 mg/g of lignin which was calculated by Langmuir and Freundlich isotherms (Nakagame et al. 2011). Due to the complex nature of LCB, it is difficult to determine whether these interactions have a significant role in the non-productive binding of the enzyme or not. Apart from lignin, hemicellulose and proteins are also present in the cell wall which also contributes to the LCB recalcitrance.

2.4.2.2 Hemicellulose

Hemicellulose as a component of LCB also contributes to the recalcitrance by acting as a physical barrier. Removal of hemicellulose seems to improve the digestibility of LCB (Zhao et al. 2012a). Xylan, which is present abundantly in hardwoods, can affect the recovery of sugars after hydrolysis and the amount of enzyme required (Bura et al. 2009). The addition of enzyme hemicellulases during enzymatic digestion has also been observed to enhance the hydrolysis of cellulose. This is due to the action of hemicellulases (xylanase) on the hemicellulose which degrades to form xylose, arabinose, and the low molecular weight lignin fragments that are associated with them (Mansfield et al. 1997; Yoshida et al. 2008). However, compared to lignin, the effect of hemicellulose on biomass recalcitrance is not that significant as it is less complex and easier to remove by both the pretreatment and hydrolysis system

(Zhu 2011). Cellulose and hemicellulose are present as holocellulose in the LCB. In recent years, the studies related to the properties and valorization of holocelluloses have increased. For example, Park et al. (2017) in their work studied the effect of hemicellulose content on holocellulose fibril properties. It was observed that with the decrease in the hemicellulose content, crystallinity index, and specific surface area of holocellulose nanofibrils increased, whereas the filtration time and diameter decreased. However, increase in hemicellulose content showed a rise in elastic modulus and tensile strength of nanopaper sheets formed from holocellulose nanofibrils. In another study by Huang et al. (2020), water-soluble ammonium polyphosphate and methyl trimethoxysilane modified bamboo residue were used to obtain the holocellulose nanofibrils. These nanofibrils were further used to prepare the aerogels using the freeze-drying process. The formed aerogels were flexible, soft, and has a 3D network-like structure. The formed aerogels also have good flame retardant and hydrophobic properties. The thermal conductivity of this aerogel was 0.039 W/m K which shows its applications for preparing thermally insulative materials.

The removal of hemicellulose by the enzymatic or chemical process can reduce the biomass recalcitrance and enhance the digestibility of cellulose. The backbone of hemicellulose in LCB is present in a highly acetylated form. These acetyl groups amount to 1–6% of LCB which varies in different plant species. The acetyl moieties are considered to contribute significantly to biomass recalcitrance (Grohmann et al. 1989; Peng et al. 2011). The attachment of acetyl moieties to the cellulose decreases its enzymatic hydrolysis. From several studies, it was observed that deacetylation of LCB can increase its hydrolysis rate. This is because acetyl moieties can interfere with the recognition sites of enzymes which can reduce the rate of hydrolysis. It may also affect the hydrogen bonds-based binding of cellulose with cellulase. Acetyl moieties on cellulose can also increase the chain diameter, which provides the steric hindrance to the enzymatic systems (Pan et al. 2006; Zhu 2005).

2.4.2.3 Proteins in the Cell Wall

The proteins present in LCB also have an effect on its enzymatic hydrolysis. The functional class of proteins present in the plant cell wall are: (i) proteins acting on carbohydrates, (ii) oxidoreductase proteins, (iii) proteases, (iv) proteins with interaction domains, (v) proteins possibly involved in signaling, (vi) structural proteins, (vii) proteins related to lipid metabolism, (viii) miscellaneous proteins. Some examples of these proteins are glucoside hydrolases, peroxidases, and expansins. The type and abundance of cell wall proteins vary with biomass source and cell types in the plant (Albenne et al. 2013; Cassab 1998). They either contribute to the LCB hydrolysis or discourage it. The endogenous enzymes in the plant cell wall such as hemicellulase (endoxylanases), cellulase (endoglucanase), and enzymes that play a role in debranching of the polysaccharides (ferulic acid esterase) have a positive effect on biomass hydrolysis (Lagaert et al. 2009). The proteins that have a negative effect on biomass hydrolysis inhibit the activity of the biomass-degrading enzymes present in the cell wall. Some examples of these enzymes are xylanase inhibitors and polygalacturonase inhibiting proteins. However, the effects of these proteins can be overlooked because these proteins are active in freshly harvested biomass and during processing and storage of biomass, these proteins undergo denaturation and degradation (Han and Chen 2007; Zhao et al. 2012a).

2.4.3 Combined Effect of Physical Properties and Chemical Compositions on Recalcitrance

In the previous sections, the role of physical properties and chemical composition on the LCB recalcitrance was discussed. The chemical structures have their own set of interactions which enhances the recalcitrance. However, combined interactions of these physical properties and chemical compositions play a huge role and are interrelated. The removal of a chemical component would certainly affect the physical properties of the cell wall, whereas varying the physical properties would reflect upon the chemical compositions of LCB. For example, the removal of lignin and hemicellulose increases the porosity of biomass which has a direct effect on the ASA for enzymes (Mansfield et al. 1999). Similarly, a decrease in DP and crystallinity of cellulose results into particle size reduction and increased specific surface area. The factors that affect the accessibility to biomass can be categorized into two factors: (i) Direct and (ii) Indirect factors. In direct factors, enzymatic digestion system interacts with the ASA of LCB, which makes it one of the most important factors for enzyme hydrolysis (Jeoh et al. 2007). Indirect factors are related to the structure of the biomass. Examples of these factors are particle size, pore size and volume, DP and crystallinity of cellulose, and chemical composition of LCB. However, in some cases, the indirect factors can also affect the enzyme hydrolysis process directly. An example for this would be the cellulase adsorption by the lignin which reduces the effective enzyme concentration (Zhao et al. 2012a). It is clear from the discussion that recalcitrance in LCB is not the product of a single structural or compositional factor. The interactions between chemical components result in the formation of rigid and compact LCB structures which makes its utilization difficult in the natural form. A solution to counter this rigidity is a process called pretreatment. Pretreatment is the most significant process in the lignocellulose biorefineries, and there has been a lot of research on this process to utilize the biomass effectively. Pretreatment is a key that opens the full potential locked in the LCB for its successful valorization in biorefineries which will be discussed in detail in the next section.

2.5 Pretreatment: Introduction and Its Role

The LCB as biomass is resistant to breakdown by biological and chemical agents due to its recalcitrance, as discussed in the previous section. Pretreatment processes are required to remove this recalcitrance so that LCB can be utilized optimally in biorefineries. It influences the recalcitrance by processes such as hemicellulose degradation, lignin sheath removal, reduction in DP, and crystallinity of cellulose present in the fibers. The pretreatment process enhances the accessibility to chemicals and enzymes towards the digestion of LCB. Different biomass sources display the variation in the physical properties and composition which requires the selection of different pretreatment processes. Different pretreatment strategies induce different effect on LCB and are utilized according to their special features (Baruah et al. 2018). The goals associated with the selected pretreatment processes are (i) minimum degradation of sugars capable of fermentation, mainly the ones obtained from hemicelluloses, (ii) production of biomass that is able to give a high sugar yield on enzymatic hydrolysis, (iii) minimization of inhibitor formation such as phenolic compounds from lignin degradation, acetic acid from hemicellulose, hydroxymethylfurfural (HMF), furfurals, and other acids such as levulinic acids, formic acid from sugars as shown in Fig. 2.7, (iv) removal and recovery and of lignin for successful valorization, (v) low cost and less energy requirements, (vi) hemicelluloses removal from cellulose, (vii) removal of acetyl groups that interfere with lignocellulose recognition by enzymatic systems, (viii) reduction in particle size and increase in porosity of the biomass, (ix) enhancement of pore size of the components for efficient hydrolysis, and (x) minimization of downstream processes involved in the product recovery, which otherwise will make the bioproduction costly (Chiaramonti et al. 2012; Ramos et al. 2019; Zhao et al. 2012b). These goals are interrelated in nature meaning that changing one of these can affect the others. For example, removal of hemicellulose in LCB can also improve the pore size of the biomass which will enhance the hydrolysis yield. The increase in the porosity also affects the pore size which is a limiting factor for biomass hydrolysis. The selection of a particular pretreatment process for biomass depends on the type/source of biomass origin and the product required (Chiaramonti et al. 2012). The assessment of a particular pretreatment for a biomass can be done by parameters such as (i) the accessibility of water-washed or unwashed biomass to hydrolyzing systems, (ii) the total recoverable amount of carbohydrates released (monomeric and oligomeric units present in solid or liquid phase), (iii) the fermentation ability of hydrolysates obtained after pretreatment which can be characterized by product yields and microbial growth during fermentation, (iv) the formation of useful by-products for the synthesis of other value-added products besides the main intended product (Ramos et al. 2019). Pretreatment is one of the most important processes in biorefineries and needs strategic planning as it determines the economic viability of the process. The energy balance, chemical consumption, production of enzymatic and fermentation inhibitors, and environmental effects are some other factors that are considered before selecting the appropriate pretreatment process

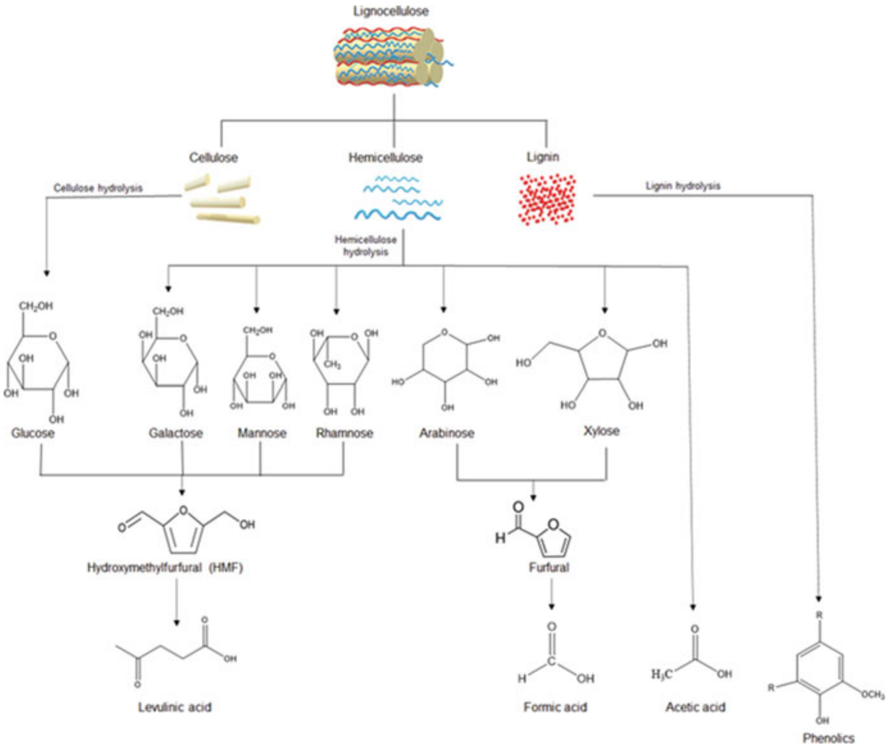

Fig. 2.7 Schematic representation of by-products and inhibitors produced from lignocellulosic biomass valorization and the respective products that can be obtained with them

(Kapanji et al. 2019; Ng et al. 2019). The selection of the pretreatment also influences the upstream and downstream systems that are applied during the processing of LCB. For example, in upstream processes, the choice of the pretreatment process can influence the harvesting and storing conditions of biomass and the chemical and techniques utilized for it. Similarly, the pretreatment process applied can also influence the enzyme loading needed for hydrolyzing the substrate, downstream processing utilized for recovery and isolation of the product, and wastewater generated from the process that can be recycled (Bensah and Mensah 2013; Harmsen et al. 2010). The types of pretreatments utilized in biorefineries are physical, chemical, physicochemical, biological, and combined pretreatments. Physical pretreatment processes, as the name suggests, use the physical and mechanical processes to bring down the recalcitrance of LCB. It reduces the particles size and increases ASA for hydrolysis. These methods are generally used in combination with other pretreatment methods. Some examples of physical pretreatments are milling, radiation pretreatment, extrusion, freezing, and pyrolysis (Zhao et al. 2012b). Chemical pretreatment uses the chemicals for pretreatment of LCB under defined conditions. The mechanism of chemical pretreatment varies with the type of chemical utilized. Some examples of chemical pretreatment are acid pretreatment, alkaline pretreatment, sulfite pretreatment, oxidative pretreatment, ozonolysis, organosolv pretreatment, and ionic liquid-based pretreatment (Bhardwaj et al. 2020a; Kumar et al. 2018; Soltanian et al. 2020). Physiochemical pretreatment methods use physical and chemical methods in combination to increase the efficiency of the pretreatment. Some examples are ammonia fiber explosion (AFEX), steam explosion, liquid hot water pretreatment, wet oxidation, and ultrasonication (Chiaramonti et al. 2012). Biological pretreatment processes use the application of biological agents such as microorganisms or enzymes to reduce the recalcitrance possessed by LCB. Some examples of this pretreatment are fungal, bacterial, enzymatic, and microbial consortium-based pretreatment (Kumar et al. 2018; Bhardwaj and Verma 2020; Bhardwaj et al. 2020b; Soltanian et al. 2020). The last category in pretreatment processes would be the combined pretreatment. The different pretreatment strategies have their own shortcomings and to reduce this, two or more pretreatments could be applied to the biomass. This will help in increasing the efficiency of the pretreatment by improving sugar production, less time consumption, and less production of inhibitors. It also helps in improving the economic viability and product yield. Some examples are combined CO_2 and steam explosion pretreatment, combined biological and dilute acid pretreatments, combined alkali and ionic-liquid pretreatment, and microwave-assisted alkali pretreatment (Kumari and Singh 2018). This information about the main products that are generated in different pretreatment processes from the individual biomass component can supplement in choosing the right pretreatment method for a particular product. For example, in cellulose, acid hydrolysis generates glucose; pulping, bleaching, and enzymatic hydrolysis yield cellulose nanocrystals whereas pulping, bleaching, and mechanical processing produces cellulose nanofibers. For hemicellulose, acid hydrolysis generates monosaccharides that constitute xylose arabinose, etc., autohydrolysis and mild acid hydrolysis generate oligosaccharides whereas partial acid hydrolysis and functionalization produce hydrocolloids. For lignin, oxidation forms vanillin, acid or alkaline hydrolysis produces phenolic acids, and sulfite pulping produces lignosulfonates (Ramos et al. 2019).

Based on the discussion above, it can be concluded that pretreatment is a crucial step in LCB valorization in biorefineries. Some of the examples of pretreatment used for lignocellulosic biomass are presented in Table 2.1. along with the methodology and sugar yield obtained. In recent years, the development of a low-cost and efficient pretreatment process has been researched thoroughly and the pretreatment strategies available at present allow excellent performance in biomass utilization. However, these strategies still have some obstacles that are needed to be solved such as high energy and chemical demands, waste production, efficient recovery of LCB components, and production of inhibitors. The role of pretreatment in biorefineries is huge and contributes largely to the cost associated and therefore requires careful selection. Selecting the right pretreatment process is not an easy task and requires the understanding of economic and sustainability aspects, biomass used, products required, and optimum conditions for operation.

Table 2.1 Examples of different pretreatments processes applied to lignocellulosic biomass along with their methodology and respective yield

Substrate	Pretreatment	Type of pretreatment	Methodology	Yield	References
Rice hulls	Acid hydrolysis	Chemical pretreatment	H_2SO_4 (0.3 %), solid: liquid ratio 5: 95, 152 °C, 33 min	Glucose 47.2 g/100 g glucan; xylose 86.3 g/100 xylan	de Moraes Rocha et al. (2011)
Corn stover	Supercritical CO_2 explosion	Physicochemical pretreatment	5g raw material, 165 °C, 34.5 MPa, 60 min	Total sugar 37 g/100 g raw material	Huisheng et al. (2013)
Switchgrass	Ammonia fiber explosion	Physicochemical pretreatment	Ratio: 1.5:1 ammonia: biomass loading (w/w), 140 °C, 20 min	Glucose 69.3 g/100 g glucan, xylose 67.7 g/100 g xylan	Garlock et al. (2012)
Sorghum bagasse	Alkaline hydrolysis	Chemical pretreatment	Ammonium hydroxide (28% v/v), 130 °C, 1 h	Glucose 42 g/100 g raw material	Chen et al. (2012)
Sugarcane bagasse	Liquid hot water	Physicochemical pretreatment	High pressure CO_2, solid: liquid ratio: 1:12, 115 °C, 60 min	Glucose 30.43 g/L, xylose 9.82 g/L	Gurgel et al. (2014)
Rice straw	Ionic liquids	Chemical pretreatment	1-ethyl-3-methylimidazolium acetate, 5% solid, 120 °C, 5 h	Glucose 450 g/kg rice straw	Poornejad et al. (2014)
Sitka spruce	Organosolv	Chemical pretreatment	Ethanol: water 60:40 (H_2SO_4, 1%), solid: liquid ratio 1:10, 180 °C, 60 min	Glucose 38.6 g/100 g biomass, Ethylglycosides 12.5 g/100 g raw material	Bouxin et al. (2014)
Mandarin peel	Steam explosion	Physicochemical pretreatment	Hot popping: 150 °C, pressure: 15 kgf/cm	Glucose 45.1 g/100 g raw material; fructose 18.4 g/100 g raw material	Choi et al. (2013)
Japanese cedar wood	*Ceriporiopsis subvermispora*	Biological pretreatment	8 weeks at 28 °C, 70% moisture content	35% and 5% conversion of holocellulose to methane with and without pretreatment, respectively	Wagner et al. (2018)

2.6 Pretreatment-Induced Changes on LCB

LCB in its natural form shows recalcitrance towards enzymatic and chemical hydrolysis which is the basis behind the use of pretreatment in biorefineries. The pretreatment processes applied to LCB change its chemical composition and physical properties. Generally, pretreatment disrupts the physical barriers of the cell wall, removes lignin and hemicelluloses, alters the cellulose crystallinity, helps in swelling of pores, and increases porosity as shown in Fig. 2.1(b). The pretreated biomass due to these changes becomes different from the natural LCB which could be observed from variation in physical properties of kraft pulp before and after pretreatment as shown in Table 2.2. (Popescu et al. 2009).

Physical pretreatment changes the crystallinity, particle size, and surface area whereas chemical pretreatment generally focuses on swelling of cellulose and lignin removal (Mussatto 2016). Considering physical pretreatments, the ball milling process performs the size reduction (~78%), decreases cellulose crystallinity (from 74.2% to 4.9%), and DP, with ASA of~ 2.13–2.26 m^2/g (Yeh et al. 2010; Zhu 2011). Another physical pretreatment based on radiation-based, significant hemicellulose (xylan increase 13.9–16.3%) and lignin removal (26.3–6.8%) is observed. In terms of physical properties, it enhances the ASA and decreases the cellulose crystallinity (27.3–24.6%) and DP (1920–170). The ball milling process does not degrade the components of biomass; however, physical pretreatment affects the chemical composition of the LCB (Shin and Sung 2008; Zheng et al. 2009). Ultrasound-based physical pretreatment modifies the structure by cavitation and breaks LCC complexes. For the chemical pretreatments, dilute acid shows significant removal of Kalson lignin and partial degradation of hemicellulose (xylan 8.1–5.5%) which almost disrupts the structure completely. It removes almost all the acetyl groups too (up to 90%), decreases crystallinity (up to 4.4%), and DP (up to 84.7%) of cellulose. In concentrated acid hydrolysis, swelling of cellulose, partial hydrolysis of hemicellulose, and coalescence and condensation of lignin are observed. In alkali pretreatment, significant removal of lignin (>50%) with partial degradation of hemicellulose disrupts the physical structure of LCB. It also removes the acetyl groups completely, increases ASA significantly, with notable and some decrease in the cellulose crystallinity and DP, respectively. In supercritical CO_2 pretreatment, partial hydrolysis of hemicellulose, and an increase in ASA and pore volume are

Table 2.2 The change in physical properties of unbleached and bleached kraft pulp (Popescu et al. 2009).

Properties	Unbleached kraft pulp properties	Bleached kraft pulp fibers
Viscosity (L/g)	1.10	0.728
Density (bulk) (m^3/kg)	0.0019	0.0018
Water retention value (kg/kg)	1.59	1.43
Elastic modulus (N/mm^2)	2420	2129
Tensile strength (kN/m)	1.92	1.74
Kappa number	26.8	3.2

observed. In oxidative delignification, significant removal of the lignin (~50%) is seen with almost complete removal of hemicellulose. It also removes acetyl groups partially, increases ASA significantly, decreases DP of cellulose. Ionic liquid pretreatment partially removes the lignin (15.6–36.3%) (Sathitsuksanoh et al. 2014; Zhao et al. 2012b). It significantly increases ASA, completely removes acetyl groups, converts crystalline cellulose to amorphous, and shows a decrease in cellulose DP (1198–812). Organosolv pretreatment (organic acid-based) shows significant lignin removal (60–90%) and almost completely degrades hemicellulose. It shows a significant increase in ASA with some decrease in cellulose DP. Physiochemical pretreatments such as stream explosion almost completely remove hemicellulose (80–100%) and partially removes lignin (26–50%), however, cause significant changes in redistribution and structure. For physical properties, it significantly removes the acetyl groups and increases ASA significantly. In liquid hot water pretreatment, partial lignin removal (35–60%) happens with significant changes in structure and redistribution of the components with significant and almost complete degradation of hemicellulose (90%). For biological pretreatments, in fungal degradation, partial removal of lignin (13–41%) and good recovery of hemicellulose (81%) is observed with some cellulose degradation. It enhances the ASA and reduces the cellulose DP to some extent. For enzymatic pretreatment, lignin and hemicellulose degrading enzymes such as laccases, peroxidases, and xylanase comes into play that potentially degrades the lignin and hemicellulose in the LCB and increase ASA for its access to the chemical and enzymatic hydrolysis system (Zhao et al. 2012b). Figure 2.8 shows the different physical, chemical, physiochemical, and biological pretreatment methods available for LCB and the changes in biomass induced by them.

Wheat straw as a lignocellulosic substrate when undergoing thermal pretreatment, several changes are observed in the LCB composition. At 180 °C temperature, an increase in the cellulose content is observed, from 34.5% to 47%. At this temperature, a reduction in the hemicellulose content was observed. The reason could be the generation of hydronium ions which could have degraded the materials, generating simple compounds from complex LCB components. Significant removal of lignin was also observed at this temperature. The results also show an increase in crystallinity from 39.7% to 48.5%. The reason for the increase in crystallinity could be a decrease in hemicellulose, lignin, and amorphous cellulose content in the biomass. The fracture of lignin and hemicellulose structure also changes the chemical structure of the biomass, resulting in the change in chemical bonding which was found by Fourier-transform infrared spectroscopy spectra (FTIR) (Rajput and Visvanathan 2018). Bagasse which is obtained from the hybrid of wild and commercial sugarcanes (energy cane bagasse) when undergoes the pretreatment with ionic liquids such as [EMIM][OAc] shows a significant removal of lignin (~32%) with slight xylan and glucan degradation (14% and 8.8%, respectively). The treatment also improved the enzymatic digestibility of the energy cane bagasse. After pretreatment, a disordered and loose structure of biomass was observed from scanning electron microscope (SEM) observations. The crystallinity of cellulose in the biomass also decreased from 56.28% to 24.52% (Qiu et al. 2012). Rice straw

Fig. 2.8 Schematic representation of changes induced after pretreatment of lignocellulosic biomass

when pretreated with alkali shows a significant change in the biomass composition. At 12% NaOH pretreatment for 1 h, the glucan content in the biomass increased from 34.99% to 64.96% whereas the xylan content decreased from 21.55% to 9.07%. Lignin content and extractives also decreased from 24.28% to 4.96% and 16.05% to 14.85%, respectively, during these conditions. The effect of pretreatment in changing the physical properties and chemical composition of the biomass is quite evident and is proven with several studies on different substrates (Kumar and Verma 2019; Harun and Geok 2016). Each pretreatment applies a unique set of changes to the biomass. The innovative pretreatment methods that allow better accessibility to biomass and minimize the waste is a topic of interest from a research perspective and is expected to grow more in the future to make a zero-waste biorefinery. The biorefinery-based production is although classified into various types depending on the feedstocks utilized, pretreatment processes involved, and types of intermediates generated. However, the biorefineries can be divided into different phases such as phases I, II, and III. Phase I biorefineries use single feedstock and produce a single product (e.g., pulp and paper, biodiesel) whereas phase II biorefineries utilize a single substrate to generate multiple products (e.g., bioethanol production). Phase III biorefineries use various feedstocks to produce multiple type of products (LCB biorefinery, whole crop biorefinery). The innovation that has been introduced in the LCB biorefinery in recent years is also starting to gain industrial attention. This has led to a variety of LCB biorefinery products adapted by industries (e.g., succinic acid, ethanol, and lactic acid) which projects new prospects for this area in the coming future with unlimited possibilities (Takkellapati et al. 2018).

2.7 Conclusion

The rapid consumption of natural petroleum-based reserves to obtain fuels and materials is leading to their quick depletion and huge environmental pollution. It is high time to search for alternative natural substrates to obtain these products which will reduce the dependence on petroleum reserves and pollution caused by them. In recent decades, lignocellulosic biomass from wood has been identified as a suitable substrate for this purpose which can replace the conventionally used petroleum-based raw materials. However, the inherent resistance or recalcitrance of the biomass protects it from biological and chemical agents and suppresses its utilization at full potential. To counter this, pretreatment processes are used in biorefineries that make the LCB more susceptible to the degradation process and facilitate its optimal utilization in biorefineries. The pretreatment processes are of different types that change the physical properties and chemical composition of biomass depending on the biomass used and the pretreatment process and conditions. The ongoing research is towards the development of innovative pretreatment methods with high efficiency for pretreatment that can increase the economic value of LCB-based biorefineries and industries.

Acknowledgment R.R is thankful for the junior research fellowship from Department of Biotechnology, Govt. of India (DBTHRDPMU/JRF/BET-20/I/2020/AL/07). P.D. is grateful for the Ramalingaswami fellowship and the research grant obtained from the Department of Biotechnology, Govt. of India (BT/HRD/35/02/2006). The authors are grateful to School of Biochemical engineering, Indian Institute of Technology (IIT-BHU), Varanasi for their kind support which made this work possible.

Competing Interests All the authors declare that they have no competing interests.

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Chapter 3
Understanding Biomass Recalcitrance: Conventional Physical, Chemical, and Biological Pretreatment Methods for Overcoming Biomass Recalcitrance

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Abstract Pretreatment of lignocellulosic waste is one of the costliest phases in transforming cellulosic material into fermentable sugars. It represents one-third of the overall process cost, and about 90% of the dry weight constitutes cellulose, hemicellulose, lignin, and pectin. Hydrogen bonds and some covalent bonds bind the carbohydrate polymers to lignin firmly. The existence of lignin in lignocelluloses barricades the plant cell against the breakdown action by fungi and bacteria. The purpose of the pretreatment procedure is to disrupt the crystalline phase of cellulose and disintegrate the lignin structure, improving the porosity of the lignocellulosic material.

It further provides acids and enzymes access to hydrolyze cellulose by expanding the porosity of the lignocellulosic material so that it readily attacks to break down the cellulose. Pretreatment is therefore done: (i) to facilitate hydrolysis for the formation of sugars, (ii) to keep away the decaying or waste of carbohydrates, (iii) to prevent the creation of by-products that hinder the hydrolytic activities and fermentation that follow, and (iv) make it economical. Numerous pretreatment protocols are employed for treating biomass to overcome the problem faced during pretreatment. In this

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
https://doi.org/10.1007/978-981-19-4312-6_3

study, we have dealt with various pretreatment adopted against lignocellulosic biomass, which is a measure of their potential as feedstock for biofuels.

Keywords Lignocellulosic waste · Pretreatment · Cellulose · Lignin

Abbreviations

AFEX	Ammonia fiber explosion
HMF	5-hydroxymethylfurfural
HPSE	High-pressure steam explosion
OLP	Oxidative lime pretreatment

3.1 Introduction

Rapid population expansion, drop-in biodiversity, and natural resource switches in pollution and climate (Correa et al. 2019) have prompted academics and policymakers to focus on sustainable energy policies to reduce greenhouse gas emissions (Andrée et al. 2017). Furthermore, the depletion of fossil deposits is occurring faster due to an increased demand for fossil fuels due to global industrialization and motorization (Perin and Jones 2019). Fossil fuels are still the world's principal energy source, responsible for more than 88% of primary energy consumption (Li et al. 2019). Their burning releases greenhouse gases, mainly CO_2 (Alalwan et al. 2019; Goswami et al. 2020). As a result, substituting fossil fuels with renewable energy sources allow us to fix these problems by reducing global temperature rise (Scaramuzzino et al. 2019; Goswami et al. 2021). Renewable energy is the proportion of renewable energy to total primary energy consumption, which comprises the equivalent of direct energy from hydroelectric sources (excluding storage through pumping), geothermal, solar, wind, tidal, and wave energy other factors. Power is provided by solid biofuels, biodiesel, different liquid biofuels, biogas, and the renewable component of municipal garbage.

On the other hand, biofuels are fuels generated directly or indirectly from biomass (OECD 2019; Goswami et al. 2022a, b). Biomass is the largest and most important renewable energy source today, after coal, oil, and natural gas (Azevedo et al. 2019; Kumar and Verma 2020a). It can generate various energy sources because the carbon dioxide released during combustion is equivalent to the amount absorbed by the plant throughout photosynthesis, so biomass can be termed carbon neutral (Ibarra-Gonzalez and Rong 2019). Lignocellulosic biomass, the world's most cost-effective and highly renewable natural resource (Hernández-Beltrán et al. 2019; Agrawal and Verma 2020; Goswami et al. 2022c) is the most significant potential feedstock for bioenergy production.

3.2 Pretreatment and Hydrolysis of Biomasses: Overview

Pretreatment or fractionation is a valuable technique for changing the structure of lignocellulosic biomass (Fig. 3.1) and making the holocellulose (cellulose + hemicellulose) bioavailable for bioconversion (Rajendran et al. 2018; Bhardwaj et al. 2021). Pretreatment's primary goal is to break down the cell wall's physical barriers, allowing it to depolymerize and lower cellulose crystallinity (Karimi and Taherzadeh 2016; Kumar et al. 2020). Depending on the type of biomass, pretreatment has been recognized as a crucial stage in the bioconversion of lignocellulosic biomass for utilization in biorefineries (Mupondwa et al. 2017). Pretreatment must be cost-effective, as operational and capital expenditures could account for more than 40% of total processing costs (Bhutto et al. 2017). There have been various studies on biomass pretreatment methods, which can be divided into four categories: (1) mechanical processes; (2) chemical processes; (3) physicochemical processes; and (4) biological processes, which employ microbial consortia or enzymatic means (Fig. 3.2).

3.2.1 *Physical/Mechanical Pretreatment*

Physical approaches can improve lignocellulosic biomass's pore size and surface area while reducing cellulose crystallinity and polymerization. Milling, sonication, mechanical extrusion, and irradiation are physical pretreatment.

Mechanical pretreatment minimizes the size of the particles by milling, chipping, or grinding (Kumari and Singh 2018). Pretreatment with mechanical equipment is a well-known way of enhancing biogas production, but due to its high energy requirements, it is still a costly method (Veluchamy and Kalamdhad 2017).

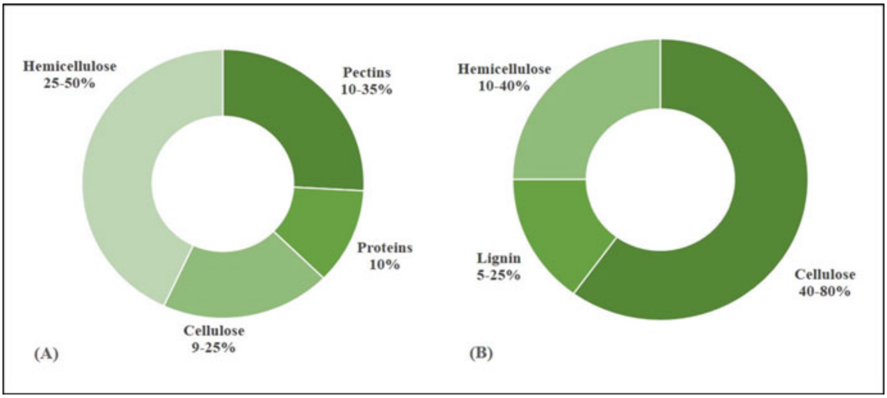

Fig. 3.1 (**a**) The primary cell wall, (**b**) secondary cell wall of the plant's cell wall

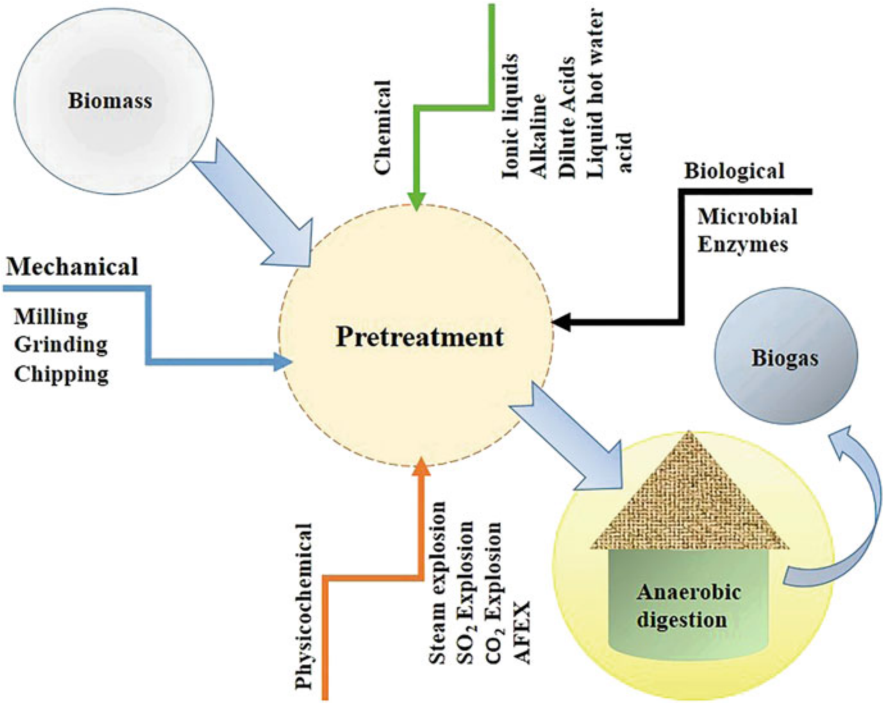

Fig. 3.2 Bioavailability of lignocellulosic biomass after pretreatment

To improve lignocellulosic biomass's accessible surface area and porosity, it must first be reduced in size, lowering cellulose crystallinity and improving the accuracy of the following processing phase and the overall production line (Rodriguez et al. 2017).

Mechanical pretreatment benefits from not producing any secondary inhibitory compounds, implying that they might be used for methane synthesis or other bioprocesses (Dahunsi 2019a). Mechanical processing of six distinct lignocelluloses produced structural material degradation and enhanced methane output by 22%. However, excessive lignocellulosic biomass size reduction can impair methane generation efficiency (Kumari and Singh 2018). Operational variables such as particle size, mechanical pretreatment processing time, and mechanics all affect the performance of the operation in terms of cost energy. According to the literature, there is no standard particle size acceptable for the methanation process, and it varies depending on the type of substrate and the biomethanation procedure. Dumas et al. (2015) found no correlation in wheat straw biogas production with particle sizes ranging from 0.7 to 0.2 mm, and that methane output did not go up at 0.048 mm. The impacts of various particle sizes of wheat straw, rice straw, Mirabilis leaves, cauliflower leaves, *Ipomoea fistulosa* leaves, dhub grass, and other agricultural residues were investigated at 0.088, 0.40, 1.0, and 6.0 (Sharma et al. 1988). They also stated that the biogas yield difference between 0.4 and 0.088 mm was not statistically significant. De la Rubia et al. (2011) found that particle size 1.4–2.0 mm produced the maximum methane yield in sunflower oil cake, 17% greater than particle size 0.355–0.55 mm. Compared to both straws' particle size of 0.75 mm, the particle size of 0.30 mm of wheat and rice straw did not exhibit any substantial improvement in methane yield, according to Chandra et al. (2015). Both particle sizes, however, increased as compared to the untreated particle size of 1.5 mm.

Tsapekos et al. (2015) studied six different mechanical pretreatments that produced particle sizes ranging from 0 to >20 cm. They found that mechanical pretreatment that made particle sizes greater than 20 cm, which accounted for 33% and 41% of the overall biomass, did not yield over untreated biomass. The proportion of biomass with more than >20 cm particle sizes was only around 22% of the total biomass; the methane output was significantly higher and enhanced by 25%. Herrmann et al. (2012) revealed a substantial connection between particle length and methane yield when evaluating different particle lengths of similar agricultural material. Two particle sizes, 2 mm and > 20–100 mm, on various substrates, including softwood, hardwood, and cotton, were studied by Krause et al. (2018) and discovered that lowering particle size enhanced methane output.

On the other hand, particle reduction processing time is essential for energy and the efficiency of lignocellulosic biomass bioconversion (Bhutto et al. 2017). Rodriguez et al. (2017) evaluated 30 and 60 min of mechanical pretreatment and found that 60 min resulted in a 21% increase in methane output, while 30 min did not. The milling equipment's speed must be addressed in order to reduce the cost of energy utilized in mechanical pretreatment (Tsapekos et al. 2017) investigated the effect of different milling speeds, ranging from 200 to 1200 rpm, on CH_4 production through meadow grass and found that the milling rates studied made no difference. Treatments resulted in a 27% enhancement in CH_4 output compared to untreated material.

There was also a drop in methane yield when particle sizes were greater or lower than the range of 2–5 mm (Chandra et al. 2015; Menardo et al. 2012; Dell'Omo and La Froscia 2018). According to Menardo et al. (2012), increasing the particle size of wheat straw to 2 mm increased CH_4 production by 83%. Similarly, at particle sizes of 5 mm and 20 mm, barley straw increased methane output by 54% and 41%, respectively (Menardo et al. 2012). Because of the differences in particle size, milling time, and milling speed, the optimal mechanical pretreatment technique appears to depend on the type of lignocellulosic material, and no general strategy can be advised.

Waste liquid streams from pulp and paper factories are attracting a lot of attention in Northern Europe. On steam-pretreated birch wood, Lamb et al. (2019) employed ultrasonication, a Fenton-like reaction, or a combination of the two to see if a favorable influence on biomethane generation could be obtained. A Fenton reaction uses iron ions and hydrogen peroxide to oxidize organic pollutants like inhibitors and poisonous compounds that can harm microorganisms. Birchwood was steam processed for 10 min at 210 °C in the study. After that, the STEX material was ultrasonicated for 2 h at a pH of 4, with or without the addition of hydrogen peroxide and $FeCl_3$. The findings imply that a strong ultrasonication combined with a

Fenton-like treatment negatively influenced biogas generation, but a softer treatment increased production. They led to a shorter residence time to get near the maximum BMP, which has a significant impact on reactor size (or biogas capacity), which is the most expensive part of a biogas plant.

3.2.1.1 Milling

Milling can make lignocelluloses more accessible to cellulases based on the intrinsic cellulose ultrastructure and crystallinity degree. Cellulases are enzymes that catalyze the breakdown of cellulose; however, for the enzymes to operate optimally, substrate supply must be increased. Before introducing lignocellulosic materials to enzymatic hydrolysis, they should be milled and size reduced.

Colloid mills, dissolvers, and fibrillation are suitable for wet materials, while hammer mills, extruders, cryogenic mills, and roller mills are suitable for dry materials. Ball milling can be used for both wet and dry materials. Hammer milling is the best pretreatment method for wastepaper. By lowering the crystallinity and size of the material, milling promotes enzyme degradation. Particle size reduction of near 0.2 mm can be achieved through milling and grinding. Particle size reduction is possible to a degree; then, particle size reduction does not influence the pretreatment procedure.

Small particle sizes corn Stover of 53–75 m is more productive than corn stover with large particle sizes, 475–710 m. Because of the variation in particle size, productivity has a considerable impact on the pretreatment process. (Bondy et al. 1998; Taherzadeh and Karimi 2008; Walpot 1986) found that ball milling reduces the crystal index from 4.9% to 74.2%, making it pretty appropriate for straw saccharification under mild hydrolytic circumstances with more fermentable sugars yield.

Grinding and milling procedures are not the only types of physical preparation. Falls et al. (2019) investigated the impact of "shock treatment." For example, the method depended upon the effects of an immediate shock wave on material when treated with enzymatic hydrolysis. They investigated various lignocellulosic materials in the study, including bagasse, corn stover, poplar wood, sorghum, and switchgrass. One of the objectives was to examine the digestion of oxidative lime pretreatment (OLP) substrates by glucan enzyme after ball milling and shock treatment. All substrates responded better to shock treatment than ball milling at a hydrolysis time of 24 h. Ball milling outperformed shock treatment when the residence duration was increased. There was a significant improvement in digestibility compared to solely OLP substrates, leading to increased glucose production (Galbe and Wallberg 2019).

Milling is a technique that can be employed in conjunction with enzymatic hydrolysis to improve hydrolysis results. It is possible to carry out mechanical action, mass transfer, and enzymatic hydrolysis in parallel when two techniques are coupled. Compared to biomass pretreatment without milling technology, small enzyme feeding is required in a bill mill reactor. Numerous ball beads contribute a critical part in cellulose hydrolysis, and a 100% hydrolysis rate can be obtained.

3.2.1.2 Irradiation

Microwave irradiation is a commonly used irradiation technology for plant biomass processing. This pretreatment approach has several advantages, including the convenience of use, higher heating capacity, quick processing time, minimum inhibitor generation, and lower energy use. In 1984, a group of researchers from Kyoto University in Japan reported the first case of microwave irradiation in a closed container. In the presence of water, they microwaved sugarcane bagasse, rice straw, and rice hulls. Glass jars of 50 mL, 2450 MHz energy, and 2.4 kW microwave irradiation were utilized for microwave therapy (Azuma et al. 1985).

Traditional pretreatment procedures used high pressures and temperatures. In response to the extreme heat, chemical connections between lignocellulosic materials break down, boosting substrate availability for enzymes. In traditional healing processes, lignocellulosic material is heated to temperatures between 160 and 250 °C using an injection of high-pressure steam or indirect heat. However, to avoid temperature gradients, lignocellulosic material must be crushed into small particles.

Microwave is a suitable alternative for avoiding significant temperature gradients since it evenly distributes heat and prevents lignocellulosic material breakdown into humic acid and furfural. For effective degradation, microwave irradiation is paired with a mild alkali agent. Alkali and irradiation combination pretreatment of switchgrass resulted in 70–90% (Hu and Wen 2008). Microwave irradiation is done at a high temperature, requiring using sealed containers to attain that temperature.

Microwave demonstrates three properties: penetration, reflection, and absorption. Penetration, reflection, and absorption are three characteristics of the microwave. Microwaves penetrate through glass and plastic, acquiring energy from water and biomass, whereas metals reflect them. Microwave reactors can be classified into two sorts based on these characteristics: those that allow microwaves to flow through and those that reflect them. The first type of microwave reactor is glass or plastic, whereas the second type is steel.

Microwaves can enter the reactor through quartz windows, which are positioned in the reactor. For microwave irradiation pretreatment, a closed, sealable, pressure-resistant glass tube container with a Teflon gasket can be utilized at a high temperature of 200 °C. The temperature of the microwave is controlled and maintained using sensors. Due to their features like thermostability, corrosion resistance, and zero absorbance, Teflon-coated sensors are an ideal choice.

Some scientists utilize Teflon vessels in microwave ovens because of their beneficial features (Komolwanich et al. 2014; Azuma et al. 1984). The size of a ship might range from 100 mL to several hundred milliliters. On the top of Chen and Cheng's microwave (Chen and Cheng 2011), a 650 mL vessel with a 318 mm length, a connected nitrogen bottle, gauges, and thermometers are installed.

Aside from glass jars and stainless-steel tanks with temperature and pressure sensors, a microwave input control system and a mechanical stirrer are also used.

3.2.1.3 Expansion and Extrusion

When materials travel through a die with a defined cross-section, they emerge with a fixed, definite profile. Sugar is extracted from biomass using the extrusion method. Mechanical extrusion pretreatment has several advantages: adaptability to changes, no degradation products, a regulated environment, and high throughput. Extruders are divided into two types: single screw and twin screw.

3.2.2 Physicochemical Pretreatment

Physicochemical approaches are utilized to dissolve lignocellulosic parts of the structure based on moisture levels, allowing the lignocellulosic content to be conveniently available for the hydrolysis step while preventing inhibitor development. Although these approaches are more difficult to apply, their significant impact on lignocellulose substrate pretreatment assures high production in the following bioprocesses (Theuretzbacher et al. 2015; Kumar et al. 2020). Physical pretreatment, in general, necessitates more expenditure of energy, making it a costly procedure that is not very economical on an industrial level. As a result, the focus of many previous studies is on process optimization and the criteria for lowering the energy, time, and costs of this treatment.

3.2.2.1 Explosion

High-pressure Steam Explosion (HPSE)

This approach involves treating lignocellulosic biomass with high-pressure saturated steam and then rapidly lowering the pressure, resulting in explosive decompression of the biomass. The temperature of the steam explosion is set to 160–260 °C, and the pressure is set to 0.69–4.83 MPa for a few seconds to minutes, after which the biomass of lignocellulosic plants is exposed and held at atmospheric pressure, triggering hemicellulose hydrolysis and ending the process with explosive decompression. The opportunity for cellulose degradation grows as cellulose breaks and lignin converts due to the high temperatures. Acid and many other acids generated throughout the steam explosion pretreatment played a part in the breakdown of hemicellulose. Because of turbulent material flow and rapid material flashing to air pressure, lignocellulosic material fragmentation occurs (Jørgensen et al. 2007; Li et al. 2007). H_2SO_4 or CO_2 is utilized in steam explosion pretreatment to reduce time and temperature and inhibit product generation while increasing hydrolysis efficiency, leading to 100% hemicellulose removal. For softwoods, steam explosion pretreatment is ineffective; nevertheless, adding an acid catalyst throughout the procedure is required for the hydrolysis of the substrate through the enzyme. Biomass can be treated by steam at a specific temperature without the need for extensive dilution. At the end of the process, a sudden pressure release quenches the entire process and decreases the temperature. Rapid heat expansion opens the particle structure of biomass, which is employed to stop the reaction: moisture content, residence duration, size of the chip, and temperature all impact the steam explosion. Optimal hemicellulose hydrolysis and solubilization can be done in two ways: Low temperature and lengthy residence time vs high temperature and short residence time. Steam explosion pretreatment has an intense energy need. However, mechanical pretreatment requires 70% more energy than steam explosion pretreatment to achieve a similar reduction in particle size. So far, steam explosion pretreatment with the inclusion of a catalyst has been tried, and due to its cost-effectiveness, it has the best chance of being scaled up at a commercial level. Steam explosion pretreatment is being employed on a small scale at the Iogen demonstration plant in Canada. Steam explosion pretreatment is an effective technique for hardwood and agricultural wastes.

Ammonia Fiber Explosion (AFEX)

The AFEX technique is a physicochemical pretreatment technique. This low-temperature technique uses concentrated ammonia (0.3–2 kg ammonia/kg dry weight) as a catalyst. In a high-pressure reactor, ammonia is introduced to biomass; pressure is swiftly removed after 5–45 min of cooking. This operation is usually carried out at a temperature of roughly 90 °C. Because of its volatility, ammonia can be collected and reused. AFEX works on the same idea as a steam explosion. Apparatus such as a reactor, thermocouple well, pressure gauge, pressure relief valve, needle valve, sample cylinder, temperature monitor, and vent are used in AFEX procedures. AFEX pretreatment of several blades of grass and herbaceous crops appears to boost the fermentation rate. AFEX technology is used to treat alfalfa, wheat chaff, and wheat straw. AFEX technique cannot remove hemicellulose or lignin. Hence, only a tiny amount of material is solubilized. During AFEX pretreatment, hemicellulose is breakdown into oligomeric sugars, and deacetylation occurs, resulting in hemicellulose insolubility. Ninety percent of cellulose and hemicellulose hydrolysis was achieved after AFEX pretreatment of Bermuda grass and bagasse. The efficiency of AFEX pretreatment diminishes as the lignin amount of biomass, such as newsprint, woods, nutshells, and aspen chips, increases. The maximal hydrolysis yield for newspaper and aspen chips after AFEX pretreatment was 40–50%. As a result, AFEX pretreatment is not recommended for the processing of biomass with high lignin content.

Carbon Dioxide Explosion

The treatment of supercritical CO_2 explosions is classified as physicochemical pretreatment. Scientists attempted to generate a technique that would be less expensive than ammonia fiber explosion and work at temperatures lower than stream explosion temperatures. Supercritical carbon dioxide, which acts as a solvent, is used in this method. At ambient temperature, supercritical fluids are compressed above their critical point. Carbonic acid is formed when CO_2 is dissolved in water, with unique properties that make it less corrosive. Carbon dioxide molecules enter tiny pores in lignocellulosic biomass throughout the process because of their small size. The CO_2 pretreatment was carried out at a low temperature, which helped prevent sugar degradation by acid. When CO_2 pressure is released, the cellulosic structure is broken, making the substrate more accessible to cellulolytic enzymes for hydrolysis (Haghighi et al. 2013; Kumar et al. 2009; Kumar et al. 2009; Kumar and Sharma 2017). Dale and Moreira (1982) pretreated alfalfa with carbon dioxide and detected a 75% theoretical release of glucose. Zheng et al. (1998) conducted studies on recycled paper and sugarcane bags to compare the effects of ammonia explosion, steam pretreatment, and CO_2 pretreatment. CO_2 explosion prevention is more economical than AFEX, according to the findings.

3.2.2.2 Mechanical/Alkaline Pretreatment

Individually applied mechanical techniques are rarely appropriate (Souza-Corrêa et al. 2013). Grinding-related mechanical pretreatment has the merit of being environmentally friendly, as it does not require the use of chemicals like alkalis or acids. However, because it is an energy-intensive operation, it is best utilized with different pretreatment procedures to save energy and reduce operational expenses. Lignin creates a physical and chemical hindrance to enzyme exposure to cellulose, and mechanical therapies cannot remove it (Miura et al. 2012; Shi et al. 2015). Various kinds of ball milling and compression milling (dry/wet, centrifugal, jet, and vibratory) have been utilized in a range of research studies, either alone or in combination with other procedures (acid, enzyme, and irradiation) to make material handling easier in future processing (Licari et al. 2016; Rahmati et al. 2020).

3.2.3 Chemical Pretreatment

To chemically pretreat lignocellulosic biomass, acids, alkalis, and organic solvents are utilized. One of the most promising is (Gupta and Verma 2015; Kumar et al. 2020), which can be highly effective in breaking down more complex-structured feedstocks (Pellera and Gidarakos 2018; Bhardwaj et al. 2020a). It also improves carbohydrate bioavailability by expelling lignin and/or decreasing cellulose crystallinity and degree of polymerization (Behera et al. 2014; Kumar and Verma 2020b). Chemical pretreatment is gaining popularity since it is usually less expensive and results in a faster and more effective breakdown of complex chemical molecules.

3.2.3.1 Liquid Hot Water

This treatment process is also referred to as "hot compressed water." This type of pretreatment uses high temperatures (160–220 °C) and pressures (up to 5 MPa) to keep water in a liquid state. Chemicals and catalysts, on the other hand, aren't employed in the fluid hot water pretreatment procedure (Kumar and Sharma 2017). For around 15 min, liquid water is in contact with lignocellulosic biomass in this process. There is no need for quick leisure or extension in this pretreatment procedure because pressure prevents evaporation. This approach has proven to be extremely productive on sugarcane bagasse, wheat and rye straw, corncobs, and corn Stover. So many researchers utilize different terminology to describe this pretreatment process, such as solvolysis, aqueous fractionation, and hydro thermolysis (Kumar and Sharma 2017; Sparling et al. 2011; Zhuang et al. 2016). Depending on the direction of the biomass flow, pretreatment of liquid hot water can be done in three different manners, with the water flowing straight into the reactor. The first approach includes bringing the biomass slurry and water to a high temperature and keeping it there at pretreatment conditions for a certain period, and then cooling it down. Countercurrent pretreatment is the second approach, which involves pumping hot water against the current. The flow-through pretreatment method, which includes running hot water over lignocellulosic biomass that serves as a fixed bed, is the third alternative.

Abdullah et al. (2014) showed the impact of liquid hot water pretreatment on the varied hydrolysis rates of cellulose and hemicellulose. The optimization of different parameters was examined in two steps of the process. The first phase, hydrolyzing hemicellulose, was carried out with reduced severity, but the second step, cellulose depolymerization, was done with great seriousness. The disadvantage of using liquid hot water for pretreatment is that it uses a lot of energy. The benefit of this method is not using chemicals or catalysts and inhibitors (Sparling et al. 2011).

3.2.3.2 Acid (Weak and Strong Acid Hydrolysis)

In this treatment, acids are applied to pretreat lignocellulosic biomass. Acid pretreatment releases inhibitory compounds, making it a less desirable pretreatment option. After acid pretreatment, inhibitory compounds such as furfurals, aldehydes, 5-hydroxymethylfurfural, and phenolic acids are generated in high numbers. Based on the type of final use, acid therapies are divided into two categories. The first treatment type is short (1–5 min) but uses a high temperature of >180 °C, while the second treatment method is long (30–90 min) but uses a low-temperature 120 °C.

Because of the acid treatment, additional processes of biomass hydrolysis can be skipped although washing is required before the fermentation of sugars to eliminate the acid (Kumar and Sharma 2017; Sassner et al. 2008). Acid pretreatment necessitates the use of reactors that are resistant to corrosive, hazardous, and toxic acids; as a result, acid pretreatment is quite costly. Rectors have been produced in various ways, including flow-through, percolation, shrinking-bed, countercurrent rector, batch, and plug flow. The ability to recover concentrated acid at the end of the treatment is crucial for improving the economic viability of acid pretreatment. They concentrated on lignocellulosic biomass treatment.

Sulfuric Acid

The most often used acid is sulfuric acid. Acid pretreatment can improve the hydrolysis process for producing fermentable sugars from lignocellulosic biomass. Poplar, switchgrass, spruce, and corn stover are all commonly pretreated with sulfuric acid. The sugar content of Bermuda grass and rye was reduced by 19.71% and 22.93%, respectively, after acid pretreatment. Rice straw was processed with aqueous ammonia and dilute sulfuric acid in two phases in a percolation reactor. When using ammonia, a 96.9% reducing sugar yield was attained; however, when using diluted acid, a 90.8% yield was achieved. *Eulaliopsis binata* released 21.02% of sugars, 3.22% lignin, and 3.34% acetic acid, as well as inhibitors in trace levels when exposed to dilute sulfuric acid (Kim et al. 2011; Tang et al. 2013).

Because it is less expensive and more effective, pretreatment with a sulfuric acid concentration of 4 wt% is preferred. The dilute H_2SO_4 responsible for biomass breakdown causes xylose to be broken down further into furfural. At high temperatures, dilute H_2SO_4 hydrolysis is most efficient (Mosier et al. 2005).

Hemicellulose must be eliminated to improve glucose output from cellulose, and diluting H_2SO_4 is an essential instrument for this. For cost-effective biomass conversion, a high xylan-to-xylose ratio is mandatory. Xylan makes about one-third of the total carbohydrate in most lignocellulosic materials.

The first is characterized by intense temperature and constant flow method for modest solid loadings, whereas the second is attributed to the standard batch procedure for substantial solid loadings. The first type's temperature and solid loadings are >160 °C and 5–10%, respectively, whereas the second type's temperature and solid loadings are around 160 °C and 10–40%, respectively (Brennan et al. 1986; Esteghlalian et al. 1997).

In addition to sulfuric and hydrochloric acids, other acids such as oxalic and maleic acids are applied to pretreat lignocellulosic biomass. Oxalic and maleic acids have a higher pK_a value and solution pH than H_2SO_4. Since dicarboxylic acids have two pK_a values, they are more efficient at hydrolyzing biomass as sulfuric and hydrochloric acids.

Lower yeast toxicity, no odor, a more comprehensive pH and temperature range for hydrolysis, and no inhibition of glycolysis are other advantages. The khyd/kdeg ratio of maleic acid is high, favoring cellulose hydrolysis over glucose breakdown.

(Lee and Jefferies 2011), the impacts of oxalic, sulfuric, and maleic acid preprocessing on feedstock were investigated when the severity factor was combined (CSF). Maleic acid produces a more significant xylose and glucose amount that are higher than oxalic acid levels.

Phosphoric Acid

Another study by Geddes et al. (2010) showed the production of sugar monomers by sugarcane bagasse and found that pretreatment with 1% (w/w) H_3PO_4 at 160 °C for 10 min yielded greater monomers, which this pretreatment method was reportedly proper because it successfully hydrolyzes hemicellulose in the substrate. As a result, cellulose is more easily digestible by enzymes.

3.2.3.3 Alkaline Hydrolysis

The hemicelluloses ratio hydrolyzes under low pH, but the cellulose and lignin parts do not. Instead, at a higher pH, lignin is solubilized, which is the basis for several pulping processes used to produce high-quality journal papers. Depending on the degree of the pretreatment, the amount of solid material that dissolves varies substantially. Hemicelluloses and cellulose can be transformed to oligo- or monosaccharides when a high acid level is applied at high temperatures. In considerably more acidic circumstances, carbohydrates break down to different compounds such as furfural, 5-hydroxymethylfurfural (HMF), levulinic acid, and so on. Temperatures of 140–200 °C are typical, with a minute to hours of residence time (Galbe and Wallberg 2019). Some bases, in addition to acids, are utilized in biomass processing. The amount of lignin in the sample had a significant impact on the alkaline treatment's outcome. Although it takes days and hours, treatment with alkali necessitates minimal pressure, temperature, and environmental conditions than other pretreatment processes. Sugar decomposition is reduced in alkali treatment compared to acid treatment, and caustic salt removal and recovery are also possible and straightforward. Ammonium, sodium, calcium, and potassium hydroxides are all alkali pretreatment agents; nevertheless, the much more commonly utilized substance is sodium hydroxide alkali pretreatment agent, while the least is calcium hydroxide but the most influential of all alkali pretreatment agents.

Calcium can be bounced back in insoluble calcium carbonate by neutralizing it with CO_2. Limekiln technology can be used to renew calcium hydroxide. A temperature controller, a tank, a CO_2 scrubber, a water jacket, a water and air manifold, a pump, a tray, a frame, a temperature sensor, and a heating element are required for alkali pretreatment. Making a lime slurry utilizing water is the initial step in pretreatment. The next stage is to spray the slurries lime over the biomass and then keep it for hours or days, depending on the circumstances. Increasing temperature lowered contact time, according to Elshafei et al. (1991), Kim and Holtzapple (2006), Lee et al. (1994), and MacDonald et al. (1983). The crystallinity index rises as lignin and hemicellulose are eliminated during lime pretreatment. The structural properties that emerge from lime pretreatment influence the hydrolysis of pretreated biomass. Chang and Holtzapple (2000) discovered a connection between three structural aspects: lignin, acetyl content and crystallinity, and enzymatic digestibility. They concluded that (1) significant delignification is adequate to give high digestibility regardless of crystallinity or acetyl concentration. (2) Hydrolysis is aided by the removal of parallel barriers such as dignification and deacetylation. (3) While crystallinity has little impact on the final sugar yield, it is involved in the initial step of the hydrolysis process. Based on these principles, the lignin amount should be reduced to 10%, and it is necessary to terminate all acetyl groups through a particular pretreatment method. Consequently, alkaline pretreatment is critical for enzyme exposure to cellulose. Lignin elimination can significantly improve enzyme function by improving enzyme access to cellulose and hemicellulose while removing nonproductive adsorption sites.

Sodium Hydroxide

In another work, Harun and Geok (2016) used NaOH to pretreat rice straws. At 55 °C, the straw was prepared for 1 h and 3 h, respectively. All samples were treated with a 2–12% (w/v) NaOH solution and a 1:20 (w/v) rice straw to NaOH solution ratio. One of the outcomes was that using 1 h of 12% NaOH enhanced the glucan concentration by 85.6% (compared to untreated straw). In this setting, the delignification of the straw was likewise at its maximum, at 79.6%. Straw was treated for 3 h with 2% NaOH although it gave the highest effective total carbohydrate content, at 79.2% (Galbe and Wallberg 2019).

Hydrogen Peroxide

H_2O_2 is possible to combine the alkaline reagent and hydrogen peroxide. In a broad range of lignocellulosic materials, H_2O_2 enhances enzymatic accessibility, resulting in higher enzymatic hydrolysis yields (Dutra et al. 2018). Lignocellulosic biomass is bleached with the bleaching chemical H_2O_2. Although many free radicals are created during pretreatment, the biomass does not leave residues since it dissolves into oxygen and water with few secondary products. The oxidative fragmentation of lignin side chains leads to lignin removal from the lignocellulosic matrix (Song et al. 2013).

In terms of delignification and enzymatic digestibility, Yuan et al. (2018) discovered that alkaline hydrogen peroxide beats single alkali reagents. However, keeping a constant pH throughout the procedure for avoiding hemicellulose excision, which is an exceptionally essential criterion for process efficiency (Zhuang et al. 2016), limits this technique. Delignification using alkaline hydrogen peroxide enhances lignin depolymerization and requires gentle temperature and pressure settings (Su et al. 2015), lowering inhibitor generation (Rabelo et al. 2014).

Ayeni et al. (2019) evaluated the operating settings for alkaline hydrogen peroxide pretreatment of sugarcane bagasse. They discovered that 0.3% hydrogen peroxide concentration and 100 °C for 4.6 h were the optimal pretreatment conditions. Siciliano et al. (2016) found that treating olive mill residues anaerobically with a low oxidant concentration at room temperature increased the anaerobic treatability by up to 0.328 L/g of COD (chemical oxygen demand) removed. Katukuri et al. (2017) also discovered that treating *Miscanthus floridulus* substrate with 0.8% H_2O_2 boosted methane yield by 49% over untreated *Miscanthus floridulus* substrate.

Alencar et al. (2017), on the other hand, investigated the H_2O_2 recycling technology. They looked at the ability of recycled H_2O_2 in five different reuse cycles and discovered that each one was less efficient than the last.

Before anaerobic digestion, Dahunsi (2019b) investigated the impact of acid or alkaline H_2O_2on pineapple skip preprocessing. The temperature was adjusted around 75–115 °C, the residence period was varied between 6 and 46 min, and the H_2SO_4 concentration was 0–2% (v/v) according to response surface methods. Alkaline H_2O_2 was used in a similar technique. The study's primary findings were that enhanced alkali pretreatment resulted in lignin depletion and a biogas output that was 67% more than the treatment by acid (Galbe and Wallberg 2019).

Wet Oxidation

In this pretreatment process, biomass is treated at high temperatures (>120 °C) for half an hour at 0.5–2 MPa pressure using oxygen/air and water or hydrogen peroxide Haghighi et al. 2013; Varga et al. 2003). This kind of pretreatment is also employed for wastewater treatment and soil remediation. For pretreatment of lignin-rich biomass, this approach has proven to be quite effective. The efficiency of the wet oxidation preprocessing method is influenced by elements, for example, reaction time, oxygen pressure, and temperature. Water behaves like acid at high temperatures, inducing a hydrolysis reaction as the concentration of hydrogen ions grows with temperature, lowering the pH value. In wet oxidation pretreatment, pentose monomers are generated due to hemicellulose breakdown, and lignin is oxidized, but cellulose is unaffected. Some reports of alkaline peroxide or sodium carbonate are added to the mix. The presence of these chemical agents aids in lowering temperature reactions and reducing inhibitory compound production. Attempts to improve hemicellulose breakdown at high temperatures result in inhibitory chemicals such as furfural and furfuraldehyde. However, the number of inhibitors produced by wet oxidation pretreatment is far lower as compared to that produced by liquid hot water pretreatment or the steam explosion approach. Because of two factors, this technique has very little chance of being used on a large scale. The volatile nature of oxygen is one factor, while overprice of hydrogen peroxide utilized during the procedure is another (Bajpai 2016).

Ozonation

Pretreating lignocellulosic biomass with ozone is an ideal approach to reducing lignin. The application of ozone pretreatment to biomass improves its in vitro digestibility. This preparation does not produce inhibitors, a significant benefit because conventional chemical pretreatment leaves hazardous residues. Ozone (O_3) is used as an oxidizer in ozone pretreatment that breaks lignin. O_3 gas is a powerful oxidant that breaks down lignin and creates soluble compounds with lower molecular weight. Wheat straw, bagasse, cotton straw, green hay, poplar sawdust, peanut, and pine can all be prepared with ozone by the breakdown of lignin and hemicellulose; however, all of them are the only materials that can be O3 pretreated (Ben-Ghedalia and Miron 1981; Kumar et al. 2009; Quesada et al. 1999).

A catalytic destroyer of O_3, a trap made of iodine for measuring catalyst potential, an O_2 cylinder, an O_3 generator, a three-way valve, an O_3 UV spectrophotometer, a valve for controlling pressure, and a gas used in the process are all included in an ozonolytic apparatus. Because lignin oxidation decreases as biomass moisture content rises, moisture amount substantially influences lignin oxidation via ozone exposure.

At lower water concentrations, ozone mass transfer is reduced, which impacts its reactivity with biomass. Blocking pores by water film causes a more extended ozone residence period (Mamleeva et al. 2009). Organic acids production lowers the water pH during ozonolysis. Alkaline environments trigger delignification because lignins linked to carbohydrates are removed (Chen et al. 1984; Travaini et al. 2015).

The formation of inhibitory chemicals is linked to biomass delignification. Delignification produces several aromatic and polyaromatic chemicals (Travaini et al. 2013). In a study, Bule et al. (2013) discovered structural alterations in lignin; NMR research demonstrated different lignin subunits have aromatic opening and degradation of -O-4 moieties.

In a spectrum, the concentration of aromatic carbon signals dropped. Changes in methoxy groups were discovered, indicating that the ester-linked structure was disintegrating. Batch reactors, Drechsel trap reactors, fixed bed reactors, rotatory bed reactors, and multilayer fixed bed reactors are the reactor models applied for O_3 biomass processing. Most experts employed plug flow reactors (Li et al. 2015).

Heiske et al. (2013) investigated the properties of single-layered and multi-layered bed reactors to increase the transformation of wheat straw to biogas. A single-layered reactor produced straw with a lignin content of 16.2%, while a multi-layered reactor produced straw with a lignin content of 7.2% at the bottom layer. In ozone-pretreated wheat straw, Kádár et al. (2015) discovered that wax breakdown drives the formation of fatty acid molecules. When corn stover was processed with ozonolysis, Williams (2006) found that over 49% of the lignin was broken down.

3.2.3.4 Solvent Extraction

Scientists have been interested in the application of ionic liquids to pretreat lignocellulose over the term. Ionic liquids containing cations or anions are a new type of solvents with great thermal stability and polarity, as well as a lower melting point and vapor pressure (Behera et al. 2014; Zavrel et al. 2009). Significant organic cations and modest inorganic anions make up ionic liquids: temperature, cations and anions, and pretreatment time all impact the interaction of ionic solvents with biomass.

Ionic liquids conflict with lignocellulosic materials for h-bonding, disrupting networks.1-ethyl-3-methylimidazolium diethyl phosphate-acetate, 1-butyl-3-methylimidazolium-acetate, cholinium amino acids, cholinium acetate, 1-allyl-3 methylimidazolium chloride, and chloride are ionic liquids used to treat rice husk, water hyacinth, rice straw, kenaf powder, poplar wood, wheat straw, and pine (Kumar and Sharma 2017). Imidazolium salts are one of the commonly applied ionic liquids. Dadi et al. (2006) found that using 1-butyl-3-methylimidazolium chloride as a pretreatment doubled the output and frequency of hydrolysis.

Liu and Chen (2006) employed 1-butyl-3-methylimidazolium chloride, referred to as (Bmim-Cl), to pretreat rice straw and observed that it modified the wheat straw structure by Bmim-Cl, resulting in a considerable improvement in the hydrolysis process. Polymerization and crystallinity were reduced, thanks to Bmim-Cl. Research by Kuo and Lee (2009) found a twofold increase in hydrolysis yield from sugarcane bagasse compared to untreated bagasse. In a study by Li et al. (2010), 1-ethyl-3-methylimidazolium-acetate was used to pretreat switchgrass at a temperature of 160 °C for 3 h to eliminate lignin. Tan et al. (2011) observed that 1-butyl-3-methylimidazolium chloride pretreatment of palm trees resulted in 62.9% lignin reduction, enzymatic digestion was improved, while cellulose crystallinity was minimized. After ionic liquid pretreatment, minor changes in biomass composition occurred, but considerable alterations in biomass structure were found. Ionic liquid pretreatment is less desirable than alternative treatments due to its chemical and thermal durability, least hazardous processing circumstances, the low vapor pressure of solvents, and the ability to establish a liquid condition throughout a broad range of temperatures.

Ionic liquids are simple to recycle and don’t degrade. Cellulase unfurls and inactivates due to the incompatibility between cellulose with ionic liquids, which is a downside of using ionic liquid pretreatment. Since cellulose dissolves at less temperatures and viscosities, viscosity is an essential factor in terms of average energy consumption, ionic liquids should be addressed. Mäki-Arvela et al. (2010) proposed that high temperatures result in different side reactions and unfavorable effects, such as ionic liquid stability deterioration.

3.2.4 Biologicals Pretreatments

Pretreatment with biologicals is a viable alternative to chemical pretreatment, but it has a slower reaction rate which is inconvenient for business (Wyman et al. 2018).

3.2.4.1 Fungi

Various microorganisms, including white, brown, and soft rot fungus, are used to pretreat lignocellulose. White-rot fungi are the most well-known and influential delignification microorganisms (Raveendran et al. 2016; Agrawal and Verma 2021). Although brown rot fungi contribute to lignin degradation, white-rot fungi are the most prominent and influential delignification microorganisms. Auxiliary enzymes such as hydrolytic enzymes, cellobiose dehydrogenase, aryl alcohol oxidase, glyoxal oxidase, copper oxidase, and cellobiose dehydrogenase are released by most fungi that degrade lignocellulose, causing the concurrently or specific destruction of cellulose and hemicellulose, as well as lignin (Rudakiya and Gupte 2017; Alam et al. 2021; Verma 2022; Bhardwaj et al. 2020b).

These enzymes help break down lignin and polysaccharides by producing free radicals and intermediates. The effects of biological pretreatment with laccase, manganese peroxidase, and versatile peroxidase at different incubation times—0, 6, and 24 h—were investigated by Schroyen et al. (2014). The presence of phenolic compounds, which are methane inhibitors, was not detected in the pretreatment. The laccase enzyme increased biomethane synthesis by 25% after 1 day of the process of incubating bacteria, but prearrangement with peroxidase enzymes increased the biomethane output by 17% while decreasing the process of incubating bacteria incubation time from 1 day to 6 h.

To improve methane generation, Liu et al. (2017) used *Ceriporiopsis subvermispora* to evaluate fungal pretreatment of two forest wastes, namely hazel and acacia branches, and two agricultural leftovers, namely barley straw and sugarcane bagasse. Compared to untreated hazel, the fungus' manganese peroxidase and laccase increased methane emissions by 100%. While fungal pretreatment of lignocellulosic biomass is favorable to the environment and the economy, they are time-consuming. According to Liu et al. (2017), a unique bioreactor should develop aerobic and aseptic conditions for fungal pretreatment.

According to Van Kuijk et al. (2015), selecting substrate-specific and effective strains and recovery duration and carbohydrate losses can be reduced by changing the cultural conditions. Biogas generation from lignocellulosic biomass can be boosted via inoculation with *Neocallimastix frontalis*, an anaerobic fungus isolated from the rumen, according to Dollhofer et al. (2018).

3.2.4.2 Bacteria

Microbial pretreatment surpasses enzymatic pretreatment in the anaerobic digestion process due to their greater variety and tolerance to external parameters such as temperature and pH. Rouches et al. (2018) isolated bacterial strains from soil (*Bordetella muralis* VKVVG5), silverfish stomach (*Citrobacter werkmanii* VKVVG4), and millipede (*Paenibacillus s*p. VKVVG1) and used them to speed up the hydrolysis of water hyacinth.

Water hyacinth was pretreated for 4 days with *Citrobacter werkmanii* VKVVG4 at a rate of 109 CFU/mL, which enhanced the solvability by 33.3%. Others, on either hand, proposed using anaerobic lignocellulose degrading consortiums. According to Kong et al. (2018), in mesophilic and thermophilic settings, anaerobic consortia TC-5 decomposed wheat straw by 45.7% and increased methane output by 22.2% and 36.6%, respectively.

During 24 h of exposure, rumen fluid was proven to enhance the productivity of rapeseed stems and leaves by 47% (Baba et al. 2017). Yuan et al. (2016) pretreated cotton stalks with the thermophilic microbial consortia MC1.

The findings confirmed that the amounts of soluble chemical oxygen and volatile organic compounds rise rapidly in the early phases of the pretreatment, peaking the highest methane CH_4 output at 128 mL/g over 6 days of MC1 pretreatment. The CH_4 emission was not distinguishable between 122 mL/g and 122 mL/g. Sawdust inoculated with a microbial consortia LCDC obtained from decaying sawdust produced 72.6% more methane than control, according to Ali et al. (2017). They found a significant decline in lignocellulose contents during 10 days of treatment (Hernández-Beltrán et al. 2019).

3.3 Conclusions

The most prevalent materials for biofuel production are lignocellulosic substrates, and this digestion procedure aids in waste disposal while also providing one of the most important sources of renewable bioenergy. Because of their low bioactivity, the structure of lignocellulosic residues continues to pose technological challenges, and proper implementation of digesting technology requires the pretreatment of these resistant substrates. However, as it can be observed, the key constraints are energy expenses, operating expenses, and the generation of anti-proliferative chemicals, all of which substantially impact the downstream bioprocess for producing biofuel or additional products with enhanced value.

A mix of diverse pretreatment may provide a solution that can be tailored to the substrates and downstream bioprocesses to yield bioenergy and certain other products. Biorefineries that produce two or more bioproducts on the same system are inclusive biorefineries, which could be a potential approach for establishing the techno-economic viability of lignocellulose substrate use.

Competing Interests All the authors declare that they have no competing interests.

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Chapter 4
The Pioneering Role of Enzymes in the Valorization of Waste: An Insight into the Mechanism of Action

Anupama Binoy, Revathy Sahadevan, Suchi Chaturvedi, and Sushabhan Sadhukhan

Abstract Finite petro-based reserves and a surge in environmental pollution demands the valorization of waste into revenue streams like biofuels and other industrial commodities. Enzymatic technology provides an eco-friendly platform for the same with higher product yields. Enzymes act as a catalyst in the reaction, and the matter of value addition in this technology is its requirement in low quantity and reusability. They have been included in the valorization of lignocellulosic (woody, agro, and food) waste, treatment of wastewater, and degradation of non-biodegradable hazardous waste. Microbial flora has enormously experimented as well as explored in the conversion of this waste into valuable products. In addition to that, protein engineering and metabolic engineering have been seen as new biotechnological trends in the same field. In this chapter, we will focus on different classes of hydrolytic enzymes based on the structural composition of different types of biomass with special attention to their catalytic activity. The mechanistic action of these enzymes will also be discussed in lieu of their use at various stages in the

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
https://doi.org/10.1007/978-981-19-4312-6_4

transformation of waste to value-added substances. We will also shed light on the future advancement through the biotechnological revolution in the field of enzyme technology.

Keywords Hydrolytic enzymes · Valorization of waste · Lignocellulosic waste · Wastewater · Biorefinery

Abbreviations

AAO	Aryl alcohol oxidase
BOD	Biological oxygen demand
CAZy	Carbohydrate-active enzyme
CLEAs	Cross-linked enzyme aggregates
COD	Chemical oxygen demand
DNA	Deoxyribonucleic acid
DyP	Dye-degrading peroxidases
EG	Ethylene glycol
FAD	Flavin Adenine Dinucleotide
GH	Glycoside hydrolases
GHG	Greenhouse gas emission
GLOX	Glyoxal oxidase
GOS	Galacto-oligosaccharides
LiP	Lignin peroxidase
MnP	Manganese peroxidase
MSW	Municipality solid waste
P2O	Pyranose 2-oxidase
PAH	Polycyclic aromatic hydrocarbons
PCR	Polymerase chain reaction
PE	Pectin esterase
PE	Polyethylene
PET	Poly ethylene terephthalate
PG	Polygalacturonase
PGL	Polygalacturonate
PL	Pectin lyase
PMG	Polymethygalacturonase
PMSF	Phenyl methane sulfonyl fluoride
POPs	Persistent environment pollutants
PP	Polypropylene
PS	Polystyrene
PUs	Polyurethane
PVC	Polyvinyl chloride
RNA	Ribonucleic acid
TPA	Terephthalate
VP	Versatile peroxidases;
XYNII	Endo-1,4-ß-xylanase II

4.1 Introduction

The global surge in population and simultaneous automation have resulted not only in depletion of petro fuels reserve but have also piled up different forms of waste globally. In the global waste management outlook, GWMO 2015 stated that the global waste piling accounts for nearly 7–10 billion tonnes which include households, commercial, industrial, and construction-based waste (Wilson and Velis 2015; Agrawal and Verma 2022). Moreover, the major issues in front of humankind have been climate change, greenhouse gas emissions (GHG), depleting resources, and increasing pollution for a long. Waste management has existed in our society for a long in the form of landfills, incineration, composting, etc. but they are least suitable for organic waste due to problems associated with them like the generation of toxic gases such as methane and toxic leachates to the underground water bodies, etc. This calls upon the urgency to frame an economy based on renewable resources fulfilling the shooting energy demands (Kuo 2019; Goswami et al. 2022; Agrawal and Verma 2021) and also builds up sustainable methods to convert our waste into valuable revenue streams. Adapting to a sustainable way can be envisioned by valorizing waste into biofuels (different forms of bioenergy to replace fossil fuels), biomaterials, and other value-added bio-ingredients. This process is commonly associated with the concept of biorefineries where the waste biomass is upgraded and transformed into a spectrum of invaluable and marketable commodities. Waste can be of different forms. The most common and important problem faced during the valorization of waste is the complexity of the composition of waste. Organic or biomass waste is solid or liquid waste that can be found in many forms like agro and food waste, forestry residues, waste generated from food processing industries, etc. The basic units of the biomass waste are rich in protein, sugar, and fat, which indeed make them an ideal feedstock for enzymatic valorization. Enzymes are introduced at various steps in the process of valorization. For instance, the lignocellulosic mass from the agro-waste is subjected to pretreatment by exposing them to delignifying enzymes which removes the protective lignin component. Thus, enabling the hydrolyzing enzymes to easily solubilize the polymers like cellulose, and hemicellulose into their monosaccharides and oligosaccharides. These monomer units are either subjected to fermentation using microbes for the production of biofuels or enzymatic modification like oxidation/phosphorylation for valorizing into valued products (Andler and Goddard 2018; Bhardwaj and Verma 2021). Enzymes are molecular catalysts triggering biochemical reactions. They catalyze the reaction with high substrate and product selectivity at optimum temperature and pressure. Reusing enzymes for several reactions further makes the procedure cost-effective. All this opens up an opportunity for introducing greener processing strategies that are more sustainable for the ecosystem (Kennedy et al. 2006). Enzymes are ubiquitous in all forms of life performing different purposes and therefore can be extracted from them through purification and characterization (Yada 2015; Bhardwaj et al. 2021a; Kumar and Verma 2020a). Systems biology has encompassed a role in understanding the molecular basis of different enzymes. Through various bioinformatics tools and algorithms, system biology enables us to form a link between different biological components in an organism thereby allowing us to modify and decipher newer enzyme candidates involved in waste valorization as well (Bhatt et al. 2019). Here in this chapter, we will be focusing on different enzymes which participate in hydrolysis of biomass component. As enzymes are very specific to the composition of its substrate, we will also shed light on the composition of different types of biomasses. To better understand the action of hydrolyzing enzymes and their application, it is necessary to take a glimpse at the different characteristics of enzymes and the different factors which affect the activity of enzymes. This chapter will also highlight the advanced enzyme technology and trending opinion on increasing the efficacy of enzymes for valorization of waste.

4.2 Enzymes and Their Characteristics

Enzymes are biological catalysts known to increase the rate of biochemical processes happening inside a living organism (Blanco and Blanco 2017). They were first introduced by Frederick W. Kuhne as molecules of higher molecular weight that help in the fermentation of sugar to alcohol. Enzymes are mostly composed of proteins except for some RNA which exhibit enzymatic characteristics in certain biological processes. Enzymes are associated with cofactors (inorganic metal ions like Cu^{2+}, Zn^{2+}, Mn^{2+}) and/or coenzymes (organic or organometallic complexes) for their activation and function (Renneberg et al. 2017). An enzyme without the cofactor or coenzyme is known as an apoenzyme and the complete active form is referred to as the holoenzyme (Litwack 2018). The accurate structural conformation of enzymes plays a crucial role in determining their activity and any parameters, physical or chemical, that alter the native confirmation will affect the efficiency of their catalytic activity. Based on the type of catalytic reactions, enzymes are categorized into six groups. *Oxidoreductases* catalyze oxidations or reduction reactions. *Transferases* help in the transferring of functional groups between two molecules. *Hydrolases* catalyze hydrolysis (lysis in the presence of water). *Lyases* are involved in the removal or addition of groups to form or reduce double bonds. *Isomerases* catalyze the internal arrangement of atoms in a molecule to form isomers and finally, *lipases* catalyze condensation reactions to form bonds between carbon–sulfur, carbon–carbon, or carbon–nitrogen (Blanco and Blanco 2017; Kumar and Verma 2020b).

4.2.1 Enzyme–Substrate Interaction

An enzyme facilitates a suitable environment for the substrates to form products at an enhanced rate. The substrate undergoes non-covalent interaction with the enzyme in a specific site called the active or substrate-binding site of the enzyme to form a substrate–enzyme complex. This enzyme–substrate complex later transforms into a product and releases the enzyme back. The catalytic action of enzymes is favored at optimal pH, temperature and ionic strength, etc. and any alterations will affect the catalytic activity of the enzymes. For example, a temperature rise will cause an alteration in the enzyme's native conformation (denaturation) which will reduce their catalytic activity. Small molecules can also affect the activity of enzymes and are known as inhibitors. The important difference between competitive and noncompetitive inhibitors is their preference for the binding site on enzymes. Competitive inhibitors compete for the active site on the enzyme whereas noncompetitive inhibitors engage with sites other than that of the active site. Both the inhibitors eventually bring conformational changes in the structure of the enzyme and facilitate inhibition of its activity. The active site of an enzyme has a unique and specific sequence of amino acids which in turns increases substrate specificity and selectivity. Enzyme specificity is first explained by the "Lock and Key model" introduced by Emil Fischer in 1894. The assumption of the rigid structure of enzymes was falsified later in 1958 through the "Induced Fit Model" proposed by Daniel Koshland where the concept of the transition state of the enzyme–substrate complex was introduced. According to this model, the conformation of the enzyme's active site as well as in some cases conformation of the substrate itself will undergo small changes during the formation of the enzyme–substrate complex (Blanco and Blanco 2017).

4.2.2 Enzyme Thermodynamics and Kinetics

An enzyme, just like any catalyst increases the reaction rate by lowering the activation energy of the reaction (Fig. 4.1).

The kinetics of the enzyme–substrate is explained by Leonor Michaelis and Maud Menten in 1913. Michaelis-Menten theory is based on the following reaction between enzyme (E) and substrate (S) to yield the product (P) through the formation of the enzyme–substrate complex (ES).

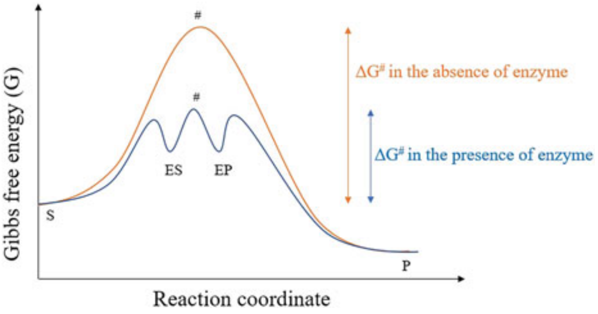

Fig. 4.1 Energy profile diagram of an enzyme-catalyzed and uncatalyzed reaction. Where S represents a substrate, ES is the enzyme–substrate complex, EP is the complex of enzyme and product just before their degradation to product, P, and # represents the transition state

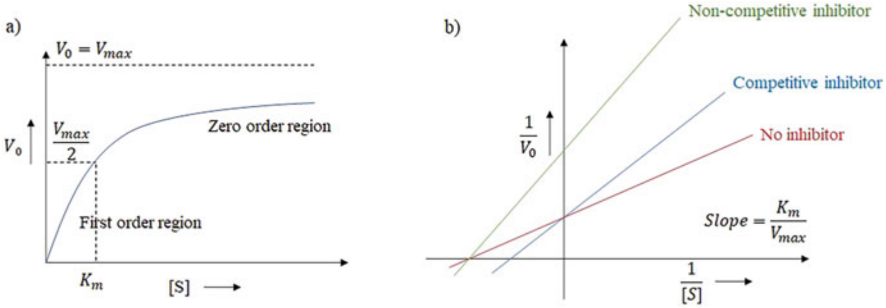

Fig. 4.2 The graphical representation of (**a**) Michaelis-Menten equation; (**b**) Lineweaver-Burk plot in the absence of inhibitor and the presence of competitive and non-competitive inhibitors

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{ES}] \overset{k_2}{\rightarrow} \mathrm{P} + \mathrm{E} \tag{4.1}$$

Michaelis and Menten derived an equation for the rate of the catalytic action of enzymes based on the assumption that the formation of ES and the reverse reaction to E and S is faster than its conversion to P and E and then applied the steady-state approximation for ES complex. The Michaelis-Menten equation is given as,

$$V_0 = \frac{V_m[S]}{[S] + K_m} \tag{4.2}$$

where V_0 is the rate at which ES converts into a product, V_m is the maximum reaction rate at the saturated concentration of the substrate, $[S]$ is the concentration of substrate, and K_m is Michaelis constant, it is the concentration of the substrate needed to acquire $V_m/2$. The graphical representation of this equation, V_o *vs* $[S]$ plot is given in Fig 4.2a. This equation is applicable to single enzyme–substrate interaction at constant enzyme concentration. At a low concentration of substrate, the enzymatic reaction follows first-order kinetics where the rate of reaction is proportional to substrate concentration. At a high concentration of substrate, the reaction follows zero-order kinetics, which means the rate of reaction is independent of substrate concentration.

Enzyme activity in the presence of inhibitors is well understood from the Lineweaver-Burk plot which is a graphical representation of the reciprocal of the Michaelis-Menten equation, as shown in Fig 4.2b.

$$\frac{1}{V_0} = \frac{1}{V_{\max}} + \left(\frac{K_m}{V_{\max}}\right)\frac{1}{[S]} \tag{4.3}$$

4.3 Chemical and Structural Factors Guiding Enzyme Hydrolysis

Biomass waste is biodegradable organic matter produced directly or indirectly by the energy utilized from the sun through the process of photosynthesis. The source of waste is very diverse and varied in terms of its composition. They are mainly composed of constituents like lignocellulosic biomass, starch, chitin, triglycerides, proteins, etc. (Tuck et al. 2012; Kumar and Verma 2020b). Due to the high fixed carbon content in them, these feedstocks have been in past and are even now used to generate energy and heat by burning them which could pose threat to the environment by the release of toxic air pollutants such as PAH (polycyclic aromatic hydrocarbons), particulate matters, POPs (persistent organic pollutant) (Sivertsen 2006). Policymakers have directed the industries to focus on the sustainable valorization of worldwide generated biomass so that such a resourceful matter is not just dumped as waste or burned into ashes. Currently, they are utilized as major feedstock in biorefineries for biofuels production, biogas, and biofertilizers.

4.3.1 Composition of Lignocellulosic Biomass

Lignocellulosic biomass is categorized based on the source of its generation. It could be organic matter from woody terrestrial forest residues, herbaceous residues from agriculture (corn cobs, sugarcane bagasse, rice and wheat husk, fruits and vegetable residues generated from fields and market), green waste from Municipality Solid Waste (MSW), animal and human sources, aquatic organic mass, and organic mass generated by anthropogenic ways as well. The sustainable utilization of biomass offers a huge advantage as they are widely available worldwide, reduces the overall cost of fuels by introducing them as an alternative source, and finally, contributes to the reduction of greenhouse gas emissions. Moreover, the overall production and process cycle of sustainable alternatives exhibit a zero-carbon dioxide balance. Lignocellulosic biomass is structurally composed of cellulose, hemicellulose, protein, lipids, etc. They also contain some active ingredients like antioxidants, polyphenols, lignin, pigments/carotenoids, etc. These constituents are arranged in layers to form the complete lignocellulosic biomass structure with lignin being the outermost layer, hemicellulose occupying the middle space, and cellulose placed at the core of the mass (Fig. 4.3).

Interestingly, cellulose is the major substrate in the biorefineries for biofuels and chemical commodities production. The percentage of these components varies based on the type and source of lignocellulosic biomass. Almost 15% of the total lignocellulosic mass comprises protein also. The lignin component renders a high resistance to cellulose access by the hydrolytic enzymes. Various pretreatment methods have been adopted to remove the lignin part to give more access to hydrolytic enzymes to degrade the high polysaccharide component of cellulose and

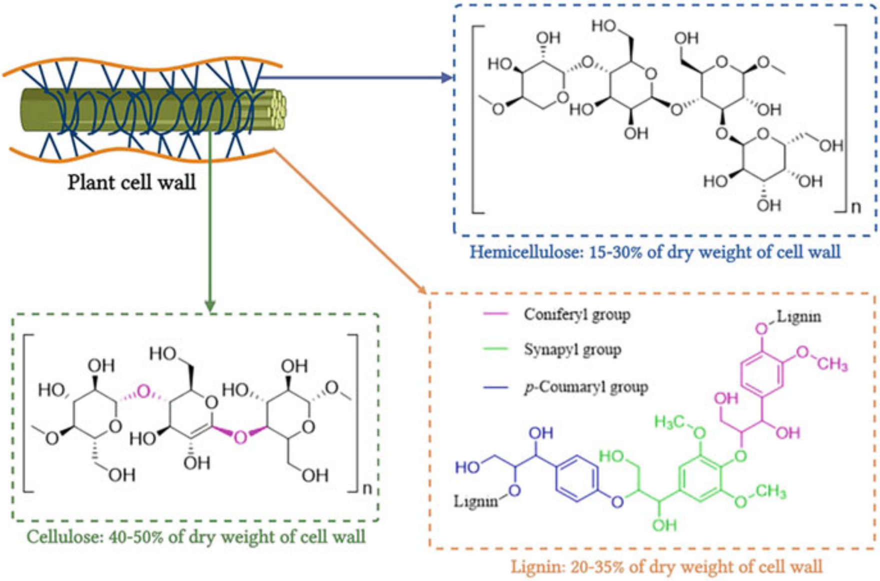

Fig. 4.3 Structural representation of lignocellulosic biomass: The plant cell wall is composed of a lignocellulosic structure where lignin forms the outermost covering, followed by hemicellulose and the most internal part is made up of cellulose components

hemicellulose. Depending upon the chemistry of the components present in the lignocellulosic biomass, enzymes are selected to degrade it.

4.3.1.1 Cellulose

Cellulose is an important cell wall component of the plant. It is a high molecular weight polysaccharide composed of D-glucose units linked with each other through β-1,4-glycosidic bonds forming the basic repeating unit called cellobiose, 4-*O*-β-D-glucopyranosyl-D-glucopyranose (structural basis of cellulose) (Fig. 4.4a). A cellulose primary chain is composed of almost 500–1400 monomer units. These primary chains are further arranged in a parallel array to form the higher structural unit called microfibril. Several microfibril units form cellulose fibril, the higher structural unit (Robak and Balcerek 2018; Bhardwaj et al. 2021b). The extensive intramolecular (O_6–O_2 and O_3–O_5) and intermolecular (O_3–O_6) hydrogen bonds and Van der Waals forces in cellulose structures give its crystalline nature, high tensile strength, and recalcitrance to hydrolysis. The amorphous cellulose corresponds to regions where the above-mentioned molecular bonds are disrupted giving twists and torsions to the structure resulting in interspersed disordered regions in cellulose. The structural or crystalline region of cellulose is highly packed not allowing even a single water

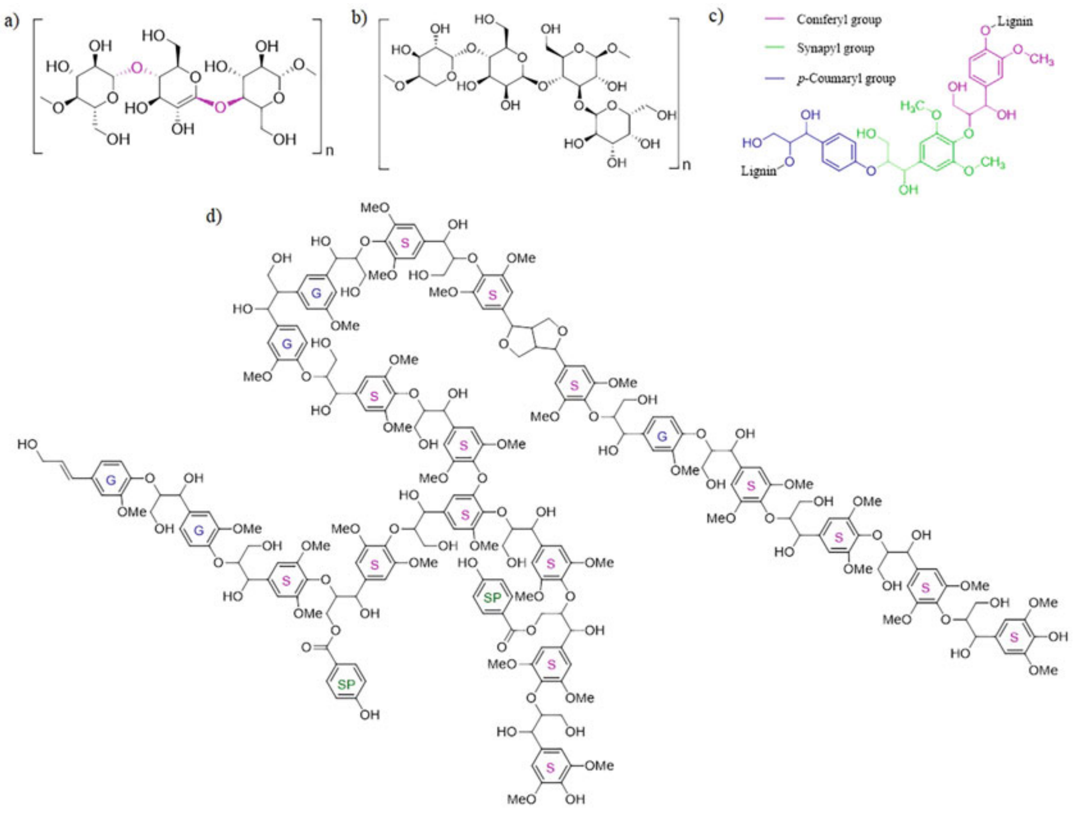

Fig. 4.4 Chemical structures of components present in lignocellulosic plant's cell wall: (**a**) basic skeletal structure of cellulose: Glucose units combined by *β*-(1,4)-glycosidic linkages; (**b**) basic skeletal structure of hemicellulose having *β*-(1,4)-xylose-*β*-(1,4)-agarose-*β*-(1,4)-mannose-*β*-(1,4)-glucose-*α*-(1,3)-galactose motifs; (**c**) basic skeletal structure of lignin component; and (**d**) Structure of lignin in poplar plant. Where S is the syringyl group, G is the guaiacyl, and SP is the synapyl basic groups

molecule to enter, but the distorted amorphous region is very easily accessible to enzyme hydrolysis (Betts 1991).

4.3.1.2 Hemicellulose

Hemicellulose stands second to cellulose in terms of its abundance on the planet. In comparison to cellulose, hemicellulose is highly branched with almost 500–3000 sugar units as monomers. Hemicellulose is a heteropolymer comprising of side chains with xylans as pentoses, mannans, and glucomannans as hexoses or arabinogalactans and galactans as galactose units. Apart from monosaccharides, they also accompany typical uronic acids like D-glucuronic, 4-*O*-methylglucuronic, and D-galacturonic acids (Fig. 4.4b).

Xylan: Xylans are water-soluble polysaccharides made up of repeating units of β-D-xylopyranose linked by β-(1,4)-glycosidic bonds. This primary chain also comprises other carbohydrates such as xylose, mannose, arabinose, rhamnose, or 4-*O*-methylglucuronic acid.

Mannan: Mannans are the most important constituent of hemicellulose which helps the hemicellulose to bind to the cellulose counterpart. They are widely found as a component in the angiosperm cell wall. β-D-mannopyranosyl units are formed by β-1,4 linkage along with a small ratio of galactans in the linear chains. There are four different types of mannans present: galactomannans, galacto-glucomannans, glucomannans, and linear-mannans.

Galactans: Galactans are made of galactose as repeating units linked through α-1, 3, and β-1,6 linkages to form 4-α-D-galactopyranosyl and 3-β-D-galactopyranosyl attached in alternate fashion. They are long polymeric chains not commonly found in all forms of plants. They are majorly found in some algae, seeds, buds, or flowers (Li et al. 2013).

4.3.1.3 Lignin

Unlike cellulose, lignin has an irregular three-dimensional structure with no specific repeating units. Lignin acts as the protective and cementing cover in plants which helps arrange the fibers together to enhance the compactness of the wood thereby making it more resistive. It helps in gluing hemicellulose with cellulose, and it resists the access of enzymes to cellulose by acting as a physical barrier. It is an amorphous organic compound comprising phenylpropanoid units with three different types of *p*-hydroxycinnamyl alcohol: coniferyl alcohol, sinapyl alcohol, *p*-coumaryl alcohol (Fig 4.4c, d). Overall lignification is species specific and is obtained by several cross-linking reactions between the radicals formed by oxidation and resonance delocalization in phenylpropanoid monomeric units. Lignin is synthesized in the plants via shikimic acid pathway. The structural integration of different cellulosic components makes it very recalcitrant to hydrolysis by enzymes. The cellulose and hemicellulose are attached through hydrogen bonds, meanwhile, lignin forms five different types of lignin carbohydrate bonds to bind to hemicellulose: γ-esters esters, benzyl ethers, phenyl glycosides, ferulate/coumarate esters, and hemiacetal/acetal linkages (Giummarella et al. 2019; Agrawal and Verma 2020a, b). The biorefineries arena focus on the effective valorization of lignocellulosic materials into valuable products by introducing controlled cleavage of carbon–carbon and carbon–oxygen bonds present in the recalcitrant lignin on the outermost coat. The focus is also maintained on getting rid of various impurities (organic and inorganic).

4.3.2 Starch

Food is stored in plants in the form of starch in seeds, roots, and a little amount in the residual biomass. It is composed of two types of polysaccharides, namely amylose and amylopectin. Amylose is formed by polymerizing D-glucose via α-1,4 linkages linearly, on the other hand in amylopectin, which has branched formation is formed by α-1,4 glycosidic bonds linearly, and α-1,6 glycosidic linkages for branched chains (Whistler and Daniel 1984).

4.4 Enzymes and their Application in Waste

Despite the sustainable availability of biomass for conversion into bioenergy, the process is expensive and time-consuming as it requires lengthy downstream processing for the collection of final products. Before subjecting the different components of waste to hydrolysis, pretreatment of the complex material is required which is the most expensive process in the transformation. It is done to remove the recalcitrant lignin component which remains the major hindrance in exposing the buried cellulose to the saccharification process. The pretreatment involves subjecting the lignocellulosic mass to either high pressure, temperature, or chemical treatment or enzymatic hydrolysis. The chemical pretreatment includes the use of chemicals like organic solvents, concentrated acids/bases, or neoteric solvents which are very harsh and corrosive. Additionally, the process becomes more tedious as many steps are required to separate the final products from the chemicals used in pretreatment. The highly concentrated and corrosive acids and alkali are damaging to the equipment too. There are a lot of unwanted products formed during the process of pretreatment with chemicals that can act as inhibitors to the microbial enzymes used for fermentation. Therefore, the use of hydrolytic enzymes proves to be useful as it poses less cost and also reduces the difficulties faced in the downstream process (Manisha and Yadav 2017). As discussed earlier, the most resourceful feedstock for the production of green fuel is biomass waste, and it has been in regular consideration and experimentation under the biorefinery concept (Azapagic 2014). To switch to industrial symbiosis, i.e., waste from one sector is used as feedstock in another

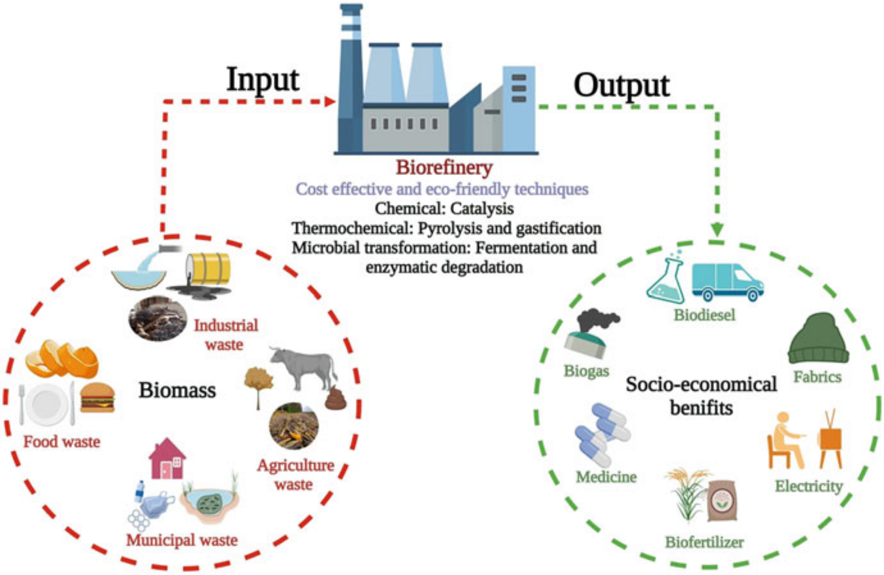

Fig. 4.5 A model of biorefinery concept: Biomass feedstocks from various sources are taken as raw material in biorefinery and converted into various forms of bioenergy and other value-added products

industry; therefore, it is very necessary to identify, characterize, and quantify the residues present in the waste stream (Fig. 4.5).

Microorganisms and their enzymes have long been core tools in the biofuel refineries, being present in all stages, starting from pretreatment, hydrolysis, and fermentation. They can be introduced as biocatalysts with the substrates where they are produced in situ by microorganisms or they are added ex situ in purified form or as enzyme cocktails. In this section, we will be considering the important enzymes, especially the hydrolytic type in saccharification of polymers into monomers and will also discuss the mechanism of their actions.

4.4.1 Hydrolytic Enzymes Involved in the Valorization of Lignocellulosic Waste

The main source of lignocellulosic biomass is the organic residues obtained from human activities such as agricultural waste and food processing industries. Moreover, solid municipal waste which mostly comprises paper and organics can be included as an important lignocellulosic waste stream for valorization into valuable products. The biopolymers included in lignocellulosic biomass constitute cellulose, hemicellulose, and lignin. The major enzymes required to saccharify these polymers are cellulases, hemicellulases, and lignin-degrading enzymes. These enzymes are classified under the single-family of glycoside hydrolases (glycosidases or carbohydrases), E.C 3.2.1, and are involved in the catalysis of *O*-glycosidic bond hydrolysis (van Wyk et al. 2017; Bhardwaj et al. 2020). The gene corresponding to this class of enzyme is present in all living organisms except in some Archaeans and some unicellular parasites. Glycoside hydrolases cleave the glycosidic bonds via two different mechanisms based on the status of the anomeric configuration during the reaction. The net inversion of an anomeric configuration is achieved as a result of a one-step double displacement reaction between the acidic and basic amino acid groups whereas the retention of the anomeric configuration happens via a two-step double displacement reaction involving acid/base and nucleophilic assistance provided by amino acid residues (Naumoff 2011). All the information concerning genomic, structural, and functional aspects of glycoside hydrolases and their family members is available in a highly curated, knowledge-based database known as the carbohydrate-active enzyme (CAZy) database. This database states that glycoside hydrolases (GHs) are categorized into 135 different families and 14 clans. This classification was based on their overall structural confirmation, amino acid sequence, and function (Lombard et al. 2014).

4.4.1.1 Cellulases

Cellulase is a class of enzymes that hydrolyzes the β-1,4-glycosidic bonds in polysaccharides like cellulose to glucose units and is grouped among glycoside hydrolases (GH). Cellulose from fungus has two domains, namely a catalytic domain, which performs the catalytic activity, and a cellulose-binding domain, which anchors the enzyme to the cellulose substrate. Both the domains are linked together through a linker domain. The hydrolytic action depends upon the synergistic action of three major enzymes, cellobiohydrolase/exoglucanase (E.C 3.2.1.176)/(E.C 3.2.1.91), endocellulase/endoglucanase (E.C 3.2.1.4), and β-glucosidase (E.C 3.2.1.21) (Horn et al. 2012; Kostylev and Wilson 2014). Endocellulases hydrolyze the amorphous area of cellulose to release long-chain oligomers with non-reducing ends which are then acted upon by exocellulase or cellobiohydrolases on the β-1,4-glycosidic bonds liberating β-cellobiose. Cellobiohydrolases act on the oligomers from the reducing ends whereas exocellulase act on the non-reducing ends. β-glucosidase hydrolyzes the smaller glucans or disaccharide cellobiose into the monomeric glucose (Juturu and Wu 2014) (Fig. 4.6a).

Several microorganisms have been found to produce cellulose enzymes. Among bacteria the most important are *Clostridium* species, *Pseudomonas* species, and *Trichoderma reesei* whereas the major cellulose-producing fungi belong to *Aspergillus species*, *Fusarium species*, *Penicillium species*, *Schizophyllum commune*, and *Melanocarpus species.* In anaerobic bacteria, cellulose occurs as cellulosomes, an extracellular aggregated enzyme structure. Endocellulase or endoglucanase belonging to the family glycoside hydrolases (GH) 5 comprises a single catalytic subunit made up of 335 amino acids folding into the active enzyme. The structural

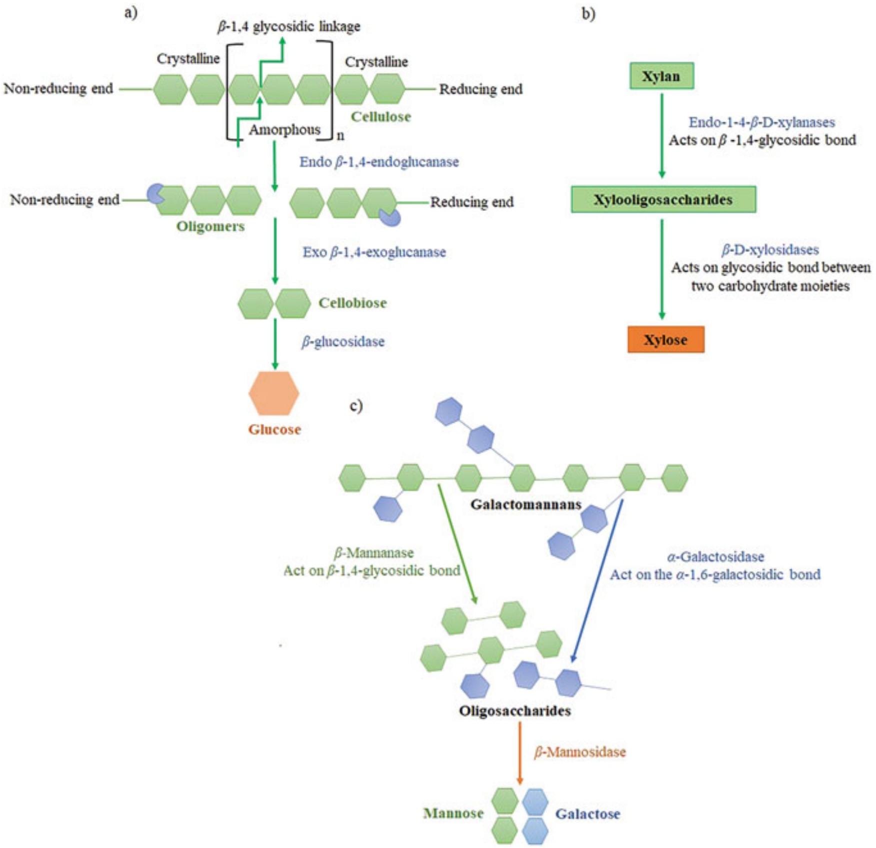

Fig. 4.6 Mechanism of action of cellulases and hemicellulases: (**a**) Endocellulase, exoglucanase, and β-glucosidase act in synergy for the degradation of cellulose. (**b**) The mechanism of action of endoxylanase and β-glucosidase on the degradation of xylan to xylose; and (**c**) synergistic action of β-mannanases, β-mannosidase, and α-galactosidases on the degradation of various units in mannan component of hemicellulose

architecture of endoglucanase has eight $(\beta/\alpha)_8$ barrel-shaped loops along with a short double-stranded anti-parallel β sheet and three single turns helices. The catalytic substrate-binding site has two glutamate amino acid residues at positions 133 (acid-base) and 240 (nucleophile) which are highly conserved and decisive in the first step of the reaction (Lo Leggio and Larsen 2002) (Fig. 4.7a). Cellobiohydrolases the exoglucanases belong to the family GH 7. The three-dimensional structure of cellobiohydrolases is made up of 431 amino acid residues and exhibits a β-jelly roll structure with two anti-parallel β-sheets to each β-jelly roll. Each β-sheet curves to form concave and convex shapes which are connected through four α-helices. Amino acid glutamine at positions 207 and 212 at the active site of the enzyme participates in the acid-base reaction mechanism (Fig. 4.7b) (Muñoz et al. 2001). β-

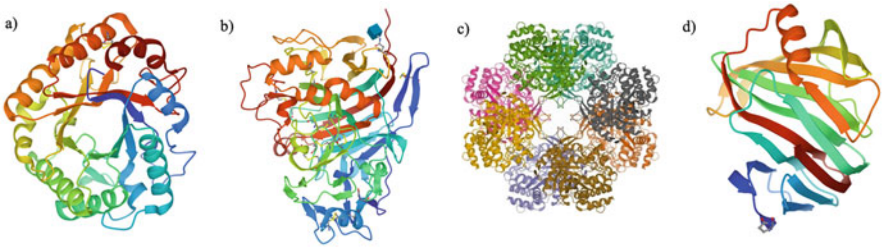

Fig. 4.7 Crystalographic structure of (**a**) endoglucanase enzyme obtained from *Thermoascus aurantiacus* (PDB I.D: 1GZJ) (Lo Leggio and Larsen 2002); (**b**) exoglucanase enzyme obtained from *Phanerochaete Chrysosporium* (PDB ID: 1GPI) (Muñoz et al. 2001); (**c**) *β*-glucosidase enzyme obtained from *Bacillus polymyxa* (PDB ID: 1BGA) (Sanz-Aparicio et al. 1998); (**d**) endo-1-4-β-D-xylanases enzyme obtained from *Trichoderma reesei* (PDB I.D: 1ENX (Törrönen et al. 1994)

glucosidase from the strain *Bacillus polymyxa* (BglA) exists in a tetramer of dimers arranged in an octameric confirmation. The enzymes form aggregates due to their intracellular localization. The substrate-binding site of the enzyme accommodates Glutamine at 166 and 352 which acts as acid/base and nucleophile in hydrolysis reaction, respectively. The substrate binding is also influenced by Histidine residue at 121 as well as tyrosine residue at 296 positions (Sanz-Aparicio et al. 1998) (Fig. 4.7c). Cellulases have been utilized widely in various industries like brewery distilleries, textile processing, paper pulp industries, detergent production, cattle feed processing, and recently been introduced in the production of biofuels.

4.4.1.2 Hemicellulases

This class of enzyme is also known as hemicellulose degrading enzymes. They are involved in the depolymerization of components present in the hemicellulose portion of lignocellulosic biomass such as galactans, xylans, mannans, and arabans. Mannanases, *α*-glucuronidases, and *α*-arabinofuranosidases are widely discussed as well as utilized enzymes.

Xylanases: Xylanase enzymes constitute two major enzymes which include endo-1-4-*β*-D-xylanases (EC 3.2.1.8) and *β*-D-xylosidases (E.C. 3.2.1.37). The endoxylanases hydrolyze xylan into xylooligosaccharides which are further acted upon by xylosidases to yield monomeric xylose (Fig. 4.6b). The structural analysis of endo-*β*-1,4-xylanase II (XYNII) from *Trichoderma reesei* reveals that the enzyme exists as a single domain with 190 amino acid residues folded into two anti-parallel *β*-sheets arranged parallel to each other (Fig. 4.7d). The active site cleft is formed by twisting the β-sheets, and it accommodates two glutamic acid residues at positions 86 and 177 (Törrönen et al. 1994). Some of the accessory enzymes like acetyl xylan esterase (E.C 3.1.1.72), *p*-coumaric esterase (3.1.1.B10), *α*-glucuronidases (E.C 3.2.1.139), *α*-l-arabinofuranosidases (E.C. 3.2.1.55), and ferulic acid esterase (E.C

3.1.1.73) are necessary to hydrolyze the remaining component or side chains of the hemicellulose structure such as glucuronic acid, galacturonic acid, arabinose, galactose, ferulic and coumaric acids (Bhardwaj et al. 2019; Gírio et al. 2010; Beg et al. 2001). The action of α-glucuronidase, α-l-arabinofuranosidases, and acetyl xylan esterase is to remove acetyl and phenolic side branches whereas p-coumaric esterase and ferulic acid esterase cleave the ester bonds in xylose. The synergistic enzyme activity of all the xylanases proves significant in opening up the xylan component of the lignocellulosic biomass (Moreira and Filho 2016). The presence of xylanases has been found in many organisms ranging from microorganisms like fungi, bacteria, and yeast to crustaceans, insects, and seeds (Beg et al. 2001). Microbial xylanases are preferred over animal sources. The most notified, experimented, and applied xylanases are from the organisms from the genus *Bacillus, Chaetomium, Nonomuraea, Arthrobacter, Clostridium, Thermomonospora, Dictyoglomus, Fusarium, Streptomyces, Aspergillus,* etc. (Bhardwaj et al. 2019; Sunna and Antranikian 1997).

Mannanases: These enzymes are involved in the depolymerization of mannans which are an integral part of the hemicellulose portion of the cell wall. 1,4-β-D-mannohydrolases or β-mannanases (E.C 3.2.1.78) are endo-acting mannanases that cleave the internal glycosidic bonds on the linear chains liberating short oligosaccharides like β-1,4-manno-oligosaccharides. On the other hand, β-1,4-D mannopyranoside hydrolases or β-mannosidases (E.C 3.2.1.25) are exo hydrolases that choose to act on the non-reducing ends of mannobiose to degrade it into individual mannose units. Lastly, β-1,4-D-glucoside glucohydrolases or β-glucosidases (E.C 3.2.1.21) act on the products liberated from the cleavage of glucomannan and galactoglucomannan specifically cleaving the β-1,4-glucopyranose units from the non-reducing terminal (Dhawan and Kaur 2007; Moreira and Filho 2008). α-galactosidases (E.C 3.2.1.22) and acetyl mannan esterases (E.C 3.1.1.6) are some of the accessory proteins which are required to excise the additional side chains or groups present occasionally on the mannans (Malgas et al. 2015) (Fig. 4.6c).

Mannanase is classified under different GH families (like GH 1–3, GH 5, 26, 27, 113, etc.). Their primary structure is different while they share common spatial arrangements. They all have a canonical $(\beta/\alpha)_8$-barrel protein fold in their active site and based on that they have been included in clan GH-A. The central active site cleft contains two glutamate residues at the C-terminal side (Dawood and Ma 2020). Mannanase is the second most important industrial enzyme after xylanases and has been explored in various industries like textile and paper industries, pharmaceuticals, food, feedstock industries, etc. The bacterial degraders for mannanases among Gram-positive bacteria are from *Bacillus* species, and *Clostridia* species, whereas from Gram-negative bacteria are from *Vibrio*, *Pseudomonas, Klebsiella,* and *Bacteroides.* Among fungal counterparts *Aspergillus, Agaricus, Trichoderma,* and *Sclerotium, Penicillium* species are mostly reported. Actinomycetes from *Streptomyces* species have also been shown to be mannan degraders (Dhawan and Kaur 2007; Chauhan et al. 2012).

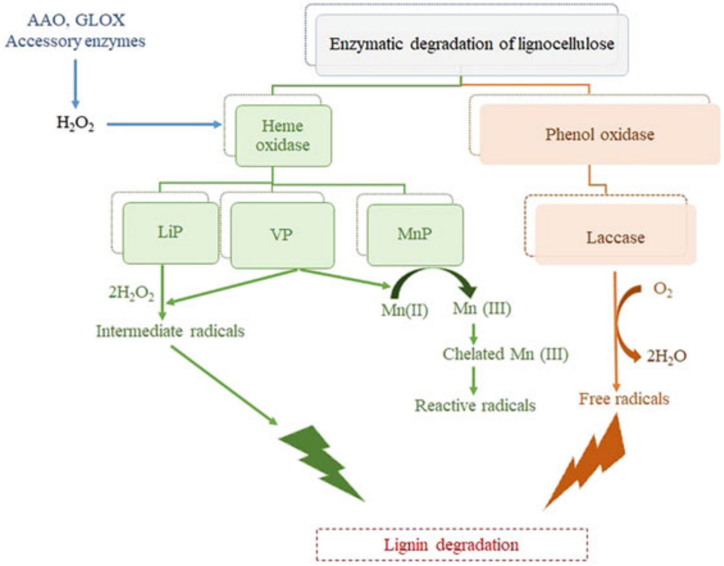

Fig. 4.8 Lignin hydrolysis by lignin-degrading enzymes: Diagram depicting the mechanism of action of different lignin-degrading enzymes for hydrolyzing lignin component

4.4.1.3 Lignin-Degrading Enzymes

They catalyze the conversion of lignin present in lignocellulosic biomass into small aromatic molecules. Lignin is a phenolic polymer containing phenylpropanoid aryl-C3 units links. These can be degraded by the synergistic action of two groups of enzymes, namely lignin-modifying and lignin-degrading auxiliary enzymes. The former includes laccase or phenol oxidases (E.C 1.10.3.2), lignin-modifying peroxidases such as lignin peroxidase (LiP) (E.C 1.11.1.14), versatile peroxidases (E.C 1.11.1.16), dye-degrading peroxidases (E.C 1.11.1.19), and manganese peroxidase (MnP) (E.C 1.11.1.13). All the peroxidases have a unique prosthetic group in the form of protoporphyrin IX (Pollegioni et al. 2015). Auxiliary enzymes in lignin degradation on the other hand include glucose oxidase (E.C 1.1.3.4), cellobiose dehydrogenase (E.C 1.1.99.18), glucose oxidase (E.C 1.1.3.4), aryl alcohol oxidase (E.C 1.1.3.7), pyranose 2-oxidase (E.C 1.1.3.10), and glyoxal oxidase (E.C 1.2.3.5) along with some other enzymes like alkyl aryl etherase, and aryl alcohol dehydrogenase (Bilal et al. 2019; Zhang et al. 2020a, b; Levasseur et al. 2008; Agrawal and Verma 2020a, b) (Fig. 4.8).

Basidiomycetes white-rot fungus is extensively investigated for the production of these auxiliary enzymes (Garcia-Ruiz et al. 2014). Hofrichter and Ullrich stated an action of a new enzyme heme-thiolate haloperoxidases, catalytically identical to other heme-containing oxidoreductases (cytochrome P450 monooxygenases and catalases), as lignin degrading in cultures of *Ceriporiopsis subvermispora* (Hofrichter and Ullrich 2006).

Although the crystal structure and catalytic cycle of all the ligninolytic enzymes are well-reviewed (Chen et al. 2012; Pollegioni et al. 2015; Wong 2009; Janusz et al. 2017), we have attempted to briefly touch on some of the important aspects in understanding the mechanism of these enzymes.

Laccases: Laccases fall in the group of oxidoreductases that uses oxygen as an oxidizing agent. The four copper ions at the active center of laccases help the enzyme in oxidizing most of the phenolic and aromatic compounds present in the lignin (Mai et al. 2000; Pollegioni et al. 2015). Some metal ions and organometallic compounds are also been reported as the substrate of laccases (Garcia-Ruiz et al. 2014; Zimmerman et al. 2008). All these four copper ions at the T2/T3 site (the T1 Cu and the tri-nuclear Cu cluster (T2 Cu, T3α Cu, and T3β Cu)) have a different electro-paramagnetic resonance which is key to their unique reaction with the random polymeric nature of lignin. The fungal laccases are known to comprise ~520–550 amino acids residues with glycosylation as primary modifications. The three-dimensional structure of fungal laccases demonstrates three tightly arranged cupredoxin-like domains having β-barrel symmetry. The third domain holds the T1 Cu near the surface of the protein, and the T2 Cu, T3 (α and β) Cu are located at the junction of the first and the third domain (Mehra et al. 2018; Sitarz et al. 2016). Laccases are extracellularly, intracellularly as well as periplasmically produced depending on the type of microorganisms producing them. It is found mostly in fungal and bacterial cells.

Lignin Peroxides (LiP): LiPs are generally known to oxidize phenolic and non-phenolic organic compounds instead the enzyme specificity is relatively poor. The structural analysis of LiP isolated from *Phanerochaete chrysosporium* revealed its globular nature. The active site pocket is formed of two domains organized of eight α-helices (major and minor) with restricted β components enclosing a heme-chelating ferric ion (Choinowski et al. 1999). The three-dimensional structure of LiP is further stabilized by four disulfide linkages, two calcium ions, and two glycosylation-specific post-translational sites. Although their enzymatic mechanism is similar to other peroxidases in the same class, they stand effective catalytically due to their very high redox potential when it comes to oxidizing the recalcitrant lignin component (Sigoillot et al. 2012).

Manganese Peroxidases (MnP): MnP was isolated and studied initially from the fungi *Phanerochaete chrysosporium*. Supplementation of Mn ions and other organic compounds like 2-hydroxybutyrate, malonate, glycolate, or glucuronate in the growth medium stimulated the production of MnP in white-rot fungus (Mester and Field 2006). These molecules in particular stabilized the structure of the enzyme. A molecule of heme (iron protoporphyrin IX) is sandwiched between the two domains formed by α-helices very similar to that of the structure of LiP. Very close to the heme porphyrin lies the binding site of Mn^{2+} ion which constitutes one aspartate and two glutamate γ-carboxylic groups. Slightly different from the structure of LiP, MnP consists of five disulfide bridges and two Ca^{2+} ions. The active cycle of MnP varies from that of LiP, in the oxidation of lignin compounds involving the conversion of $Mn^{2+}$to Mn^{3+}ions (Niladevi 2009).

Versatile Peroxidases (VPs): This enzyme represents a cocktail of LiPs and MnPs. It also constitutes a heme porphyrin group close to the catalytic site. The active center is made of 11–12 α-helixes with four disulfide bridges, two Mn (II) binding sites and two Ca(II) binding sites. This enzyme is capable of oxidizing methoxybenzenes and various non-phenolic lignin compounds with high affinity. The multi-step reaction mechanism of VPs is similar to other peroxidases.

Dye-decolorizing peroxidase (DyP): These enzymes are different from the classical lipid-modifying peroxidases like LiP, MnP, and VPs. They can decolorize a range of molecules including dyes, β-carotene, and aromatic sulfides (Zámocký et al. 2015). They were first investigated and isolated from the cultures of the fungus *B. adusta* (Fernandez-Fueyo et al. 2015). DyPs can oxidize non-specifically all peroxidase substrates and also possess hydrolase and oxidase activity. The structural analysis of DyPs demonstrates the presence of two domains. The catalytic site lies in the cavity of the two domains accommodating the heme cofactor (Colpa et al. 2014).

Glyoxal Oxidases (GLOX): Lignin components like methylglyoxal and glyoxal can be oxidized by the GLOX. These enzymes proceed with the oxidation of their substrate with the formation of extracellular hydrogen peroxide (Yamada et al. 2014). They are moreover required to regulate the peroxidase activity of the lignin-modifying peroxidases. The active center of GLOX is occupied by a copper ion which helps in the aldehyde oxidation of its substrate (Yin et al. 2015).

Aryl Alcohol Oxidase (AAO): This enzyme is a member glucose-methanol-choline oxidase/dehydrogenase family. Structurally, this enzyme is a monomer with two domains non-covalently bound with the FAD cofactor (Fernandez et al. 2009). AAO substrates include various aryl-alcohols (phenolic and non-phenolic), aliphatic (polyunsaturated) primary alcohols, or aromatic secondary alcohols present in the lignocellulose biomass. It also oxidizes the radical intermediates produced by laccase enzymes like guaiacol, sinapic acid, etc. (Mathieu et al. 2016). The oxidative dehydrogenation reaction of AAO is an NADP-dependent reaction and produces H_2O_2 (Ferreira et al. 2010).

Pyranose 2-Oxidase (P2O): These oxidoreductases are involved in the oxidation of aldopyranose compounds. It is produced periplasmically and transported in membrane-associated vesicles (De Koker et al. 2004; Prongjit et al. 2009). They are homotetrameric and have three major conserved regions, namely the binding site for FAD, the substrate-binding region, and the flavin attachment loop. The threonine hydroxyl of Thr169 present at the active site is very important for the oxidation of sugars and flavin molecules. The P2O catalyzes the oxidation of its substrate at the C2 position via a Ping-Pong type reaction mechanism at pH 7 (two half-reactions). The end products are the 2-keto-sugars and hydrogen peroxide. First, a hydride equivalent from the sugar substrate is donated to the protein-bound flavin with the generation of a reduced FAD (FADH) and the 2-keto-sugar, and secondly, a reduced flavin is oxidized by donating two electrons to O_2 thereby forming H_2O_2 (Pitsawong et al. 2010).

4.4.2 Hydrolytic Enzymes Involved in the Valorization of Food Waste

Food waste origin is marked starting from the agriculture sector, packaging, and retail, finally till household consumption. These waste streams generated are rich in biodegradable organic matter, which due to their peculiar chemical characteristics like high biological and chemical oxygen demand, content-rich in carbon and nitrogen, are deleterious to the environment when discarded in landfills and aquatic streams. They may cause aquatic pollution, harmful toxic leaching into ground and surface water, altered soil composition, etc. The food processing industries and so their waste is categorized based on the food material they process. Baiano et al. (2014) assessed and estimated the approximate percentage of waste generated by different food processing units or industries (Baiano 2014). According to them, the beverages manufacturing industry generates 26% of food waste, dairy industries make up 21%, fruit/vegetable, cereal edible oils manufacturing and processing as well as meat and fish product processing and preservation industries constitute (12.9%), (3.9%), (8.4%) of food waste, respectively. However, valorization of these compounds to revenue streams like biofuels, other food, and non-food commodities is possible by introducing enzymes catalysis at various steps of their conversions (Andler and Goddard 2018). For instance, esterification of different waste components like oil, sugar, starch, and even flavonoids help in enhancing their values through converting or valorizing them into value-added products like biodiesel, surfactants, biodegradable plastics, and this indirectly prevents their direct disposal to wastewater treatment facilities.

Pectinases: The industries processing vegetables and fruits are rich in crude dietary fibers, carbohydrates, polyphenols, flavonoids, triglycerides, or plant-based fatty acids, etc. The by-product of these industries can be widely valorized through enzymatic and also through other physico-chemical extraction into value-added revenue streams like novel pharmaceuticals, animal feeds, etc. (Mourtzinos and Goula 2019; Fierascu et al. 2020). For instance, soluble and insoluble dietary fibers from citrus fruit pulp have been investigated by a group of researchers to replace fat content in ice cream because of their high phenolic and carotenoid content and more importantly because of their high water and fat retention capacity (de Crizel et al. 2014). Fierascu et al. (2020) have also extensively reviewed the current opinions on utilizing the waste generated from fruits processing industries into useful commodities (Fierascu et al. 2020). Pectinases are important fibrinolytic enzymes, and they are widely utilized in beverages industries for clarification as well as enhancement of color purposes. These enzymes help dissolve pectin structures (Micheli 2001) and are categorized based on their mechanism of bond cleavage: (1) pectin esterases and (2) depolymerase enzymes. Depending upon the substrate on which the pectinases act, pectin esterases are of two types, i.e., pectin acetylesterases (E.C 3.1.1.6) and pectin methylesterase (E.C 3.1.1.11). Pectin depolymerase, on the other hand, are hydrolases, for example, polygalacturonase, PG (E.C 3.2.1.15), and lyases or transeliminase comprising pectin lyase, PNL (E.C 4.2.2.10), and pectate lyase, PL

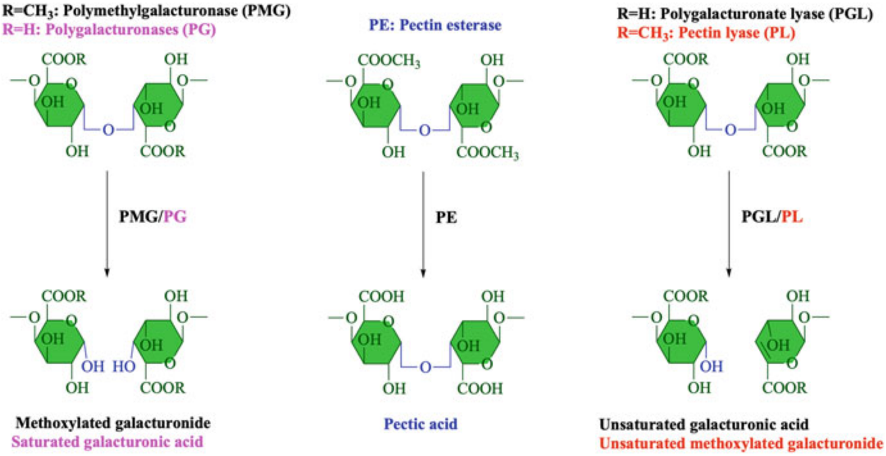

Fig. 4.9 Action of pectinases: Mechanisms of action of polymethylgalacturonase, polygalacturanase, pectin esterases, polygalacturanase, and pectin lyase on their specific pectin substrate

(E.C 4.2.2.2) (Sharma et al. 2013). Pectin methylesterases (E.C 3.1.1.11) convert the methyl groups into pectic acid and the depolymerase enzyme further disintegrates pectic acid into simpler carbohydrates (Fig. 4.9).

Pectinases in common consist of only one domain termed parallel β-helix making a right-handed cylinder. The structure contains three parallel β-sheets. These β-sheets arrange themselves to form a prism-like structure with two β-sheets forming an anti-parallel sandwich while the third one remains perpendicular to the axis. The active site of the enzyme is formed on the exterior side of the parallel β-helix. This structural model is most similar and closest to the structures demonstrated in the referred articles through crystallographic studies in pectinases from various strains (Jenkins et al. 2001; Pickersgill et al. 1994, 1998; Petersen et al. 1997).

Inulinase: Inulinase acts upon the β-2,1-linkage between the fructose units present in the inulin molecule. The polyfructose chain is terminated with a glucose unit attached with α-1, β-2-glycosidic linkage. Inulin is a stored carbohydrate found commonly in roots and tubers of plants like onion, garlic, and also there are reports of bacterial inulin which are comparatively highly branched in nature. Inulinase enzyme is classified into two classes: an endo-inulinase called 2,1-β-D-fructanfructohydrolase (E.C 3.2.1.7) and an exo-inulinase called β-D-fructanfructohydrolase (E.C 3.2.1.80) (Neeraj et al. 2018). The structural analysis of inulinase from *Aspergillus awamori* reveals the presence of two catalytically important residues (Asp41 and Glu241) at the substrate-binding site of the enzymes. These residues play a vital role in the double displacement reaction at the initial hydrolysis step (Nagema et al. 2004). Modern nutrition prospects recommend artificial sweeteners in the place of sucrose in diet to people looking for maintenance of weight/weight loss and lowering blood sugar levels in diabetes. Fructose products have also made their place as sweeteners in prebiotics popularly known as Greek yogurt. Here's where Inulinase yields its importance in industries generating fructose or fructose oligosaccharides as artificial sweeteners. Inulinase has also been established in the production of a plethora of commercially important products like citric acid, tetrahydrofuran, mannitol, sorbitol and 2,3-butanediol, etc. (Chi et al. 2009).

Lipolytic Enzymes: Wastewater generated from the slaughterhouse, poultry, and fish farms are rich in biodegradable organic matter like oil and grease waste which can result in high BOD and COD. As a consequence, there is an increase in the growth of filamentous microorganisms (bulking), floating and clogging of sludge in the treatment plant, and unpleasant odor. This demands the hydrolysis of the organic matter before its release into the treatment plants for further processing. Even though there are various methods like dissolved air flotation systems, tilted plate separators, grease-trap, and physical-chemical treatment (aerobic and anaerobic pretreatments) employed for the removal of these biodegradable organic matters from the wastewater, their proper implementation counters several setbacks. Therefore, effluents from several origins can be subjected to enzymatic hydrolysis by lipase. Treatment of domestic wastewater rich in oil and grease with lipase obtained from *Candida rugosa* (Jaeger and Reetz 1998) and *Pseudomonas aeruginosa* (Dharmsthiti and Kuhasuntisuk 1998) has been vastly investigated. Lipases are chemically known as triacylglycerol hydrolases (E.C. 3.1.1.3) which catalyze the hydrolysis of triacylglycerol. The active site of lipases is decorated with amino acids like serine, aspartate or glutamate, and histidine (Mateos et al. 2021). They exist as monomeric proteins folded to form β-sheets in the center enclosed by α-helix. The lipase activity is considered maximum at the oil-water interface which is dependent upon its change in conformation from closed to open form upon coming in contact with a hydrophobic surface. Apart from hydrolysis, lipases can catalyze other reactions like esterification, transesterification, acidolysis, and aminolysis.

Lactases: Dairy industries are also major contributors of proteins, fatty acids, and lactose in liquid waste. The major portion of which is considered to be deproteinized cheese whey obtained from cheese producing industries all over the world, which despite no toxic content is a major concern to environmental preservation and safety (Lappa et al. 2019). The lactose component in cheese whey has been elaborately investigated for the production of several commodities like bioethanol, artificial sweeteners, green plastics/polyhydroxyalkanoate polyesters, etc. (Koller et al. 2012), and there are reports of its valorization into disinfectants, electron donors for electricity generation through single chamber microbial fuels cells as well (Banaszewska et al. 2014; Pescuma et al. 2015; Yadav et al. 2015). Lactases are known as β-D-galactohydrolase/β-galactosidases (E.C 3.2.1.23), and they catalyze the cleavage of lactose into glucose and galactose. The most demanding prebiotics, lactulose, and galacto-oligosaccharides (GOS) are produced by lactose through the action of β-galactosidases. Lactose is transgalactosylated by β-galactosidases to produce a mixture of non-digestible forms of mono-, and oligosaccharides that form the GOS. In the reaction, lactose acts both as the donor and acceptor of transglycosylated galactose. Whereas in lactulose synthesis, lactose only acts as a donor of galactosyl glucose, and the fructose acts as an acceptor.

Protease: Proteases are classified into different groups based on the activity of proteases under various parameters like acidic, alkaline, or neutral conditions as well as the composition of their substrate-binding site (Panda et al. 2013). Alkaline serine protease (E.C.3.4.21–24.99) is most active at pH ranging from neutral to alkaline (Singhal et al. 2012; Varela et al. 1997). Other proteases are the neutral and acidic proteases (Razzaq et al. 2019). Proteases are proven to be a significant tool in bioremediation as well as valorization of waste to value-based products (Page and Cera 2008). The most exploited and studied microorganism for the production of alkaline protease and neutral proteases are *Bacillus species* and acidic proteases are known to be produced by the fungus. These proteases can be efficiently inactivated by PMSF (phenyl methane sulfonyl fluoride). Protein-rich waste is responsible for increasing the biological oxygen demand of aquatic waste. As discussed in earlier sections, the waste aquatic stream is drowned with effluents from food processing industries which constitutes waste from dairy products, waste from poultry, and fish industries as well as textile and leather industries. Leather industries involve alkaline protease with keratinolytic activity to hydrolyze keratin content present in the hair residues for increasing the surface area of the skin. They are also used in bating and clearing undesirable pigments during the preparation of clean skin and hides (Bhaskar et al. 2007; Shankar et al. 2011). Alkaline protease preparations of *Bacillus species* are enormously used in poultry industries to get rid of the feather waste generated in the slaughterhouse. The keratinolytic capability of these proteases has been best utilized in cleaning drainage pipes clogged with hair residues. A cocktail of protease preparation from *Streptomyces species, Bacillus subtilis*, and *Bacillus amyloliquefaciens* along with thioglycolate mixture is available commercially in the market. Alkaline proteases find a crucial place in the degradation of plastics as well as X-ray photographic sheets, particularly for the silver recovery. The active site of the alkaline protease comprises catalytic triad formed by Aspartate and Histidine residues along with Serine residue. Proteases based on their structural and sequence similarity can be obtained and assessed from the database called MEROPS (Rawlings et al. 2006) database. Table 4.1 comprehensively covers the application of different enzymes in the valorization of waste.

4.4.3 Hydrolytic Enzymes in Biodegradation and Valorization of Non-biodegradable Plastics Waste

The monomers utilized for the preparation of most plastics, ethylene, and propylene are derived from petroleum. The most commonly used are polyethylene, polystyrene, polyurethane, polypropylene, polyvinyl chloride, poly (ethylene terephthalate), etc. Out of the total production worldwide, only a small fraction around 20% is getting recycled, thus plastic remains a long-lasting, and major threat to the

Table 4.1 Listed applications of different hydrolytic enzymes in the valorization of waste and their microbial sources

Sl. No.	Name of the enzymes	Microbial source	Industry	Application	Reference
1	Cellulase	Bacteria: *Clostridium species, Pseudomonas* species, *Bacillus species* Fungus: *Aspergillus species*, *Penicillium species, Melanocarpus species, Trichoderma species, Schizophyllum commune* Actinomycetes: *Cellulomonas species, Streptomyces species, Thermomonospora species*	Pulp and paper industry, Textile industry Agricultural, and Food Industry Other	Deinking, pulping, bleaching, improve the quality and strength of pulp fibers, reduce the use of energy and chlorine, production of biodegradable sanitary napkins, papers, etc. Bio-stoning of jeans, softening of garments, biopolishing of textile fibers, enhancing quality, stability, and absorbance property of textile fibers, removal of excess dye from fabrics, and restoration of color brightness. Improve seed germination, plant growth and flowering, disease and plant pathogen control, and improve soil quality. Bioethanol production, bio-detergent production	Pere et al. (2001), Kuhad et al. (2011), Singh et al. (2016)
2	Xylanase	Bacteria: *Arthrobacter* species, *Geobacillus species, Pediococcus acidilactici, Bacillus species, Paenibacillus species, Rhodothermus marinus, Staphylococcus aureus, Pseudomonas species* Fungus: *Talaromyces species Thermomyces lanuginosus*, *Thermoascus sp,*	Agricultural, Food Industry, Pulp and paper industry, Textile industry, and Pharmaceutical industry	Improve fermenting process, improve animal feed digestibility, biogas, and bioethanol production, clarification, and maceration of fruit juice, brewing, hydrolysis of agro-residues. Bio-bleaching of pulp, Deinking Textile processing, desizing, and bioscouring. XOS production.	Beg et al. (2001), Bhardwaj et al. (2019)

		Melanocarpus albomyces *Chaetomium species*, *Fusarium species Humicola* species *Paecilomyces sp.*, *Scytalidium sp.*			
3	Mannanase	Bacteria: *Agaricus bisporus, Aspergillus species, Bacillus species, Bacteroides species, Clostridium species* Fungus: *Aspergillus species, Agaricus species, Trichoderma species*, *Sclerotium species*	Pulp and paper industry, Textile industry, Agricultural and Food Industry	Bleaching of softwood pulps using enzymes, eliminates the use of chlorine and hydrogen peroxide, and enhance the brightness of paper. Desizing and bioscouring, reduce the viscosity of the print paste. Oil extraction from coconut, food additives, oil drilling, improve the nutritional value of animal feed.	Dhawan and Kaur (2007)
4	Aryl alcohol oxidase	Bacteria: *Sphingobacterium* species Fungus: *Thermothelomyces thermophilus, Coprinopsis cinerea, Phanerochaete chrysosporium*	Food and beverages, Polymer industry, and Pharmaceutical industry	Food flavors, e.g., vanillin. Production of bio-based polymer. Production of health beneficial compounds, e.g., to cuminaldehyde (therapeutic effects against cancer and diabetes).	Urlacher and Koschorreck (2021), Serrano et al. (2019), Li and Jiang (2004)
5	Lactase	Bacteria: *Bifidobacterium infantis* *Fungus: Lactobacillus thermophiles, Kluyveromyces fragilis, Aspergillus foetidus*	Food and beverages	Production of lactose-free products reduces the crystallization of ice creams and condensed milk	Saqib et al. (2017), Porta et al. (2010)
6	Alkaline protease	Bacteria: *Bacillus pumilus* Fungus: *Streptomyces fungicidicus*, *Myceliophthora species*	Leather Industry, Cosmetic sector, Pharmaceutical Industry and	Helps in effective bating. Formulation of cosmetic products. Development of ointment compositions, gauze, and new bandage material. Detergents and silver recovery.	Baweja et al. (2016), Sharma et al. (2019), Razzaq et al. (2019)

(continued)

Table 4.1 (continued)

Sl. No.	Name of the enzymes	Microbial source	Industry	Application	Reference
			Other applications		
7	Esterase	Bacteria: *Lactobacillus casei, Pseudomonas species* Fungus: *Aspergillus niger*	Pharmaceutical industry, Paper and pulp industry	Production of chiral drugs, detoxifying toxic residue. Reducing pitch problems during paper manufacture.	Panda and Gowrishankar (2005)
8.	Lignin-degrading enzymes				
	Lignin peroxidase, Manganese peroxidase (MnP), and Glycol oxidase (GLOX)	Fungus: *P. chrysosporium Trametes versicolor, Phlebia radiate, Trichoderma viride, Trametes suaveolens, Phanerochaete sordid* Bacteria: *Bacillus anthracis and Bacillus cereus* Fungus: *Rigidoporus Lignosus* and *Ceriporiopsis subvermispora* Bacteria: *Streptomyces lividans* Fungus: *P. chrysosporium, Pycnoporus cinnabarinus, Bjerkandera adusta, Dichomitus squalene*	Textile industry, Cosmetic industry, Pulp and paper industry, Polymer industry, Food industry, and Other application	LiP and MnP: Decolorize dyes and degradation of a xenobiotic compound. LiP: Decolorize synthetic melanin an alternative to hydroquinone cream. Lip and MnP: Biopulping, biobleaching, delignification in the paper industry. Lip and MnP: Polymerization of acrylamide into a thermoplastic resin (polyacrylamide). LiP and MnP: Delignification of lignocellulose. GLOX: Oxidize aldehydes to a variety of organic acids, carboxylic acids, pyruvic acid, oxalic acid, and formic acid, source of H_2O_2 production during lignin degradation	Marco-Urrea and Reddy (2012), Abadulla et al. (2000), Joon Sung (2020), Agarwal et al. (2018), Iwahara et al. (2000), Daou and Faulds (2017), Falade et al. (2017), Januz et al. (2017)

9	Pectinase	Bacteria: *Bacillus subtilis, Saccharomyces cerevisiae* Fungus: *Aspergillus niger*, *Rhodotorula* species	Food and beverages, Textile industry, and Other applications	Reducing the viscosity and turbidity of freshly collected juice, removing the mucilage from the coffee beans. Bioscouring of cotton fibers, degumming, and retting of fiber crop, oil extraction. Purification of plant viruses.	Nighojkar et al. (2019), Sharma et al. (2019)
10	Insulinase	Bacteria: *Streptomyces species* Fungus: *Kluyveromyces marxianus, Aspergillus niger.*	Food and beverages	Production of metabolites, e.g., lactic acid, sorbitol syrup, and high fructose syrup and oligosaccharides	Singha et al. (2017)

environment, especially to the aquatic streams (Kaushal et al. 2021). Plastics are categorized into two ways: (1) Thermoplastics whose chemical composition remains unchanged at high temperature and have mostly linear carbon chain backbone and (2) Thermosets which are made of other elements along with carbon possess highly cross-linked anatomy and their chemical conversion at high temperatures is irreversible. One of the most common thermoplastics used worldwide is polyethylene (PE). It is composed of ethylene as a monomer unit and is highly crystalline in structure which makes it recalcitrant to biodegradation. Based on the pattern of the linear chain and different densities, PE can be low-density PE (LDPE), high-density PE (HDPE), and also low molecular weight PE (LMWPE) Polypropylene (PP), yet another thermoplastic made by polymerizing propylene gas. PP differs from PE in having a methyl group instead of one hydrogen atom at an alternate carbon atom in the linear carbon backbone. This chemical structure gives it more rigidity in comparison to PE. Both these plastics are included in the category of polyolefin due to their inert and resistant nature to most heating, biological and chemical treatments. It is abundantly utilized as packaging plastics in various industrial sectors (Zheng et al. 2005). Polyvinyl chloride is yet another synthetic plastic that is used in rigid or plasticized forms. They are formed by polymerizing vinyl chloride or chloroethene in linear form. The pollution caused by PVC plastics is noticeable as burning these plastics emits hydrogen chloride fumes which pose serious health hazards. They are more prone to microbial degradation in comparison to other plastics due to the high percentage of plasticizers added to them (Webb et al. 2000). Polystyrene is synthesized by polymerizing styrene as repeating units. They could be thermoplastics or thermosets. They are also widely used in packaging industries due to their foam-like appearance (Tokiwa et al. 2009). Polyurethane and PET (polyethylene terephthalate) both have improved thermostability as they are hetero-atomically branched. PET is the most abundantly produced and used plastic in the modern era. Researchers have claimed that global warming caused by enormous CO_2 emissions and promiscuous usage of PET plastics are two of the most alarming situation in the biosphere (Wang et al. 2020). It is a high molecular weight thermoplastic composed of terephthalate (TPA) and ethylene glycol (EG) via an ester bond. This polymer has great tensile strength, and durability and its production cost are also low. Their structure contains large aromatic rings which make them rigid and resistant to biodegradation (Webb et al. 2013). Polyurethane has heteroatoms with carbamate linkage which could be either ester or ether bonds. They form the major constituents of microplastics making them the most concerning issues in the aquatic system (Shah et al. 2013). Mitigation of these plastics from the environment is carried over by certain physical and chemical methods like incineration, recycling, and dumping them into landfills. All of these methods are not environmentally friendly and they are not even cost-effective. The introduction of plastic hydrolyzing enzymes has opened up hopes for eco-friendly treatments to get rid of this dire environmental pollutant (Verma et al. 2016) (Table 4.2). Varieties of microorganisms like fungi, bacteria, actinomycetes, and algae have been investigated as well as reported to exhibit plastic polymer degrading capacity. Plastic degrading enzymes are mostly obtained from microbial organisms, and therefore they are studied under two categories: intracellular and

Table 4.2 Plastic degrading enzymes and their microbial sources

Sl. No	Enzyme	Microorganism	Plastic substrate	References
1	Laccase	*Rhodococcus ruber* C208 (Mesophilic bacteria) *Bacillus cereus* (Bacteria)	Polyethylene (PE)	Santo et al. (2013), Vimala and Mathew (2016)
2	Manganese peroxidase	*Phanerochaete chrysosporium* ME446 (White-rot fungus) *IZU-154* (Fungi) *Bacillus cereus* (Bacteria) *Penicillium simplicissimum* (Fungi)		Iiyoshi et al. (1998), Sowmya et al. (2015)
3	Lignin peroxidase	*Streptomyces (Bacteria)* *Phanerochaete chrysospo*rium MTCC-787 (Fungi)		Jeon and Kim (2015), Mukherjee and Kundu (2014)
4	Alkane hydroxylase	Recombinant AH from *Pseudomonas species* E4 expressed in *Escherichia coli* BL21 (Bacteria)		Yoon et al. (2012)
5	PETase	*Chlamydomonas reinhardtii* (Green algae)	Polyethylene terephthalate (PET)	Kim et al. (2020)
6	Cutinase-like enzyme/ IsPETase	*Ideonella sakaiensis* 201-F6 (Bacteria)		Han et al. (2017)
7	Lipase	*Pseudomonas chlororaphis* (Bacteria)	Polyurethanes	Stern and Howard (2000)
8	Polyurethanase	*Serratia marcescens* (Bacteria)		Mankoci et al. (2019)
9	Protease and esterase	*Pseudomonas fluorescens* (Bacteria) *Pseudomonas chlororaphis* (Bacteria)		Hung et al. (2016), Shah et al. (2008), Nakajima-Kambe et al. (1995)
10	Polyurethanase (PUase)	*Curvularia senegalensis* (Fungi)		Crabbe et al. (1994)
11	Polyhydroxyalkanoate depolymerase	*Alcaligenes faecalis* (Gram-negative, rod-shaped bacteria)		Gamerith et al. (2016)
12	Polyester Polyurethane (PUR) esterase	*Comamonas acidovorans TB-35* (Bacteria)	Polyester polyurethane	Akutsu et al. (1998)
13	Phenylacetaldehyde Dehydrogenase	*Pseudomonas fluorescens ST (Bacteria)* *Pseudomonas putida S12 (Bacteria)* *Xanthobacter species 124X (Mesophilic bacteria)*	Polystyrene	Oelschlägel et al. (2018)

(continued)

Table 4.2 (continued)

Sl. No	Enzyme	Microorganism	Plastic substrate	References
14	Cytochrome P450 CPY152A1	*Bacillus subtilis (Gram*-positive, catalase-positive bacteria)		Shoji et al. (2007)
15	Cytochrome P450 CPY152B1	*Sphingomonas paucimobilis (G*ram-negative bacteria)		Fujishiro et al. (2012)
16	AlkB (alpha-ketoglutarate-dependent hydroxylase	*Pseudomonas putida* GPo1 (Bacteria)		Hou and Majumder (2021)
17	Alkane monooxygenase	*Geobacillus thermodenitrificans* NG80–2 (Thermophilic bacteria)		Li et al. (2008)
18	Hydroquinone peroxidase	*Azotobacter beijerinckii* HM121 (Lignin decolorizing bacteria)		Nakamiya et al. (1997)

extracellular enzymes. Extracellular enzymes are involved in the depolymerization of long-chain polymers into smaller fractions, viz. oligomers, dimers, etc. Whereas the intracellular enzymes participate in the final conversion of intermediates into the forms which can be assimilated by the microbes as a sole source of carbon. As a result of this process, a valuable emission gas, i.e., methane is released as metabolic products which can be used as fuels and can further be utilized as precursors for the production of organic acids (Amobonye et al. 2021). Furthermore, the wax moth *Galleria mellonella* is known to depolymerize plastics with the help of their gut microbiota containing the fungus *Aspergillus flavus* (Zhang et al. 2020a, b). All these enzymes involved in degrading plastics are hydrolases that catalyze the cleavage reaction in the presence of water (Müller et al. 2005). Esterases, cutinases, laccases, lipases, and PETases are the most extensively studied hydrolytic enzymes concerning the degradation of plastics. Microbial valorization of plastics into value-added chemicals is elaborately reviewed in Ru et al. (2020). The reviewer explained elaborately the microbial metabolic pathway involved in the depolymerization of ester/urethane-containing plastics, aromatic plastics, and linear aliphatic plastics into its monomer constituents and their further assimilation by microbes for the production of value-added chemicals. The chemical structure such as linkages in petro plastics, linearity or branching in carbon chain, type of linkage (ester, ether, or carbamate linkage between the monomers), presence of hydrophobic functional groups, and physical properties like rigidity (crystalline/amorphous) and density plays a significant role in engineering enzymes suitable for biodegradation (Mohanan et al. 2020). Ongoing and present studies for identification of plastic degrading microorganisms and modification of these microbial enzymes through genetic engineering provides a wide opportunity to efficiently recycle or remove plastic from the environment. Yet advantageous is when these plastics can be converted into more valuable and marketable products.

4.5 Recent Biotechnological Trends in Increasing the Efficacy of Enzymes in the Waste Valorization

Enzymes have been central in various industries like food processing, beverages distilleries, leather, textile, and paper industries for a long time (Sheldon and Woodley 2017). Their involvement in the production of biofuel and value-added products is tremendously surging in recent times (Chapman et al. 2018). Consequently, for obtaining optimal bioprocesses involving enzymes, further enhancement of enzyme stability and functionality is indispensable. Biotechnological breakthrough offers a great deal for enhancing the power of existing enzymes as well as identifying newer enzyme candidates.

4.5.1 Techniques to Decipher Newer Biocatalyst Candidates

Conventionally, enzyme discovery was done by cultivating microorganisms, fractionating cell-free extract, followed by the screening of the enzyme activity, and then recovered enzymes through purification are subjected to mass spectrometric analysis after trypsin digestion. The identified short peptides are then utilized to decipher the corresponding gene from the genomic DNA. Although these methods are dependent on the use of cultivable microorganisms, a significantly important set of enzymes were discovered using this process. State-of-the-art tools are now assessable to scrutiny and tap the vast microbial biodiversity present in nature (Rinke et al. 2013). The introduction of omics such as metagenomics and metatranscriptomics presents a big potential to analyze the diversity of complex microorganisms. These tools help in the development of genomic libraries from environmental DNA for function or sequence-based similarity screening of the enzymes (Gilbert and Dupont 2011; Uchiyama and Miyazaki 2009). For example, a collection of hydrolytic enzymes such as amylase, lipase, oxidoreductase, and epoxide hydrolase have been deciphered using this technique (Knietsch et al. 2003; Rondon et al. 2000). Several bioinformatics strategies such as in silico data mining, the Catalophore™ approach, and de novo enzyme design tools are also helpful in this process (Handelsman 2004). Progressive success in developing methods for genome sequencing like next-generation sequencing has opened up newer approaches to hunt for putative enzymes. Here, genome hunting is based on either searching for the open reading frame or homology alignment of sequences.

4.5.2 Isolation of Enzymes from Extremophiles

Enzymes that can withstand extreme parameters like higher temperature and pH as well as harsh chemicals like a high concentration of salts, metal ions, organic solvent, etc. have great value at industrial levels. There is a large diversity of organisms in the extremophilic regions and as most of these organisms have not been yet cultivated in pure cultures, the characterization of their enzymes from them is comparatively difficult (Pikuta et al. 2007; Cavicchioli et al. 2011). The bacterial isolates obtained from the extremophiles have displayed properties of different hydrolytic enzymes such as amylase, protease, lipase, and xylanase. Extreme thermophiles are widely present in bacterial species like *Thermus, Thermotoga, Clostridium, and Bacillus. Pyrococcus, Thermococcus, or Methanopyrus* belongs to hyperthermophilic Archaea. Hydrolytic enzymes such as Amylase, Xylanase, Lipase, and Protease enzymes are isolated from some halophilic bacterial species like *Halobacterium, Halobacillus, and Halothermothrix* (Moreno et al. 2012).

4.5.3 Genetic Engineering or Recombinant DNA Technology for the Production of Recombinant Protein in a Microbial Host

To obtain desired efficacy in the expression of enzymes, gene-based technology like recombinant DNA technology can be used. In this technology, the desired gene or gene of interest is inserted into the organism *via an* appropriate vector. The gene of interest can be manipulated through the addition of the desired sequence in the endogenous gene or deletion or knockout of undesirable sequence through recombining genes and elements. Rational redesigning and direct evolution are the two different methods that are adapted for modifying enzymes to their desired characteristics. Rational redesigning utilizes site-directed mutagenesis to target amino acid substitution effectively at the active site of the protein for evolving the enzyme into a more efficient one. Whereas the direct evolution method includes repeated oligonucleotide-directed mutagenesis, random mutagenesis through error-prone polymerase chain reaction (PCR), or modification through chemical agents (Manisha and Yadav 2017; Wiltschi et al. 2020) (Table 4.3).

4.5.4 Immobilization of Enzymes

The major confrontation in enzyme technology and its application in industries is bulk production and the question of reusability. These problems can be easily dealt with the immobilization technique. Enzymes can be immobilized by tethering or encapsulating them in an appropriate material that has desired physical, chemical,

Table 4.3 Genetically engineered microbes for increasing the efficacy of expressed hydrolytic enzymes in the valorization of waste

Sl. No.	Enzymes	Improved properties	Organism	References
1	Cellulase	Increased the inherent ability of *Lactiplantibacillus plantarum's* lignocellulose degradation	*Thermobifida fusca*	None and Yadav (2017)
2	*β*-glucosidase	Improve enzyme activity and thermostability	*Trichoderma reesei*	Lee et al. (2012)
3	Xylanase	T_m improved by 25 °C	*Thermotoga thermarum*	Yang et al. (2017)
4	Laccase	3-fold improved kcat and thermostability	*Bacillus* HR03	Mollania et al. (2011)
5	Lipase	2-fold increase in amidase activity	*Pseudomonas aeruginosa*	Fujii et al. (2005)
6	Lipase B	20-fold increase in half-life at 70 °C	*Candida antarctica*	Siddiqui and Cavicchioli (2005)
7	Pyranose 2-oxidase	Increased thermostability and the catalytic properties	*Trametes multicolor*	Spadiut et al. (2009)
8	Endoglucanase	Increase hydrolytic activity on cellulosic substrate	*Thermoascus aurantiacus*	Srikrishnan et al. (2012)

electrical, or mechanical properties. These materials increase the stability as well as efficacy in terms of better catalytic activity of the immobilized enzymes. Moreover, immobilization can reduce the steps required to separate them from the reaction mixture as well allows substantial reusability without affecting the activity allowing them to be compatible in a continuous process. To examine the enzyme activity of immobilized enzymes two kinetic parameters, namely the Michaelis constant, K_m, and maximal reaction velocity, V_{max} is often examined and compared with the non-immobilized counterpart. The three widely used immobilization techniques are encapsulation or entrapment, carrier-bound attachment, and the formation of cross-linked enzyme aggregates (CLEAs). Encapsulation or entrapment technique, as the name suggests is the immobilization of enzymes using material of varying degrees of porosity and permeability (Bezerra et al. 2015; Jesionowski et al. 2014). Various materials such as a variety of carriers, for example, sol–gels, hydrogels, polymers as well as nanomaterials have been experimented with immobilization of enzymes via encapsulation technique. Carrier-bound immobilization of enzymes is done by physisorption or chemisorption of enzymes on prefabricated organic or inorganic materials. Materials like metal oxides, nanomaterials, ceramic, or silica gels are used for this purpose. Chemisorption technique is preferred over physisorption as covalent attachment reduces the chances of enzyme leaching from the matrix. CLEAs technique is a very recently utilized technique where the soluble enzyme is aggregated using precipitating agents like alcohol, acetone, ammonium sulfate, etc., and then subsequently cross-linked or co-polymerized with cross-linking agents like glutaraldehyde (Sheldon 2010). Hence, immobilizing enzymes can be well exploited for obtaining desired characteristics to bring increased efficacy in the use of enzyme technology in the industrial arena as well as biorefineries.

4.5.5 Cell Surface Engineering

Genetic technological advances have let us modify microorganisms to express our genes of interest (Table 4.3). Cell surface engineering is another biotechnology tool where the particular microorganism is tailored to express the desired number of enzymes on its surface. This is technique is advantageous in biorefineries where there is a need for multiple enzymes for the conversion of biomass to biofuels. The most utilized and engineered organism includes *Saccharomyces cerevisiae*. Naturally, yeast can ferment sugars to produce alcohols, but it does not possess the enzyme required for saccharification of complex sugars present in the cell wall of the biomass. Cell surface engineering enables the arming of yeast and other organisms with a cocktail of enzymes that help the production of biofuels and other value-added products (Kuroda and Ueda 2013; Ueda 2016; Ueda and Tanaka 2000).

4.6 Conclusions

Developing sustainable approaches toward building a circular economy and safeguarding mother nature has become the need of the hour. Toward achieving this, biomass waste from various sectors like agro-forest, solid municipal waste, food manufacturing, and processing industries can be utilized and profitably and competently converted to bioenergy and value-added products. To reduce the losses incurred by the use of traditional chemical processes in the treatment of waste biomass, enzymes are introduced for the economic and easier hydrolysis of the different waste components. The major portion of waste generated is composed of biodegradable biomass as well as non-biodegradable plastics. Different microbial sources of hydrolytic enzymes are exploited for the valorization of these wastes into value-added products and bioenergy. Cellulases, hemicellulases, lignin peroxidases, pectinases, amylases, proteases, etc. enzymes are widely utilized in this concern. The biorefinery concept is structured to use the by-product from one industry as feedstock for another industry to produce more value-added goods in addition to conversion of waste to bioenergy. Various technological advances like genetic engineering, cell surface engineering, and immobilization of enzymes are exploited to increase the efficacy of the hydrolytic enzymes obtained from microbial sources. Identification of new sources of these enzymes through metagenomic analysis is relevant and very necessary to keep the reservoir filled. In addition to that further improvement of these enzymes could be done through techniques like metabolic engineering and chemical modification of the enzyme.

Acknowledgments The authors gratefully acknowledge the financial and infrastructural support from the Indian Institute of Technology Palakkad and Department of Science and Technology (DST)-SERB, Govt. of India for conducting research work. AB is supported by the National Post-doctoral fellowship granted by DST-SERB, (PDF/2020/001950) Govt. of India, RS is supported by a scholarship from Council of Scientific and Industrial Research, MHRD, Govt. of India (09/1282 (0003)/2019-EMR-I) and SC is supported by DST-INSPIRE (IF-18022) fellowship, Govt. of India.

Competing Interests There is no conflict of interest.

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Chapter 5
Thermochemical Conversion of Biomass into Value-Added Materials for Effluent Treatment Applications

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Abstract Lignocellulosic biomass has been explored for the synthesis of various value-added materials due to its wide availability and environment-friendly nature. Apart from being studied as a potential feedstock for the synthesis of fine chemicals and generation of biofuels, these biomasses have also shown a wide range of applications in effluent treatment processes. Many agricultural waste biomasses had shown potential in effluent treatment, even in their raw form. Activated carbon prepared by the pyrolysis of biomass has yielded promising results as adsorbents and catalysts support the removal of both conventional and priority pollutants from effluents. Moreover, composite materials including metal oxide composites, magnetic materials, catalyst supports, polymer composites, and graphene composites prepared by the thermochemical conversion of biomass are being explored in tertiary treatment processes for the removal of targeted pollutants from the aqueous phase. Hence, this chapter is aimed to discuss the application of biomass-based value-added materials for effluent treatment applications.

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
https://doi.org/10.1007/978-981-19-4312-6_5

Keywords Thermochemical conversion · Biomass-based composites · Activated carbon · Effluent treatment · Emerging contaminants

Abbreviations

AC	Activated carbon
BiOBr	Bismuth oxybromide
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
EIA	Energy Information Administration
TDS	Total suspended solids

5.1 Introduction

Humanity dates back to not a decade or a century but a millennium. Since existence began, the production of wastes in many forms originated particularly from natural sources. The most popular form of waste would be wood or of plant origin. In general, the term "Biomass is defined as matter originating from living plants, including tree stems, branches, leaves as well as residues from agricultural harvesting and processing of seeds or fruits" (Pang 2016). Biomass is considered to carry energy in the form of chemical bonds among hydrogen, carbon, and oxygen moieties (Pang 2019). The sources of biomass are plant products, the residue of crop farming and processing industries, fruit and vegetable waste, agro-industrial waste, household waste, urban waste, and animal waste (Wormeyer et al. 2011). Figure 5.1 shows the classification of biomass resources. They include materials consisting of cellulose, hemicellulose, and lignin (Mohan et al. 2006). As for the elementary composition, 90% of the typical biomass contains 51% carbon, 42% oxygen, and trace amounts of hydrogen, nitrogen, and chlorine (Mandapati and Ghodke 2021b). The biomass resources were calculated to be 146 billion tonnes/annum. Tropical countries like India contribute to the production of about 500 million metric tonnes/year of biomass. This natural carbonaceous resource is mostly used or exploited as a source of fuel.

5.2 Biomass as a Source of Fuel

The rapid consumption of fossil fuel has led to its depletion (Mandapati and Ghodke 2021a; Agrawal and Verma 2022; Kumar and Verma 2021a). Various renewable resources which include biomass-based reserves, wind, solar, and geothermal resources have been explored as alternative fuels. Among these renewables,

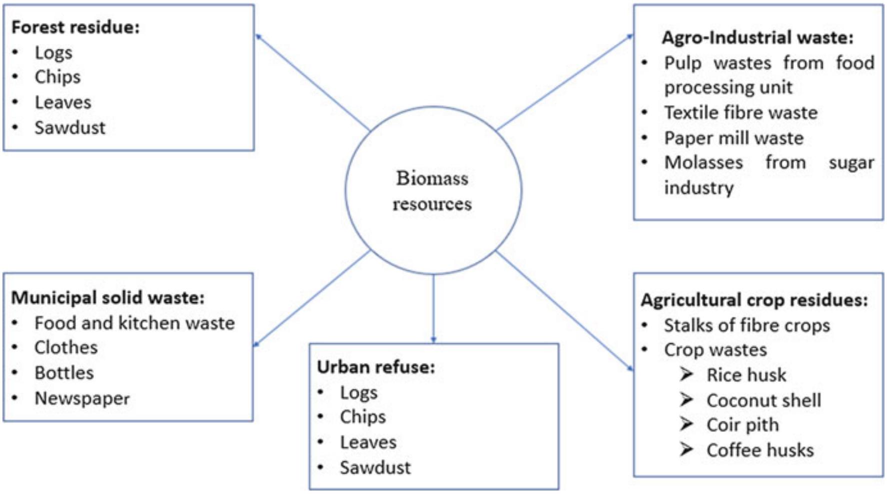


Fig. 5.1 Classification of biomass resources

bioenergy is renewable energy sourced from biomass that is abundant and has a high utilization potential to produce energy (Pang 2019; Kumar et al. 2020; Kumar and Verma 2021b). If 10% of the biomass is exploited for energy production with 50% efficiency, it may have the potential to churn out 3.1 trillion tonnes of oil equivalent energy. This would account for the availability of 200 times the energy consumed worldwide currently (Energy Information Administration, EIA, 2017). On the other hand, the utilization of 10% of biomass for organic chemical synthesis at a 10% conversion rate will lead to the production of 1.6 billion tonnes of chemical feed materials (Pang 2019). Generally, in developing countries, 38% of the energy consumed is primarily from bioenergy produced from biomasses (Sarkar and Praveen 2017).

Biomass is a clean energy source is produced by plants by consuming CO_2 from the atmosphere through photosynthesis (Tekin et al. 2014). Moreover, these biomasses are produced in short duration ranging from months to years when compared to unsustainable fossil fuels which usually require millions of years (Collard et al. 2012). Hence, renewable energy from biomasses proves to be a sustainable source of energy supply that can also address environmental concerns.

5.3 Value-Added Pathway from Biomass for Different Applications

Biomass conversion pathways through various processes are shown in Fig. 5.2. The widely used thermochemical conversion technologies for the conversion of biomasses include but are not limited to gasification, pyrolysis, hydrothermal

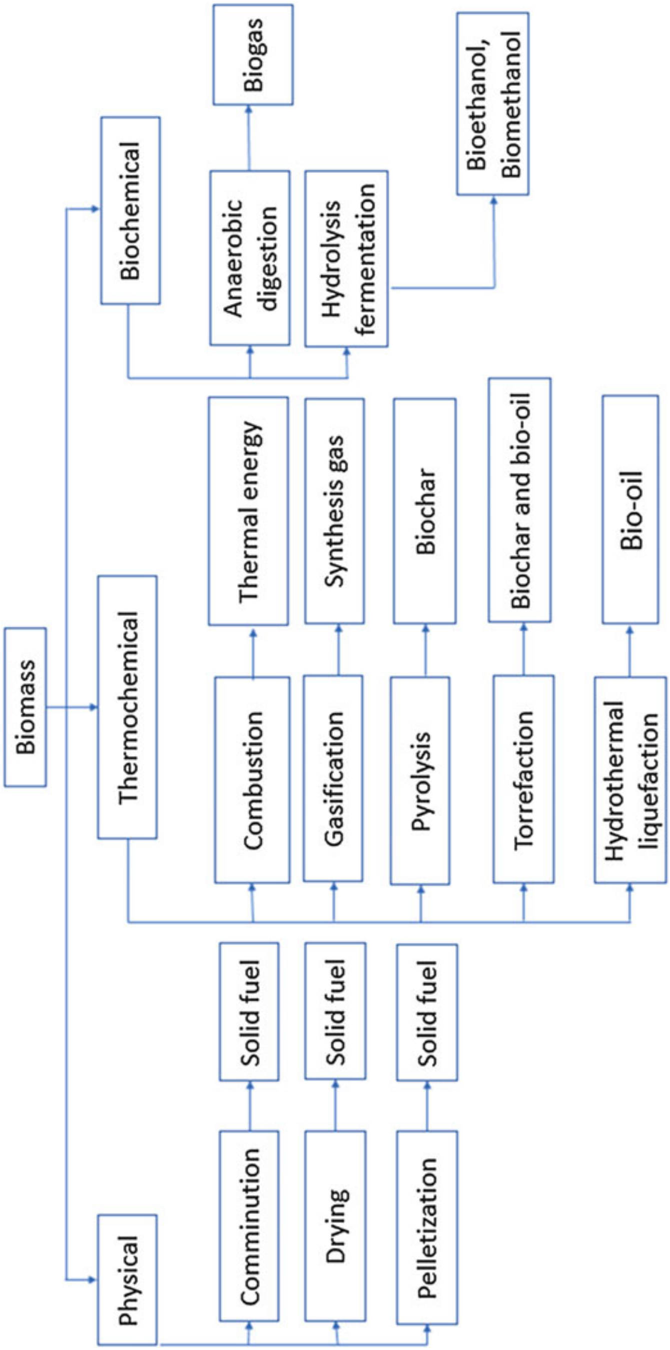


Fig. 5.2 Biomass conversion pathways

liquefaction, and torrefaction (Goswami et al. 2020, 2021a). Torrefaction is a thermal pre-treatment process used in the combustion, pyrolysis, gasification, and liquefaction of biomass (Ghodke and Mandapati 2019). Pyrolysis is heating the biomass at elevated temperatures (573–973 °K) to obtain biochar and bio-oil. The hydrothermal liquefaction process is operated between 523 and 647 °K within the pressure range of 4–22 MPa for the production of bio-oil. Gasification involves the conversion of biomass into syngas at temperatures higher than 973 K.

5.4 An Alternate Strategy for the Utilization of Waste Biomass

Biomass has a great potential to be used as a source of biofuel (Bhardwaj et al. 2021). The total biomass power generation potential of India is estimated to be 17,500 MW. However, at present, only 2665 MW of power is being generated (Kumar et al. 2015). Hence, due to the availability of abundant waste biomass materials, the management or disposal of these substances is itself a major task for environmentalists. In the global arena, “Waste to Wealth” is a term coined to utilize waste material for useful resources. Since the resource is inexpensive, green, and renewable, environmentalists focus on such processes to reduce pollution. There are several studies, where the waste biomass and its derivatives were used as a precursor material for effluent treatment processes. The biomass could be converted into a base material for catalyst preparation in the form of support or as an adsorbent material. They can be utilized for the treatment of effluents by the process of adsorption or by using an advanced oxidation process (AOP). Wherein the preparation of heterogeneous catalyst by supporting the active material on carbon support derived from biomass reduces the cost of the effluent treatment process. Hence, this chapter is aimed to discuss the thermochemical conversion of biomass into value-added materials for effluent treatment applications.

5.5 Biomass for Effluent Treatment Processes

It has been reported that every day two million tons of waste from various sources are discharged into water bodies worldwide. This created an impact that one in eight people worldwide are deprived of safe and clean drinking water as reported in World Water Assessment Programme, World Water Development Report1: “Water for People, Water for Life,” Paris (2003). Water pollution is found to be the major reason for diseases and subsequently deaths worldwide (Vairavel and Murty 2020; Goswami et al. 2021b). In India alone, it has been estimated that approximately 580 people die due to water pollution-related illnesses every day (Clark et al. 1996). Major contaminants found in wastewater include but are not limited to dyes and pigments, heavy metals, phenolic compounds, pharmaceuticals, agrochemicals, and endocrine disruptors (Akhil et al. 2021; Kumar et al. 2019; Kumar et al. 2021). Effluent treatment plants comprise physical, chemical, and biological treatment systems. Generally, all these treatment methods are grouped under primary, secondary, tertiary, and advanced treatment processes. Primary treatment processes aim to remove contaminants by the physicochemical processes like primary clarification (gravity settling) and coagulation/flotation. The secondary treatment processes work on the removal of the residual organics. The secondary treatment processes employ various microorganisms for reducing the COD and BOD of the effluent. Activated sludge treatment methods such as aerobic and anaerobic digestion are some of the secondary wastewater treatment methods. Tertiary treatment methods include membrane separation processes, electrodialysis, advanced oxidation processes, adsorption, biosorption, bioaccumulation, and ion exchange (Sonune and Ghate 2004). Most of these treatment processes like adsorption, biosorption, and advanced oxidation processes utilize functional materials for their operation. These functional materials like adsorbents and catalysts in case of adsorption and oxidation processes respectively are of chemical origin, which leads to secondary pollution. However, the waste biomasses and their derivatives proved to be environmentally friendly precursor materials for the synthesis of adsorbents and catalysts support materials. A simple thermochemical modification of the lignocellulosic waste materials could yield highly functional materials for wastewater treatment processes (Liu et al. 2015).

5.6 Application of Raw Biomass in the Effluent Treatment Process

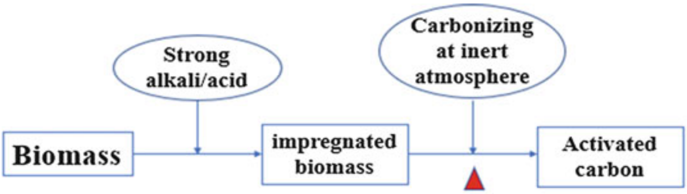
Adsorption is the most widely used effluent treatment technique This is because, the used adsorbent materials have the potential for regeneration, recovery, and recycling which proved to be an added advantage at the industrial scale of operations. It is not only used for the removal of contaminants but also could be used for the recovery of precious and costly entities from the effluents (Crini et al. 2019). The physicochemical properties of the adsorbent have a major influence on the efficacy of the adsorption process. The chosen or prepared adsorbent should be easily available, economical, non-toxic, and should have good surface characteristics. They must also have high mechanical and thermal stability (Reddy et al. 2017). The lignocellulosic waste biomasses, in their raw or modified form, proved to be potential candidates for the preparation of economical and sustainable adsorbents for effluent treatment (Bhatnagar et al. 2015). Plant and agricultural waste products have earned increased interest for dye and heavy metals removal by adsorption from the aqueous solution because of their natural availability and higher removal efficiency (Garg et al. 2019; Agrawal and Verma 2021). The inexpensive waste products, after basic cleaning or some minor treatment, were explored as adsorbents. Agricultural by-products especially those containing cellulose exhibit good adsorption potential for removing various toxic pollutants from effluents. There are numerous studies reporting the application of raw lignocellulosic materials like rice husk, oil cakes, banana peel, sugarcane bagasse, powdered leaves, etc. for the removal of different types of dyes, heavy metals, and other priority pollutants. This method of exploiting raw biomass as functional adsorbent materials proved to solve disposal problems associated with the abundant availability of these waste biomasses (Moorthy Rajendran et al. 2020). Few of the studies which deal with the application of these raw biomass materials for effluent treatment is tabulated in Table 5.1.

5.7 Biomass-Derived Activated Carbon for the Effluent Treatment Process

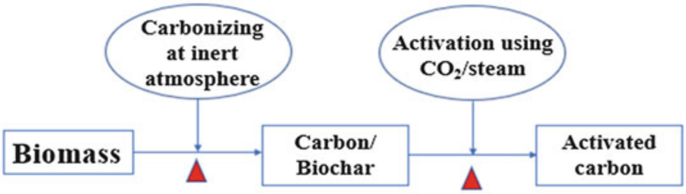
Many studies reported raw agricultural biomass as an adsorbent for the removal of organics and inorganics from simulated effluents. However, most of these raw biomasses were found to lack desired adsorption efficiency and were mechanically unstable. The efficiency of these biomasses could be enhanced by carbonization and activation using thermal and chemical treatment methods. The physical treatment includes carbonizing the material at a temperature of around 500 °C under an inert atmosphere using nitrogen or argon supply. The carbonized material is then activated at higher temperatures using suitable activating agents like steam or CO_2. The chemical treatment method involves the impregnation of the cellulosic biomass with various strong acids and bases like NaOH, KOH, HCl, H_2SO_4, $ZnCl_2$, etc. The impregnated material is then carbonized at higher temperatures at around 500 °C to obtain activated carbon (AC) (Rodríguez-Reinoso and Molina-Sabio 1992). The schematic for the preparation of AC through physical and chemical methods is presented in Fig. 5.3. AC is proved to have superior adsorptive and mechanical properties when compared to raw biomasses owing to increased surface area and porosity (Zhang et al. 2019). AC derived from different biomass has varying properties. The properties of AC depend on the precursor material, type of carbonization and activation, and activation temperature and duration. AC is the widely studied adsorbent material for treating effluents which contain all types of pollutants including the emerging contaminants from effluents (Yahya et al. 2015). Moreover, AC also finds its application as catalyst support in many reported studies in advanced oxidation processes which are discussed in Sect. 5.8.4. The application of biomass-derived AC is not limited to effluent treatment methods, and thus they are used in various fields such as gas purification (Ma et al. 2008), supercapacitors (Yang et al. 2014), and medicinal applications (Lakshmi et al. 2018). Few of the studies on the application of biomass-derived activated carbon for water and wastewater treatment is summarized in Table 5.2.

Table 5.1 Application of raw biomass for effluent treatment

Raw biomasses	Target pollutants	Maximum monolayer adsorption capacity "q_m" (mg/g)	References
Dyes			
Guava leaves	Remazol brilliant blue-R	93.12	Debamita et al. (2020)
Coffee husks	Congo red	38.65	Vairavel et al. (2021)
Neem leaf powder	Coomassie violet	39.64	Divya et al. (2020)
Sugar cane bagasse	Congo red	38.20	Zhang et al. (2011a, b)
Almond shells	Direct red 80	22.42	Ardejani et al. (2008)
Jujuba seeds	Congo red	55.55	Reddy et al. (2012)
Jackfruit peel	Methylene blue	285.71	Hameed (2009)
Lotus leaf	Congo red	45.89	Meghana et al. (2020)
Heavy metals			
Neem leaf	Cd(II)	157.80	Sharma and Bhattacharyya (2005)
Cucumis melo rind	Fe(II)	4.98	Othman and Asharuddin (2013)
Coffee residues	Cd(II)	39.52	Boonamnuayvitaya et al. (2004)
Coconut husk	Pb(II)	2.75	Abdulrasaq and Basiru (2010)
Durian shell	Cr (VI)	117	Edokpayi et al. (2015)
Sugarcane bagasse	Cd(II)	189	Karnitz et al. (2007)
Cassava tuber bark waste	Zn(II)	83.3	Horsfall et al. (2006)
Wheat bran	Cd(II)	101	Ozer and Pirincci (2006)
Phenol			
Tea waste	Phenol	154.39	Pathak et al. (2020)
Garlic peel	Phenol	14.48	Muthamilselvi et al. (2016)
Rice straw	Phenol	5.78	Sarker and Fakhruddin (2017)
Lantana camara	Phenol	112.5	Girish and Murty (2014)
Vegetal cords	Phenol	6.21	Cherifi et al. (2009)
Endocrine disruptors			
Barley husk	Bisphenol A	19.94	Balarak (2016)
Walnut shell	Bisphenol A	38.5	Dovi et al. (2021)
Raw fibric peat	Bisphenol A	6.48	Zhou et al. (2011)



Chemical Activation



Physical Activation

Fig. 5.3 Chemical and physical activation methods for the preparation of biomass-derived activated carbon

5.8 Biomass-Based Composite Materials for Effluent Treatment

Biomass-based materials either in their raw form or with thermal and chemical modification demonstrated to be an efficient low-cost material for the adsorption of various organics and inorganics from simulated effluents. Furthermore, recent studies suggest that these biomasses can also be fused with other functional materials and could be actively applied in various treatment processes. These biomass-based composites include but are not limited to metal oxide composites, magnetic materials, polymeric materials, and graphene-based composites. The schematic representation of the same is presented in Fig. 5.4.

5.8.1 Biomass-Based Magnetic Materials for Effluent Treatment

Generally, nanoparticles have promising potential to be used in various effluent treatment technologies. However, the application of these nanoparticles in water and wastewater purification is limited. This is due to the fact that, the spent nanomaterials after application tends to escape into the aquatic environment causing secondary pollution. The removal and recovery of the spent materials in their nanoform is not economical. Recently, materials coated with magnetite nanoparticles are considered

Table 5.2 Biomass-derived activated carbon for effluent treatment

Biomass-derived activated carbon	Target pollutants	Activation of adsorbents				Maximum monolayer adsorption capacity "q_m" (mg/g)	References
		Physical		Chemical			
		Temperature (K)	Activating agent	Temperature (K)	Chemicals used		
Dyes							
Pomegranate peel	Direct blue 106	–	–	773	$ZnCl_2$, H_3PO_4,	54.05	Amin (Amin 2009)
Orange peel	Direct navy blue 106	–	–	393	H_2SO_4	107.53	Khaled et al. (Khaled et al. 2009)
Pineapple waste	Methylene blue	–	–	773	$ZnCl_2$	288.34	Mahamad et al. (2015)
Rice husk	Acid yellow 36	373	steam	–	–	86.9	Malik (2003)
Sugarcane bagasse pith	Reactive orange	–	–	873	H_3PO_4	3.48	Amin (2008)
Grape processing waste	Methylene blue, Metanil yellow	–	–	873	$ZnCl_2$ $ZnCl_2$	417 386	Saygili et al. (2015)
Apple pulp and peel	Methylene blue	–	–	–	H_3PO_4	278	Hesas et al. (2013)
Palm flower	Amido black 10B	–	–	413	H_2SO_4	4.03	Nethaji and Sivasamy (2011)
Heavy metals							
Dairy waste Sugar beet	Pb(II) Pb(II)	873 873	– –	– –	– –	248 197	Inyang et al. (2012)
Hazelnut shell	Ni(II)	–	–	423	H_2SO_4	11.64	Demirbas et al. (2002)
Canna indica	Cd(II)	–	–	873	HCl	189	Cui et al. (2016)

Corn straw	Cu(II) Zn(II)	– –	– –	873 873	– –	12.5 11.0	Chen et al. (2011)
Pine bark Oak bark	Pb(II) Pb(II)	723 723	– –	– –	– –	3.0 13.1	Mohan et al. (2007)
Peanut shell	Pb(II)	–	–	823	H_3PO_4, HNO_3	35.5	Xu and Liu (2008)
Corn stalk	Cd(II)	–	–	873	$ZnCl_2$	32.4	Youssef et al. (2004)
Phenols							
Bamboo charcoal	Phenol	473	–	–	–	24.96	Ma et al. (2013)
Banyan root	Phenol	–	–	773	KOH	26.95	Nirmala et al. (2019)
Date-pit	Phenol	1173	CO_2	–	–	262.3	El-Naas et al. (2010)
Rattan saw dust	Phenol			973	KOH	149.25	Hameed and Rahman (2008)
Dates' stones	Para-chlorophenol	–	–	773	$ZnCl_2$	102.04	Aldoury and Sabeeh (2014)
Corn husk	Phenol Para-nitrophenol	– –	– –	773 773	$FeCl_3$ $FeCl_3$	8.445 11.668	Mishra et al. (2019)
Pharmaceutical wastes							
Pine sawdust	Sulfamethoxazole	–	–	923	$FeCl_2$, KOH, KNO_3	`19.09	Reguyal and Sarmah (2018)
Tea waste	Sulfamethazine	973	Steam	–	–	10	Rajapaksha et al. (2016)
Giant reed	Amoxicillin	973	Microwave	–	–		Chayid and Ahmecd (2015)

(continued)

Table 5.2 (continued)

Biomass-derived activated carbon	Target pollutants	Activation of adsorbents				Maximum monolayer adsorption capacity "q_m" (mg/g)	References
		Physical		Chemical			
		Temperature (K)	Activating agent	Temperature (K)	Chemicals used		
Cassava waste	Oxytetracycline	–	–	773	KOH	3.33	Luo et al. (2018)
Olive stones	Paracetamol	–	–	773	H_3PO_4	108.3	Garcia-Mateos et al. (2015)
Moringa seed	Diclofenac	–	–	723	H_3PO_4	121.112	Bagheri et al. (2020)
Cauliflower roots	Chlortetracycline	773	–	–	–	81.30	Qin et al. (2017)
Wheat straw	Ketoprofen	–	–	973	HCl	72.46	Wu et al. (2018)
Endocrine disruptors							
Agave Americana leaf fibers in combination with tannin	Tetracycline	1173	–	–	–	87.21	Selmi et al. (2018)
Argun nut shells	Diuron	573	–	–	–	833.33	Zbair et al. (2020)
Argun nut shells	Bisphenol A	573	–	–	–	1162.79	Zbair et al. (2020)
Pistachio nut shells	Caffeine	–	–	493	HNO_3	22.6	Roman et al. (2018)
Montmorillonite/rice husk hydrochar	17α-ethynyl estradiol	–	–	452	Methanol	138	Tian et al. (2018)
Sawdust hydrochar	Tetracycline	–	–	1073	KOH	423.7	Chen et al. (2017)

Potato peel hydrochar	Pramipexole Dorzolamide	– –	– –	473 473	KOH KOH	66 60	Kyzas and Deliyanni (2015)
Rice straw hydrochar	Tetracycline	–	–	573	K_2CO_3	714	Liu et al. (2014)

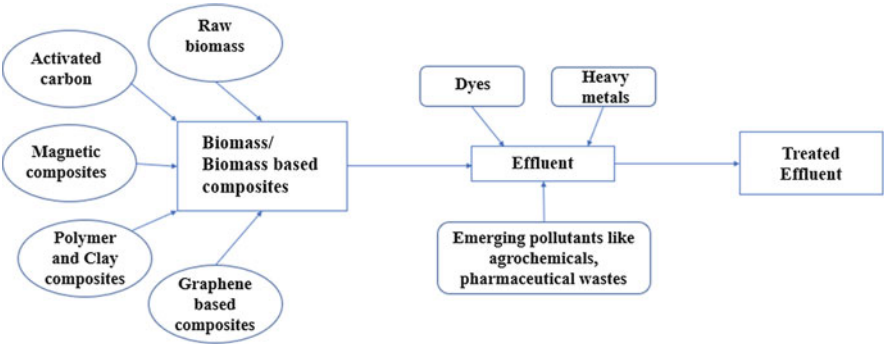


Fig. 5.4 Biomass-based composites for effluent treatment

very promising in the environmental remediation process. Since the magnetic particles are superparamagnetic (they are magnetized only with the external magnetic field), they can be recovered easily by the external magnetic field and reused without any loss of the functional materials (Nethaji et al. 2013). Hence, magnetic materials like iron oxide nanoparticles are extensively studied as functional materials for their application in water treatment owing to their magnetic properties. However, these iron oxide nanoparticles tend to agglomerate in the solution, thereby decreasing their efficiency. Hence, biomass-based materials supported by iron oxide nanocomposites were studied and successfully applied to overcome these drawbacks (Mehta et al. 2015). Biomass-based magnetic composites are mainly used in the adsorption process, and there are few studies which deals on the application of these materials in photocatalytic oxidation (Pang et al. 2016). Though several methods like hydrothermal reactions, sol-gel methods were reported, the co-precipitation method is most commonly employed for the preparation of magnetic composites. In the co-precipitation method, the biomass, or biomass-derived materials like activated carbon (AC) are dispersed along with the iron precursors like ferric chloride or ferrous sulfate. The iron salt in the precursors is then reduced using various reducing agents under continuous stirring, thus depositing the iron oxide nanoparticles onto the matrix of the raw biomass or AC derived from the biomass (Nethaji et al. 2013). The efficiency of these magnetic composites expended for the adsorptive/oxidative treatment of various pollutants from the aqueous phase along with the experimental conditions are shown in Table 5.3. The application of magnetized adsorbents derived from raw biomass and AC is presented in Fig. 5.5. Most of the studies reported an enhanced removal efficiency of the magnetic nanocomposites in comparison with the unmagnetized materials. Few adsorption studies reported a slight decrease in the efficiency, owing to the reduction in the available surface area due to the impregnation of iron oxide particles into the matrix of the biomass. Nevertheless, the ease of separation of the functional material improved considerably, thereby aiding in the regeneration and reusability of the nanocomposite materials.

Table 5.3 Biomass-based magnetic composites for effluent treatment

Biomass-based magnetic adsorbents	Precursor biomass materials	Target pollutants	Surface area (m^2/g)	Maximum monolayer adsorption capacity "q_m" (mg/g)	Inferences	References
Dyes						
Magnetic Corn cob-derived carbon (MCA)	Corn cob	Methylene Blue	153.89 (MCA) 69.45 (unmagnetized carbon)	163.93 (MCA) 103.09 (unmagnetized carbon)	The efficiency of the magnetized and unmagnetized adsorbent derived from corn cob was compared. The magnetized carbon possessed better surface area and adsorption efficiency for the sorption of methylene blue dye.	Ma et al. (Ma et al. 2015)
Magnetic graphene oxide-biomass activated carbon composite	Palm Kernel Shell (PKS)	Acid Blue 113	280.39	32.2	The adsorbent had the saturation magnetization value of 33.74 emu/g as characterized by a Vibrating Sample Magnetometer. A comparison study was also carried out to prove that the magnetized graphene oxide-PKS-derived carbon composites had better removal efficiency than the raw precursor and graphene oxide.	Ying et al. (2020)
Magnetic activated carbon from peanut shell	Peanut shell	Malachite Green	722.34 (CO_2 activation) 448.70 (Without CO_2 activation)	747.03 (CO_2 activation) 270.28 (Without CO_2 activation)	Studies were performed by increasing the iron oxide content in the matrix of the carbon derived from the peanut shell. The surface area, porosity, and adsorption efficiency increased with the increase in the iron oxide impregnation proving that the degree of magnetization is one of the most important parameters.	Guo et al. (2018)

(continued)

Table 5.3 (continued)

Biomass-based magnetic adsorbents	Precursor biomass materials	Target pollutants	Surface area (m^2/g)	Maximum monolayer adsorption capacity "q_m" (mg/g)	Inferences	References
Heavy metals						
Magnetic biochar composites (MB)	Phoenix tree leaves	Chromium (VI)	83.6	55 (Magnetized Biochar) 39.8 (Unmagnetized Biochar) 26.5 (Fe_3O_4 nanoparticles	Magnetized biochar was prepared by hydrothermal method. The O_2 containing groups on the surface of the biochar provided growth sites for Fe_3O_4 nanoparticles.	Liang et al. (Liang et al. 2019)
Magnetic nanoparticle (Fe_3O_4) impregnated onto tea waste	Tea waste	Nickel (II)	22.3 (tea waste) 27.5 (magnetized tea waste)	38.3	This study does not involve the preparation of activated carbon from tea waste. Tea waste is directly incorporated with Fe_3O_4 nanoparticles. The incorporation of iron oxide nanoparticles had a negligible impact on the surface area.	Panneerselvam et al. (2011)
EDTAD-modified magnetic baker's yeast biomass (EMB)	Baker's yeast	Lead (II)/cadmium (II)	–	89.21 (Pb^{2+}) 41 (Cd^{2+})	EMB could be regenerated using both HCl and EDTA with an efficiency of greater than 90% without disturbing the morphological characteristics.	Zhang et al. (2011a, 2011b)
Emerging contaminants						
Fe_3O_4/Douglas fir biochar	Douglas fir	Caffeine (stimulant) Ibuprofen (Inflammatory drug) Acetylsalicylic	468.2 (Douglas fir biochar) 322.0 (Fe_3O_4/Douglas fir biochar)	**Caffeine**: 23.9 (Douglas fir biochar) 73.1 (Fe_3O_4/Douglas fir biochar) **Ibuprofen:** 15.5 (Douglas fir	It was observed that the unmagnetized adsorbent exhibited better surface area when compared to the magnetized Douglas fir biochar. However, the adsorption of all the three pharmaceuticals were better	Liyanage et al. (2020)

		acid (Inflammatory drug)		biochar) 32 (Fe_3O_4/Douglas fir biochar) **Acetylsalicylic acid:** 89 (Douglas fir biochar) 126 (Fe_3O_4/Douglas fir biochar)	using the magnetized adsorbent compared to the unmagnetized char.	

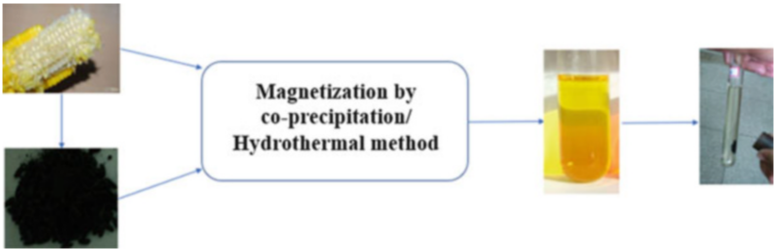


Fig. 5.5 Biomass-derived magnetic composites for effluent treatment

5.8.2 *Biomass-Based Polymer and Clay Composites for Effluent Treatment*

The efficiency of a functional material in the effluent treatment mainly depends upon its available surface area and surface functionality for adsorptive removal, and oxidative potential in case of advanced oxidation processes. Hence, polymeric materials are potential candidates to be used in the adsorption process, owing to their tunable surface properties (Pan et al. 2009). Naturally occurring biopolymers such as starch, cellulose, chitosan, and alginate were widely explored for their adsorption potential due to their high surface area and variable surface functionality. Among all the above-mentioned biopolymers, chitosan is widely explored for the removal of contaminants from simulated wastewater. It is more preferred since it contains -NH_2 and -OH functional groups on its surface which can act as chelating sites for concentrating organic and inorganic moieties (Wang and Zuang 2018). However, most of these naturally occurring biopolymers exhibit weak thermal and mechanical properties. Moreover, these biopolymers exhibit swelling phenomena when exposed to the aqueous environment. Hence, most of the studies deal with crosslinking these biopolymers with mechanically strong materials like biochar, biomass-derived AC, or clay composites. Natural clay materials like bentonite, montmorillonite, kaolinite, zeolite, etc. are mostly aluminosilicates with the presence of sodium, potassium, magnesium, and calcium. The layered morphology of these clay materials with the charged surface is ideal for the adsorption of ionic contaminants from the effluent. However, these clay minerals have poor potential for the removal of non-ionic contaminants. Nevertheless, they possess strong mechanical and thermal stability. Hence, the biopolymers are generally cross-linked with clay minerals to overcome the shortcomings of both clay and biopolymers (Unuabonah and Taubert 2014). Hence, biopolymers supported with biochar, AC, and clay minerals exhibited superior adsorption efficiency with better thermal and mechanical stability as shown in Table 5.4.

Table 5.4 Biomass-based polymer and clay composites for effluent treatment

Biomass-based adsorbent	Biomass precursors	Target pollutants	Surface area (m^2/g)	Maximum monolayer adsorption capacity “q_m” (mg/g)	Inference	References
Biopolymer composites						
Zeolite derived from chitin	Chitin	Crystal violet, methylene blue, basic fuchsin	–	124 (Crystal violet), 87.45 (methylene blue), 789.10 (basic fuchsin)	The zeolite was synthesized using biopolymer chitin as a mesoporosity agent by the hydrothermal method	Briao et al. (Briao et al. 2018)
Bacteria-derived poly(γ-glutamic acid) (γ-PGA)	*B. subtilis var.* (natto)	Auramine O, rhodamine B, safranin O	–	0.05 dm^3/mg (auramine O), 0.02 dm^3/mg (rhodamine B), 0.19 dm^3/mg (safranin O)	The kinetic data were well in agreement with Boyd’s ion-exchange model	Inbaraj et al. (2006)
Chitosan/activated carbon/iron bio-nanocomposite	Chitosan from shrimp shell, activated carbon from grape stalks	Cadmium	834 (activated carbon) 11.6 (chitosan) 419.20 (chitosan/activated carbon/iron bio-nanocomposite)	322.58	The study indicated better interactions between oxygen functional groups of AC, iron ions, and amine groups of chitosan	Sharififard et al. (2018)
Zerovalent iron encapsulated chitosan nanospheres (CIN)	Chitosan	Arsenic (V) and (III)	69 (CIN) 26 (zerovalent iron)	–	The study shows that the adsorbent is porous in nature and iron particles exist in zerovalent state and there exists a complexation reaction among iron, chitosan, and arsenic	Gupta et al. (2012)
Biopolymer clay composites						
Cellulose-montmorillonite composite	Cellulose	Chromium (VI)	87.09	22.2	The interaction between cellulose and montmorillonite has proved the potential application	Kumar et al. (2011)

(continued)

Table 5.4 (continued)

Biomass-based adsorbent	Biomass precursors	Target pollutants	Surface area (m^2/g)	Maximum monolayer adsorption capacity “q_m” (mg/g)	Inference	References
					of the material for the effective adsorption of chromium. The XRD peaks signified the ordered distribution of clay layers in the biopolymer composite	
Montmorillonite-alginate beads	Alginate	Paraquat herbicides	46	0.321 mmol/g	TGA was used to determine the thermal stability of the beads. The results proved that the thermal stability of montmorillonite-alginate beads was much better than alginate beads	Etcheverry et al. (2017)
Guar gum /bentonite bio-nanocomposites	Guar gum	Lead (II), crystal violet (CV) dye	5.533	187.08 (Pb^{2+}) 167.92 (CV)	The TGA results proved increased thermal stability of biocomposites in comparison with guar gum. FT-IR suggested the electrostatic interaction or chelation via hydrogen bond formation between Pb^{2+} or CV and active sites of bio-nanocomposites.	Ahmad and Mirza (2018)

5.8.3 Biomass-Based Graphene Composites for Effluent Treatment

Graphene is composed of single layers of carbon atoms densely packed which attracted tremendous attraction in late 2004. It is a “single layer of carbon atom densely packed in a honeycomb crystal lattice” (Li et al. 2019). Because of its good chemical stability and graphitized basal plane structure, graphene-based materials are widely used in different applications including supercapacitors, fuel cells, batteries, and as adsorbents in effluent treatment systems (Novoselov et al. 2012). Graphene or reduced graphene oxide is mostly synthesized by using Hummers or modified Hummers method. Various functional groups present on the edges of the graphitic planes aid in the interaction of the graphene sheets with the charged contaminants present in the wastewater. However, the graphene sheets generally suffer from stacking and agglomeration problems due to π–π interactions and van der Waals forces in the aqueous phase. Hence, to overcome these limitations and to exploit the desirable properties of the graphene-based materials, various biomass-based graphene composite materials were reported for the removal of organic and inorganic compounds from simulated effluents (Nethaji and Sivasamy 2017). Biomass-derived materials like biochar, AC, and other cellulosic waste biomass were used as composite materials by crosslinking with the honeycomb structure of graphene oxides. There are also studies which had reported on the utilization of iron oxide nanomaterials for acquiring the magnetic properties reducing the stacking problem of graphene layers. The application of these biomass-based graphene composite materials for the removal of organic and inorganic moieties is presented in Table 5.5.

5.8.4 Biomass-Based Metal Oxides Composites such as Catalyst and Catalyst Supports

Heterogeneous catalysis involving metal oxides is a good example of an advanced oxidation process. Literature shows a number of methods for the enhancement of catalyst activity alongside cost reduction and efficiency maximization. Though many paths are sorted for catalyst modification, synthesis of a catalyst supported on materials with a higher surface area without diminishing the activity is a greater concern. Hence, the choice of the support material comes into the picture, wherein it must be cheap, green, and environmentally friendly with enhanced activity. Hence, carbon as catalyst support derived from biomass is a better option. Wherein, the disposal problem of the biomass itself is minimized and the resulting carbon could be used efficiently. However, activated carbon in itself has been used as a catalyst. Juhola et al. (2021) had prepared biomass–metakaolin as granular composite materials for application as a catalyst for the treatment of effluents.

Table 5.5 Biomass-based graphene composites for effluent treatment

Biomass-based graphene composites	Biomass precursors	Target pollutants	Surface area (m^2/g)	Maximum monolayer adsorption capacity “q_m” (mg/g)	Inference	References
Graphene oxide-based carbonaceous nanocomposites	Rice husk	Methylene blue	936	1591	Graphene oxide/ordered mesoporous carbon was prepared from rice husk using mesoporous silica as a template source	Liou and Wang (2020)
Graphene oxide/silica nanocomposites	Rice husk	Rhodamine B	625	147.06	Silica was extracted from rice husk. The hybrid material was prepared by hydrothermal method. The study also claims that the composites not only aid in recycling agricultural waste but also help in the recovery of graphene oxide from the aqueous phase	Liou et al. (2021)
Graphene/activated carbon composite	Glucose	Lead (II)	2012	217.6	Mesoporous graphene/activated carbon composite was prepared from graphene oxide and glucose. The prepared composite had a higher adsorption capacity for Pb^{2+} when compared to the reported literature	Saeidi et al. (2015)
Nitrogen-containing carbon nano-onions-like and graphene-like materials	*Lentinus edodes*	Phenol	35.40	–	Nitrogen-containing carbon materials with different morphologies were prepared using $Fe(NO_3)_3$ through a hydrothermal method. The prepared material was used for both adsorption and photocatalytic oxidation of phenol. The photoelectrons transformed by graphite claim to be reacted with O_2 molecules to form the superoxide radicals ($^{\cdot}O_2$) for the degradation of phenol	Han et al. (2021)

Since the development of nano metal oxides as a photocatalyst under visible light irradiation for environmental remediation (Fujishima and Honda 1972). Various research has been focused on the modification of metal oxides for maximum efficiency. The preparation of metal oxide on catalyst support is highly researched. While a choice for support material activated carbon prepared from biomass is widely preferred. Devagi and Soon (2018) have reported a TiO_2/modified sago bark (biomass) for treating the sago wastewater effluent. The author chose the effluent as it had a higher chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TDS), and was acidic. The sago bark was chosen as a precursor as it is a major waste during the debarking step of the starch extraction. The modified biomass TiO_2 mixture was used as a photocatalyst for 64.92% removal with 0.2 g/L TiO_2/1% MSB (120 min of irradiation). Poudel et al. (2020) has removed As(III) from water by using agro-waste-based biomass impregnated with $TiO_{2.}$

ZnO incorporation on biomass-derived activated carbon has been widely researched by various research groups. Cruz et al. (2018) had prepared a ZnO/activated carbon (biomass derives) nanocomposite for the treatment of methylene blue dye. The ZnO nanoparticles were evenly distributed on the surface of the activated carbon. Ramya et al. (2018) has worked on the preparation of activated carbon from tannery sludge biomass. The acquired biomass was used as support material for ZnO-based nanocomposite preparation. The material was used for Cr (VI) removal from the aqueous phase. Supported biomass-based activated carbon for dye degradation has been prepared by hydrothermal technique. Waste biomass was used by Vinayagam et al. (2018) for activated carbon preparation as carbon support. Akpomie et al. (2020) recently prepared a ZnO nanoparticle along with biomass for the treatment of celestine blue dye.

Hybrid bifunctional materials have also been synthesized by various research groups comprising AC and nanomaterials which would serve both as an adsorbent and photocatalytic material. Our group has also worked in this area (Nethaji et al. 2018) and we have reported a bismuth oxybromide (BiOBr)/activated carbon hybrid material as a bifunctional nanomaterial for effluent treatment. It was a good adsorbent material and it even degraded malachite green dye under visible light irradiation. The source of AC was waste polyurethane foam trash from used car seats. The composition of the foam was a polyol with a toluene diisocyanate blend. A simple hydrothermal process was used for the preparation of the bifunctional material.

5.9 Conclusions

Biomass materials are mostly explored for their potential to be used as biofuel. However, the consumption of this biomass for the production of biofuel accounts for less than 10% of the available lignocellulosic materials. Owing to its abundant availability, most of the agricultural waste biomass is considered waste and requires a separate disposal method or a process for the same. But the utilization of these types of wastes and naturally available renewable material as a source for the production of materials for the effluent treatment itself is a boon to the environment. Most of the studies suggest that these biomasses either in their raw form or modified form proved to be an effective replacement for the synthetic materials conventionally used in effluent treatment operations. Moreover, the hybrid materials which include biomass-based composites could effectively overcome the shortcomings of their synthetic counterparts. The biomass-derived activated carbon was effectively used in various adsorptive and catalytic applications as adsorbent and catalyst support, respectively. The compatible and environmentally friendly nature of the biomasses could be explored for applications in various other unit operations in effluent treatment plants. Hence, these materials derived from the biomasses can be coined as "waste to wealth" and thus prove to be environment-friendly substitutes to treat and overcome effluent treatment problems.

Competing Interests All the authors declare that they have no competing interests.

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Chapter 6

Cellulase: A Catalytic Powerhouse for Lignocellulosic Waste Valorisation

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Abstract Cellulose is the world's most ubiquitous organic compound and has an abundant potential to be transformed into a renewable source of energy and other industrial products. To break down this complex polymer, cellulase has been conventionally used as a biocatalyst. Other than numerous industrial uses, including detergent, paper and pulp, textile, beverages, feed, baking, and biofuel, the application of cellulase for waste valorisation is also a central thrust area. The cellulolytic action of this enzyme has been explored for utilisation of widely available lignocellulosic waste. This reaction has been critical for the cellulose conversion to glucose and then to biofuel. Apart from biofuel, cellulase has also been employed to convert green waste into value-added products such as prebiotic oligosaccharides, organic acids, and biopolymers that can be integrated into the circular economy. Numerous factors affect the catalytic actions of cellulase, like pretreatment of lignocellulosic biomass, structural and compositional variation, working temperature, and pH. This chapter encompasses a detailed insight into the biocatalytic mechanism, applications, and limitations of cellulase as a potent enzyme for waste valorisation.

Keywords Cellulase · Waste valorisation · Lignocellulosic biomass · Circular economy · Biorefinery

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Abbreviations

3Rs	Reduce reuse and recycle
ATCC	American type culture collection
BSG	Brewer's spent grain
CBG	Compressed biogas
CMCase	Carboxymethyl cellulase
CNCs	Cellulose nanocrystals
CNF	Cellulose nanofibrils
CO_2	Carbon dioxide
Co^{60}	Cobalt-60
FPA	Filter paper assay
FPU	Filter paper units
GHG	Greenhouse gas
IFPU	International unit of filter paper activity
IL	Ionic liquid
IU	International enzyme unit
LCA	Life cycle assessment
MNPs	Magnetic nano-particles
MPa	Megapascal
PHA	Polyhydroxyalkanoates
PLA	Poly-lactic acid
RSM	Response surface methodology
SDS	Sodium dodecyl sulphate
SHF	Separate hydrolysis and fermentation
SmF	Submerged fermentation
SMS	Spent mushroom substance
SmSF	Simultaneous Saccharification and Fermentation
SSCF	Saccharification and co-fermentation
SSF	Solid-state fermentation
TCA	Tricarboxylic acid
TEA	Techno-economic analysis
U/g	Enzyme unit per gram
U/mL	Enzyme unit per millilitre
USD	United States dollar

6.1 Introduction

The focus of waste treatment has now shifted to its valorisation, as it promises better management of available resources. The valorisation method, if assisted by biological techniques, becomes a better environment-friendly solution. The utilisation of biological methods for waste valorisation has spawned the concept of a bio-based circular economy. Cellulase is one such biocatalytic agent which is categorised as endoglucanase (E.C.3.2.1.4), exoglucanase, or cellobiohydrolase (E.C.3.2.1.91), and β-glucosidase (E.C.3.2.1.21).

The source of cellulase can vary from natural to commercial production (Bhardwaj et al. 2021a). The commonly reported bacteria, streptomyces, and fungi for cellulase production are Clostridia sp.*, Bacillus licheniformis, Streptomyces argenteolus*, *S. griseorubens, S. lividans, Aspergillus oryzae, Candida cylindracea, Trichoderma reesei, etc.* (Hamdi et al. 2020; López-Mondéjar et al. 2019; Saldarriaga-Hernández et al. 2020; Kumar et al. 2018, 2020a). The genetically developed producers include *E. coli* and *Pichia pastoris*.

The mechanistic insight of cellulase explains the hydrolysis process. Endoglucanase is responsible for the breakdown of β-1,4 glycosidic bond, which exposes new chain ends. The ends so produced are broken by exoglucanase/ cellobiohydrolase to produce oligosaccharides, whereas β-glucosidase causes lysis of these oligosaccharides into their monomer units. For a detailed review of the mechanism of action and structure of cellulase, an article by Rabinovich et al. can be referred (Rabinovich et al. 2002). Most of the cellulases have been found to be a multidomain proteins containing a catalytic domain, a cellulose-binding domain and an interdomain linker.

Earlier reports suggest the use of cellulase in waste management such as deinking of paper, degradation of voluminous cotton sludge, and bioconversion of sawdust, vegetable and fruits waste, rice straw, leaves and bamboo, and sawdust. Thus, cellulase-mediated waste valorisation becomes a potent tool for the proficient utilisation of agro-residues, food, paper, and textile industry waste (Khan et al. 2016; Vermelho et al. 2012). The cellulose content of municipal solid waste has also been utilised for biogas production (Demirbas et al. 2016). According to a report, about 10–50 billion tons of dry lignocellulosic waste are produced every year across the globe (Motaung and Linganiso 2018). This waste has been reported to contain about 45% cellulose, 10% hemicellulose, and 10–15% lignin. The agro-waste mainly includes sugarcane bagasse (grown in China, India, Brazil, Thailand, South Africa, and Australia), maize stalks (major crop of countries like South Africa and the United States), rice husk (grown worldwide), and sorghum stalks (tropical and subtropical regions of Asia and Africa). According to Khan et al., lignocellulosic material consists of 30% solid content composed of about 65% holocellulose and 20% lignin (Khan et al. 2016; Kumar and Verma 2021a). The meticulous design of the valorisation method can lead to the recycling of by-products with economic advantage. With the advancement of current technologies, diverse applications of these processes have been explored. These include fossil-fuel alternatives such as bioethanol, biopropanol, aviation fuel, and biogas (Kumar and Verma 2021b). Other platform chemicals, including succinic acid, butyric acid, and enzymes are also being produced by using enzymatic hydrolysis of food and agro-industrial waste. This further extends to the industrial production of innumerable polymers with various commercial applications such as polyhydroxy butyrate, poly-lactic acid, xanthan, pullan, and poly-hydroxy valerate. The application of cellulase for the valorisation of waste from different industries has been summarised in Table 6.1.

Table 6.1 Application of cellulase in the waste valorisation

Industrial waste as substrate	Source of cellulase	Value-added product formed	Method used	Reference
Lignocellulosic biomass	*Bacillus. tequilensis* G9	Bioethanol	Co-culturing of *Bacillus. tequilensis* G9 with *Saccharomyces cerevisiae*	Dar et al. (2019)
Forest waste (spruce and birch)	Obtained from NZYTech Lda.	Prebiotics	Pretreated residues were enzymatically digested by four cellulase	Karnaouri et al. (2019)
Paper sludge	Obtained from Novozymes and Sigma-Aldrich	Bioethanol production	Supplementation of β-glucosidase with a commercial cocktail of enzyme	Gomes et al. (2016)
Lignocellulosic biomass	yeast *Yarrowia lipolytica*	Lipid (ricinoleic acid) production	Consolidated Bioprocessing	Guo et al. (2018)
Sugarcane bagasse	Bacterial consortium from sugarcane bagasse and thermophilic sludge	Methane, hydrogen, and other organic acids	Bioaugmentation of cellulase producing bacteria obtained from lignocellulosic biomass with sludge	Soares et al. (2019)
Spent mushroom and food waste	*A. niger*	Lactic acid	Cellulase produced by *A. niger* led to the breakdown of waste to produce hexoses and pentoses. These were then utilised by *Enterococcus mundtii* CGMCC 22,227	Ma et al. (2021)
Textile waste (cotton-polyester 50:50 blend)	Commercial cellulase and β-glucosidase	Bioplastics, biosurfactants, and other biochemicals	Pretreatment, enzymatic hydrolysis, and recovery step include the use of activated carbon, filtration. Ion exchange chromatography and solvent evaporation	Subramanian et al. (2020)
Tapioca flour commercial waste	NA	Bioethanol gel	Pretreatment, enzymatic hydrolysis, and fermentation	Amalia et al. (2021)
Pomegranate peel	Commercial cellulase and pectinase (Novozyme)	Antimicrobial property for application in therapeutics	High-pressure extraction at 300 and 600 MPa	Alexandre et al. (2019)

(continued)

Table 6.1 (continued)

Industrial waste as substrate	Source of cellulase	Value-added product formed	Method used	Reference
Sugarcane straw	Commercial enzyme (Celluclast and Novozyme 188)	Bioethanol	Steam explosion pretreatment followed by enzymatic hydrolysis	Oliveira et al. (2013)
Sugarbeet	Accellerase (Merck-Sigma Aldrich)	Pectin, phenolic compounds, and succinic acids	Fractionation is followed by enzymatic hydrolysis. The hydrolysate was fermented by *Actinobacillus succinogenes* to produce succinic acid	Alexandri et al. (2019)

This chapter encompasses applications of cellulases in the valorisation of various waste belonging to food, textile, agricultural, and other industrial sectors. The current state of the art pushes toward a bio-based circular economy where the waste stream is maximally recycled to other production input stream.

6.2 Recent Advances in Cellulase Production and Purification

The potential of abundant natural polymer cellulose in nature has been critically known in biofuel production such as bioethanol and biobutanol. However, the major constraint is in the conversion of cellulose to fermentable sugars (saccharification) that can be overcome by treating the biomass with the cellulase enzyme. The cellulolytic enzyme can be obtained from plant, animal, and microbial sources (Zhang and Zhang 2013), among which microbial sources can be used to scale up production.

6.2.1 Microbial Production of Cellulase

Most cellulolytic microorganisms were isolated from the decaying wood and used to produce the cellulase enzyme at a large scale by either solid-state fermentations or submerged fermentations.

6.2.1.1 Solid-State Fermentation (SSF)

The type of fermentation occurs almost without free water; however, the substrate moisture must be present to assist the microorganism's growth. Hence, SSF imitates the natural habitat of maximum number of cellulolytic filamentous fungi. The critical factors that play a crucial role in the extracellular release of cellulase in SSF are moisture content, harvest time, spore count, particle size, type of substrate, incubation time, temperature, and initial pH values that render the adaptation cellulase excretion. The SSF begins with inoculating an optimised number of pure spores of filamentous fungus into the sterile solid medium under the necessary optimised conditions. The cellulase production using *Trichoderma reesei* ZU-02 through SSF by reusing solid substrates in at least three batches yielded the optimum cellulase production (158 IFPU/g koji) was obtained in the second batch of fermentation (Xia and Cen 1999). The comparative investigation of cellulase production in SSF by the two mutant strains of *Trichoderma reesei* showed to be critically varied with the physicochemical parameters like moisture content and the temperature in which *T. reesei* QM9414 strain indicated that only moisture content (70% optimum) had a major influence on the production of cellulase with maximum FPA (filter paper assay) activity (1.1635 U/g). Whereas, temperature (25°C optimum) and moisture (55% optimum) were found to be important in the extracellular cellulase production with maximum FPA activity (2.314 U/g) by *T. reesei* MCG77 strain (Latifian et al. 2007). In addition, Kim et al. had investigated the improvement of cellulase production by *Aspergillus sp.* SU-M15 with the repeated sequential treatment of mutagens Co^{60} γ-rays, N-methyl-N′-nitro-N-nitrosoguanidine, and ultraviolet irradiation to spores of *Aspergillus sp.* The production in wheat bran medium was found to be higher (82.5 U/g) than husk and sawdust by SSF (Vu et al. 2011). Sometimes, a mixture of substrates induces the extracellular cellulase production rather than the individual substrate, as investigated by Barnabe et al., who found that the mixed sludge of paper and pulp that influenced the lignocellulolytic secretions to 7.3 IU/mL from 1.5 IU/mL by *Trichoderma reesei* RUT C-30 (Lai et al. 2017). However, the cost of cellulase production is considerably reduced by utilising the waste residues or low-cost substrates from the municipal corporation, horticulture, kitchen, industrial, or open terrestrial sources as the substrates for SSF by optimising the required physicochemical environment (Bansal et al. 2012; Bharti et al. 2018; Xin and Geng 2010). The purification of extracellular cellulase enzyme can be done by extraction with the circulation of buffer and collection as a crude cellulase preparation that can be used for the saccharification of lignocellulosic materials and other applications.

6.2.1.2 Submerged Fermentation (SmF)

The type of fermentation that occurs in the presence of excess water is known as submerged fermentation (Kumar et al. 2020b). In most industrial-scale enzyme operations, the production by SmF is of priority because of ease of monitoring and operating. Most of the commercially available cellulases are produced by filamentous fungi; however, some bacteria (Ariffin et al. 2006; Ekperigin 2007; Irfan et al. 2012) and actinomycetes (Das et al. 2014; George et al. 2001; Van Zyl 1985) can also have the ability to produce but in low titre. The aerobic production by SmF depends on several factors like cellulosic substrate, nutrient availability, pH of the medium, inducer concentration, rate of oxygen supply, and fermentation temperature. The media formulation is necessary to result in optimal growth of biomass and cellulase production. The generalised medium used for the growth of filamentous fungi and cellulase enzyme production is Mandel's medium, Vogel's medium. However, to increase cellulase production, these medium needs to be optimised with respect to cellulolytic fungus. The cellulase production can be increased by genetically engineering the cellulolytic strains by either random mutation or site-directed mutagenesis. Separation of extracellular enzymes from the fermented solid biomass is carried out by centrifugation (10,000 × g, 10 min, 4°C) that can be used directly as a crude enzyme for the hydrolysis of cellulosic material (Lai et al. 2017). The cellulase production by SSF and SmF using various substrates has been listed in Table 6.2.

6.3 Immobilisation and Molecular Approaches for Enhanced Cellulolytic Action

The objectives of immobilisation of cellulase enzyme are reusability of the same enzyme for several cycles with excellent efficiency and stability that can substantially reduce the overall cost of the product. The materials used to immobilise the enzymes are both organic and inorganic, including polysaccharides, proteins, polymers, activated carbon, and metals (Datta et al. 2013; Nawaz et al. 2016; Safarik et al. 2016). There are various strategies to immobilise the enzymes, as represented in Fig. 6.1.

Recent reports suggest several methods for cellulase immobilisation for the valorisation of agro-residues, as shown in the above figure (Fig. 6.1). There have been studies for the comparison of conversion efficiency of free and immobilised enzymes for bioethanol production using lignocellulosic residues. The use of nanostructured support for the immobilisation of cellulase has been widely investigated (Ahmad and Khare 2018; Brindhadevi et al. 2020; Han et al. 2018; Husain 2016; Sillu and Agnihotri 2019). These nano-carriers impart reusability and stability of the enzyme and exhibit a larger surface area for enzyme attachment. This facilitates overcoming the mass transfer limitations by increasing the amount of enzyme that can be employed for catalytic conversion. The use of Magnetic Nano-Particles (MNPs) further improvises the process by allowing easy withdrawal of enzymes from the solution utilising an external magnetic field. In another study, the immobilisation was done on MNPs produced using green synthesis. Immobilisation

Table 6.2 Examples of cellulase production using different substrates

Substrate	Microorganism	Fermentation process	Activity			Reference
			FPU	CMCase assay	β-glucosidase	
Wheat bran	*Trichoderma reesei* RUT C30	SSF	1.14 U/mL	14.98 U/mL	0.22 U/mL	Sukumaran et al. (2009)
Enriched Mandel's cellulose medium	*Trichoderma spp.*	SmF	0.396 U/mL	0.488 U/mL	–	Chand et al. (2005)
Solka Floc	*Acremonium cellulolyticus* strain CF2612	SmF	17.8 U/mL	–	40.3 U/mL	Fang et al. (2009)
Wheat bran	*Fomitopsis sp.* RCK2010	SSF	3.49 U/g of substrate	71.6 U/g of substrate	53.6 U/g of substrate	Deswal et al. (2011)
Rice straw	*Melanocarpus sp.* MTCC 3922	SSF	25.3 U/mL	42.3 U/mL	74.1 U/mL	Jatinder et al. (2006)
Pretreated sugarcane bagasse	*Penicillium echinulatum* 9A02S1	SSF	32.89 U gdm^{-1}	282.36 U gdm^{-1}	58.95 U gdm^{-1}	Camassola and Dillon (2007)
Pretreated willow	*Trichoderma reesei* Rut C30	SmF	0.62 FPU/mL	132 U/mL	0.07 U/mL	Kovács et al. (2008)
Sugarcane bagasse	*Trichoderma atroviride* 676	SmF	0.25 U/mL	1.9 U/mL	0.17	Grigorevski-Lima et al. (2013)
Wheat bran	*Penicillium citrinum*	SSF	1.72 U/mL	1.89 U/mL	–	Dutta et al. (2008)

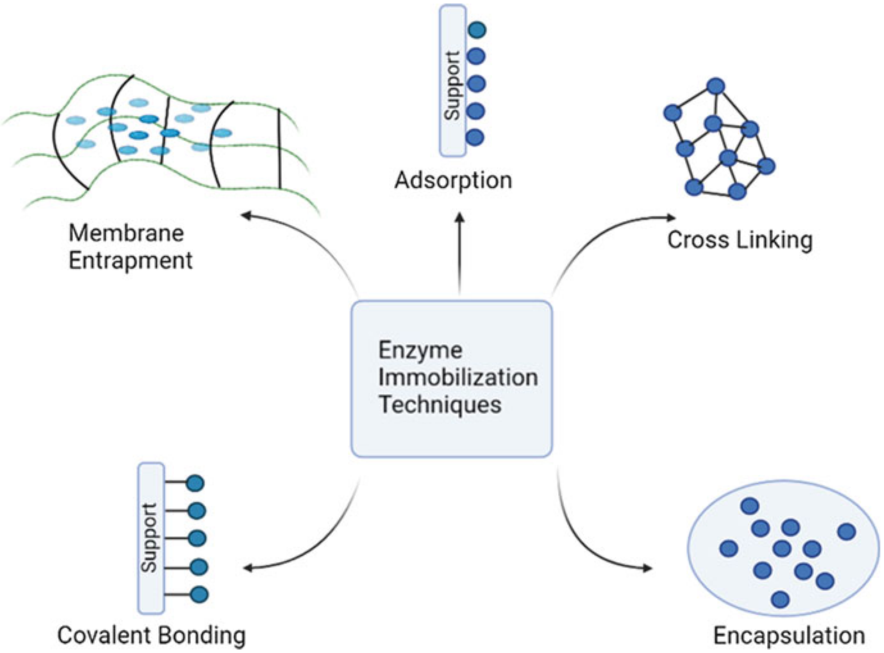

Fig. 6.1 Various methods to adopt immobilisation of enzymes

was secured by the covalent linking of cellulase to MNPs using glutaraldehyde. The results showed higher conversion efficiency of free enzymes (78%) than the covalently bonded enzymes (72%) in the first cycle, owing to the mass transfer limitation. However, subsequent cycles showed stable conversion efficiency, which ultimately is responsible for improved process economics (Ingle et al. 2017). Thus, immobilisation of cellulase contributes to its reusability, stability, and storage.

Cellulase can also be covalently immobilised using glutaraldehyde as a linker. In a significant work, it was immobilised on biochar prepared using sugarcane bagasse and coated with chitosan in different concentrations. This immobilisation process was successful in achieving 90% residual activity of cellulase even after 10 cycles of conversion (Mo et al. 2020). A detailed analysis of the pros and cons of selecting suitable micro- and nano-carriers with different methods of immobilisation is available elsewhere (Rajnish et al. 2021).

6.4 Role of Cellulase in Biorefinery Application

Cellulases are potential candidates for the bioconversion of agro-industrial wastes into several beneficial products. Such wastes are otherwise burnt or used in landfills (Singh et al. 2021). A zero-waste integrated biorefinery would involve cellulases in

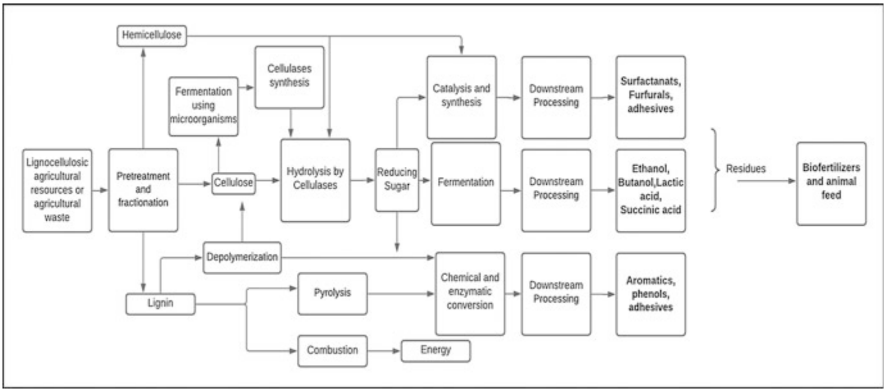

Fig. 6.2 Application of cellulases in a lignocellulosic biorefinery

the sequential production of sugar, organic acids, surfactants, furfurals, and biofuels such as bioethanol, biobutanol, biohydrogen, and compressed biogas (CBG) using agro-industrial residues, and the remaining organic matter can be used as compost or animal feed (Carrillo-Nieves et al. 2020; Kumar and Verma 2021a, b). Commercial enzyme manufacturing companies strive to manufacture enzyme cocktails for industrial biorefineries (Chandel et al. 2012). The biorefinery scheme utilising cellulases is depicted in Fig. 6.2.

6.4.1 Consolidated Bioprocessing for Biorefinery

The integrated approach to biomass conversion is known as consolidated bioprocessing. In this, a single microbe's amalgamation of saccharification and fermentation capabilities reduces environmental losses and expenses in lignocellulosic biorefineries (Bhardwaj et al. 2021a; b). The cellulase production, enzymatic hydrolysis, and bioconversion are combined (Cunha et al. 2020). The method involves hydrolysis of the structural carbohydrates to oligomers using the synthesised enzymes. The oligomers are depolymerised. The residual sugar is then fermented into various valuable products (Daniel et al. 2012). 10–30% of the pretreated liquor contributes as the carbon source for the production of enzymes and propagation of seeds. The enzyme loading is reduced to 10 mg protein/g cellulose (Scarlata et al. 2015). These modifications make the process economical and efficient. In a recent study on the biorefinery approach, consolidated bioprocessing using engineered *Trichoderma reesei* and *Saccharomyces cerevisiae* led to the highest production of 0.5 g/L glucaric acid from steam-treated corn stover in 7 days (Li et al. 2021). In another study, consolidated bioprocessing was used to produce bioethanol using surfactant (Tween 20)-assisted ionic liquid (1-ethyl-3-methylimidazolium methane sulphonate) from pretreated biomass of *Parthenium* *hysterophorus* L. The optimisation of pretreated conditions like biomass loading, pretreatment temperature, and time could increase the sugar yield by 40% during saccharification with IL-stable cellulase and xylanase enzymes produced from *Aspergillus aculeatus* PN14 (Nargotra et al. 2019). A novel consolidated bioprocessing method was developed for hyperproduction of butyric acid from delignified rice straw using co-fermentation of *Clostridium thermocellum* ATCC 27405 and *C. thermobutyricum* ATCC 49875. The butyric acid yield was increased up to 33.9 g/L by fed-batch fermentation with a selectivity of 78% (Chi et al. 2018). Therefore, consolidated bioprocessing combines many processes and reduces the overall cost of production by reducing energy requirements and contamination risk as well as maximising cost-effectiveness.

6.4.2 Cellulases in Agro-industrial Waste Biorefinery

Enzymatic pretreatment is an indispensable step of any lignocellulosic biorefinery. Using cellulolytic hydrolysis, the waste from agricultural practices and industries can be converted into several valuable products (Dragone et al. 2020). A cellulolytic enzyme derived from *Bacillus pumilus* is used for sugar production from banana-agro waste in the form of pseudostem and leaves (Kanmani et al. 2011). Cellulases synthesised by *Sporotrichum* sp. LAR5 with 7.88 IU was used to extract reducing sugar from acid-pretreated rice straw (Bajaj et al. 2014). In another instance, cellulases derived from *Penicillium decumbens* were used to hydrolysis corn cobs to produce reducing sugar used for ethanol production (Saliu and Sani 2012). The use of cellulases enzyme for the valorisation of various agricultural and industrial wastes is depicted in Table 6.3.

Cotton waste from textile industries is decomposed using cellulases for safe disposal into the environment. Waste generated from textile industries includes cotton and denim residues from the cotton machining process. These waste streams are treated with cellulase. Such industrial residues are subjected to enzymatic hydrolysis for recycling and production of valuable products such as glucose syrup (Subramanian et al. 2020). Fruit and vegetable wastes are rich in disaccharides and polysaccharides. They are also non-competitive with our food chain. Cellulases can hydrolyse the fruit and vegetable waste for further bioconversion into numerous commercial products (Srivastava et al. 2021). Hemp Hurd is a by-product of the fibre industry. Immobilised cellulase on an activated magnetic support was used to hydrolyse hemp hurds (Abraham et al. 2016). In another study, Liu et al. (2019) investigated the hydrolysis of apple pomace by pectinase and cellulase and further optimised the cellulase hydrolysis parameters by RSM after pectin hydrolysis. They obtained a maximum fermentable sugar production yield of 67.54 ± 1.45%, which provided the highest lipid production of 25.8 g L^{-1} after fermentation by a genetically modified strain *Yarrowia lipolytica* po1f (pex10−mfe− leu+) (Liu et al. 2019).

Table 6.3 Application of cellulases for treating different agro-industrial biorefinery

Agro-industrial waste	Enzyme source	Processing parameters	Observations	References
Paper sludge	Recombinant cellulase cocktail, Opt CelMix similar to Cellic CTec2 and Celluclast	0.015 g/g cellulase cocktail and 10% (w/v) biomass loaded	80% glucan conversion. High glucose yields using low enzyme loading	Malgas et al. (2020)
Newspaper waste	Celluclast 1.5 L and Novozyme 188	Pretreatment using SDS and Tween-80. 15% solid content and enzyme loading was 15 FPU/g waste	29.07 g/L reducing sugar produced after 72 h at 50 °C. 0.42 g/g ethanol produced by co-culture of *Saccharomyces cerevisiae* and *Pichia stipitis*	Xin et al. (2010)
Citrus peel waste	Indigenously from *Aspergillus niger*	30 IU g^{-1}_{Drm} cellulase, processing at 116 °C for 10 min	11.18 mg/ L reducing sugar. 30.7 g/ L ethanol and (339–356 mL/gVS methane)	Patsalou et al. (2019)
Corn stover	Commercial acidic cellulase	Steam-exploded 20 FPU/g dry stover	103 g/L reducing sugar	Lu et al. (2010)
Sugarcane bagasse	*Trichoderma reesei* and *Aspergillus niger*	2.0 IU/g cellulases	0.5 g reducing sugar obtained per dry substrate	Rabelo et al. (2008)
Wastewater sludge	Indigenously from *Trichoderma harzianum*	Bubble column bioreactor and membrane reactor for a system with 30 kDa membrane	73.5% cellulase recovery and 81.37% reduction in chemical oxygen demand	Libardi et al. (2019)
Rice husk	Celluclast	Lime pretreated biomass, 48 FPU/g	0.2 g/g reducing sugar	Saha and Cotta (2008)
Textile residues	Indigenously from *Aspergillus niger* CKB	Alkali pretreated biomass, 0.43 ± 0.01 FPU g enzyme loading	70.2% reducing sugar recovered	Hu et al. (2018)
Sorghum waste	Spezyme-*CP* and Novozyme	10% pretreated (by ammonia) fibres were hydrolysed using 60 FPU Spezyme-CP and 64 CBU Novozyme 188/g glucan	84% digested for a pretreated sample and 38% cellulose digested for untreated biomass 0.24 g ethanol per g dry biomass was obtained for the pretreated sample	Salvi et al. 2010

6.4.3 Challenges of Cellulase-Based Biorefinery

Driving down the cost of enzyme production poses the main challenge for agro-industrial biorefineries. Mass bio-prospecting programme for the discovery of efficient cellulase enzyme synthesising microbes can make the production economical in the long run (Jayasekara and Ratnayake 2019). Integrated processing techniques would also be helpful in improving cellulase production and ethanol productivity in a simplified manner (Kuhad et al. 2016). Instead of single enzymes, concoctions and cellulolytic enzyme cocktails should be explored for their applications in hydrolysis (Victoria et al. 2017). In-house enzyme production is an economical option to produce ethanol for biorefineries (Cunha et al. 2017). This would ensure waste to wealth conversion in a sustainable manner.

6.5 Role of Cellulase in Value-Added Product Formation

Lignocellulosic biomass can be transformed into value-added chemicals through various existing chemical, thermochemical, and biological routes. However, the biological method of lignocellulosic biomass conversion using enzymes is a feasible and environment-friendly, and sustainable process. Many bacterial and fungal species have the ability to breakdown the lignocellulosic biomass into simple sugars such as glucose and xylose by secreting enzymes (cellulase and hemicellulase), which can further be utilised to produce several value-added products like acids (lactic acid, citric acids, succinic acid, gluconic acids), butanol, xylitol, microbial polysaccharides, and other fine chemicals (Ning et al. 2021). In combination with other enzymes (utilised pectinase and xylanase), cellulase improves the hydrolysis efficiency and reduces the overall cost associated with the process (Bhardwaj and Verma, 2021). Some of the important value-added products derived from lignocellulosic biomass are mentioned in Table 6.4.

6.5.1 Lactic Acid

Lactic acid is used as a green solvent and building block for polylactic acid (PLA), a bio-degradable plastic alternative to petroleum-based plastic. Lactic acid can be produced from simple carbohydrates derived from the hydrolysis of agricultural lignocellulosic biomass. However, these recalcitrant lignocellulosic materials should be pretreated first to ease the cellulosic hydrolysis process governed by the cellulase enzymes. Various pretreatment such as physical (milling, grinding, shredding), chemical (acidic, alkali, ionic liquids), and thermal pretreatments can enhance the cellulosic hydrolysis process based on the nature of the lignocellulosic biomass. Yadav et al. (2021) inspected the role of imidazolium ionic liquid in the pretreatment

Table 6.4 List of some value-added chemicals produced from lignocellulosic biomass

Product	Substrate used	Microorganism	Concentration (g/L)	Yield	Reference
Lactic acid	Rice straw	*L. plantarum* SKL-22	36.75	–	Yadav et al. (2021)
Citric acid	Corn stover biomass	*Aspergillus niger* SIIM M288	136.3	74.9% of cellulose	Hou and Bao (2018)
Succinic acid	Fruit and Vegetable waste	*Yarrowia lipolytica*	43.1	0.46 gg^{-1}	Li et al. (2018)
Butyric acid	Paper mill sludge	*Clostridium tyrobutyricum*	7.0	–	Liu et al. (2018)
Gluconic acid	Microcrystalline cellulose	–	9.60	0.27 gg^{-1}	Ruales-Salcedo et al. (2020)
PHA	Brewer’s spent grain	*Burkholderia cepacia*	–	9.0 ± 0.44 mg PHA/g dry BSG	Llimós et al. (2020).

of rice straw and further saccharified with commercial cellulase enzyme for lactic acid production by *Lactobacillus plantarum* SKL-22 strain. They observed that the media optimisation using response surface methodology could enhance the lactic acid yield by 1.11%, with a final yield of 36.75% using rice straw in a single pot bioprocess.

In many bioprocesses, utilised cellulase enzymes are used repeatedly to saccharify lignocellulosic biomass to simple carbohydrates, which could be further used to produce value-added chemicals. This could be a holistic approach for upcoming biorefineries in the future and sustainable product formation. Grewal et al. (2018) explored the one-pot bioprocess of lactic acid production from ionic pretreated lignocellulosic waste saccharified by nano-immobilised cellulase enzyme. In this process, the simultaneous saccharification and co-fermentation (SSCF) process was performed by *Lactobacillus brevis*, which provided a lactic acid yield of 0.22, 0.52, and 0.49 g/g with sugars derived from ionic pretreated cottonseed cake, sugarcane bagasse, and wheat straw, respectively. To reduce a large amount of cellulase requirement in lignocellulosic-based lactic acid production, Chen et al. (2020) established the integration of fed-batch simultaneous saccharification process with membrane separation, in which residual cellulase enzyme present in the waste stream and solid-residue of corn stover were recycled and reused for successive fermentation. Around six rounds of operation were carried out, which increased the lactic acid yield (0.389 g/g) by 1.2 times higher than the conventional process and reduced the cellulase consumption, wastewater discharge and nutrient consumption by 47%, 73.7% and 86.1%, respectively.

In addition to lignocellulosic biomass, other agricultural wastes such as food waste and fungal biomass have also been utilised to produce lactic acid with the assistance of the cellulase enzyme. Ma et al. (2021) studied the co-fermentation of spent mushroom substance (SMS) and food waste to produce lactic acid. They reported that 92.62% of sugar was released from pretreated SMS by *Aspergillus niger* cellulase, which could increase the lactic acid concentration by 22.97% (Ma et al. 2021).

In another study, Abdel Rahman et al. (2019) isolated a thermo-alkaliphilic lactic acid bacterium, *Enterococcus faecium* FW26, which could produce lactic acid from mixed food waste and banana peels with a lactic acid yield of 84% g/g-consumed sugars. *Enterococcus faecium* FW26 secreted the amylase and cellulase enzyme and grew on a mixed substrate of food waste and banana peels without any treatment. In addition, the isolated strain was able to survive and facilitate fermentation under the stress of thermo-alkaline conditions, which might reduce the chances of contamination.

6.5.2 Succinic Acid

Succinic acid is a dicarboxylic acid and an intermediate compound of the tricarboxylic acid (TCA) cycle. It has various uses in the food industry as a flavouring agent, acidulant, and antimicrobial agent and is also used as a solvent additive, surfactant, foaming agent, detergent extender, coating resins, and ion chelator (Kumar et al. 2019). Glucose, maltose fructose, sucrose, and glycerol have been the most frequently used carbon sources for succinic acid production by fermentation using strains of bacteria such as *Anaerobiospirillum succiniciproducens*, *Actinobacillus succinogenes*, *Mannheimia succiniciproducens,* and recombinant *Escherichia coli* (Karthik and Rathinamoorthy 2017). However, utilisation of cheaper carbon sources such as lignocellulosic biomass with the help of cellulase enzyme could improve the overall process economics. Some microorganisms can utilise partially hydrolysed cellulose and produce valuable products. Jiang et al. (2013) performed the incomplete hydrolysis of cellulose for succinic acid production by *Actinobacillus succinogens*. A succinic acid concentration of 20 g/L with a yield of 64.7% was achieved from 18 g/L of cellobiose and 17 g/L of other sugars obtained from sugarcane bagasse hydrolysate. In another study, Li et al. (2018) hydrolysed the fruit and vegetable waste with a cocktail of enzymes (2% glucoamylase, 2% hemicellulase, 1% cellulase, and 0.25% pectinase) and obtained the final glucose titre of 56. 7 g L^{-1} and a yield of 0.46 g g^{-1}. The obtained hydrolysate was further utilised to produce succinic acid by *Y. lipolytica* PSA02004 with a titre and yield of 43.1 g L^{-1} and 0.46 g g^{-1}, respectively. They improved succinic acid productivity (0.69 g L^{-1} h^{-1}) and concentration (140.6 g L^{-1}) using in situ fibrous bed bioreactor and fed-batch fermentation. Therefore, cellulase facilitates the utilisation of agro-waste for the production of value-added chemicals through biochemical pathways with good efficiency and cost-effectiveness.

6.5.3 Gluconic Acid

Gluconic acid, a non-toxic, non-corrosive, and weak organic acid is industrially produced through the fermentation of glucose by *A. niger* or *Gluconobacter suboxydans*. The gluconic acid production was also reported by various strains of *Pseudomonas*, *Acetobacter*, and *Zymomonas*. Gluconic acid has many applications in the food industry as a flavouring agent, in dietary supplements as different salts (sodium, calcium, and iron gluconate), and in the pharmaceutical and textile industries. Microbial fermentation is the most suitable and chosen method for gluconic acid production due to being less expensive and more efficient than other methods. Large-scale gluconic acid production is mainly affected by three crucial factors: cheaper substrate, oxygen concentration, and pH. Using the lignocellulosic biomass can solve the problem of the cheaper substrate if a cost-effective enzyme production method is developed. Yu et al. (2021) explored the co-immobilisation of multienzymes (cellulase, catalase, and glucose oxidase) on reversibly soluble polymer Eudragit L-100 in a cascade reaction for the direct transformation of corn straw to gluconic acid. The gluconic acid yield was achieved at 0.28 mg/mg, and the rate of conversion of cellulose in corn straw to gluconic acid was obtained at 61.41%. Similarly, Zhou et al. (2019) studied an integrated process of co-production of gluconic acid with xylooligosaccharides from sugarcane bagasse. After the xylooligosaccharides production from the prehydrolysis, 88.6% of cellulose was converted into simple sugars in fed-batch enzymatic hydrolysis using cellulase (C2730, Celluclast®). The gluconic acid yield of 96.3% was produced by fermentation of sugars using *Gluconobacter oxydans* ATCC 621H. Therefore, approximately 105 g of xylooligosaccharides and 340 g of gluconic acid were co-produced in the integrated process from 1 kg of dried sugarcane bagasse (Zhou and Xu 2019).

6.5.4 *Citric Acid*

Citric acid is another crucial organic acid used as a preservative and acidulant in the food industries and also used as a starting material in the pharmaceutical and cosmetic industries. It is mainly produced through microbial fermentation from using carbohydrates (mainly starch) or agro-industrial waste. However, due to the restricted supply of food starch, potential alternative sources like lignocellulosic biomass are also being explored to meet future demand. Cellulase plays a vital role in the conversion of these recalcitrant compounds into simple sugars. Citric acid is produced on large scale through fermentation by *A. niger* due to its high citric acid productivity and tolerance to low pH. It is mainly produced through submerged fermentation. However, many researchers have explored the use of agro-residues and lignocellulosic biomass as the starting material for citric acid production. Hou et al. (2018) studied the simultaneous saccharification and fermentation (SmSF) of dilute acid-pretreated corn stover for citric acid production by *A. niger*. In SmSF, pretreated corn stover was hydrolysed by cellulase enzyme, Cellic CTec 2.0, from Novozymes. The highest citric acid concentration (136.3 g/L) was obtained with an overall yield of 74.9% of cellulose in the aerobic SmSF process. This study compared the citric acid production from SmSF with separate hydrolysis and fermentation (SHF) and concluded that the cellulosic citric acid production by SmSF could be highly comparable to starch-based citric acid production.

6.5.5 *Microbial Polymers*

6.5.5.1 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA) are the most potential, degradable, and environment-friendly substitute for petrochemical-based plastics. The main constraint that prevents PHA from commercialisation is the cost of production. Therefore, researchers are focusing on cheap substrates for sustainable PHA production. In this regard, lignocellulosic waste can be used as a possible substrate as it is cheap, readily available, and most importantly, it does not compete with the food requirements of humans. Nowadays, a wide range of lignocellulosic waste generated from industries, forestry, agriculture, marine biomass, etc. has gained great consideration for PHA production (Obruca et al. 2015).

PHA production using lignocellulosic biomass at the industrial level includes mainly three steps, especially pretreatment, enzymatic/acidic hydrolysis, and fermentation. Many pretreatment techniques are used before the enzymatic hydrolysis of cellulose which includes physical processes for size reduction, chemical treatment (with hydrogen peroxide, acid, alkali, or sodium chlorite) for delignification, physicochemical processes (like a steam explosion, ammonia fibre expansion, etc.) or a biological pretreatment using microbial enzymes. Further, enzymatic hydrolysis is performed for the degradation of complex carbohydrates into simple sugar, which serves as a carbon source for microbes in the successive fermentation step. Later fermentation is carried out using PHA-producing microbes (e.g., *Bacillus sonorensis, Halomonas hydrothermalis, Pseudomonas putida, Bacillus cereus*, etc.) and PHA is recovered. It was suggested that the average sugar and PHA yields were higher in the case of enzymatic hydrolysis as compared to acid-based hydrolysis and cellulase plays an important role in enzymatic hydrolysis (Al-Battashi et al. 2019).

Production of PHA without pretreatment steps is also used to decrease the cost of the process. Israni and Shivakumar (2020) used cellulase, lipase, and amylase positive *Bacillus megaterium* strain Ti3 for the production of PHA without pretreatment step. PHA was produced using 16 different lignocellulosic substrates by submerged fermentation at 30 °C for 48 h at 120 rpm. They demonstrated that ragi husk and sesame oil cake have the most influential factors on the basis of Taguchi orthogonal array. Similarly, Heng et al. (2017) demonstrated a three-step process for PHA production using *Burkholderia cepacia* USM, *Cupriavidus necator* NSDG-GG, and a genetically modified strain of *Cupriavidus necator* H16. They used rice husk as raw material and performed alkaline pretreatment followed by enzymatic hydrolysis and fermentation. For enzymatic hydrolysis, they used a cellulase-based enzymes Celluclast 1.5 L and Novozyme-188 at 50 °C 160 rpm for 72 h. They obtained the highest sugar yield of 87% after enzymatic hydrolysis and obtained 7.8 g/L of dry cell weight and 50% PHA content using a 5 L fermentor.

Llimós et al. (2020) performed two-stage valorisation using Brewer's spent grain (BSG) as a lignocellulosic substrate for PHA production. First, they produced lignocellulolytic enzymes by three fungal strains (*Trichoderma reesei*, *Aspergillus niger* and *Thermoascus aurantiacus*) through SSF of dried BSG. Then these enzyme were used for the hydrolysis of BSG and production of PHA. The PHA was produced by fermentation of sugar rich BSG hydrolysate at 30 °C and 120 rpm using *Burkholderia cepaci*a and *Cupriavidus necator*. *C. necator* cells were harvested after 48 h and *B. cepacia* cells were harvested after 72 h. The maximum yield of PHA they obtained was 9.0 ± 0.44 mg PHA/g dry BSG, and the result showed that BSG could be utilised as a suitable raw material for the production of value-added products (Llimós et al. 2020).

PHA is a potential material with a broad range of uses which includes its use as bioplastics, drug carrier, and synthesis precursor, packaging materials, biofuels, implant materials, cosmetic ingredients, disposal cups, and bottles, etc. Presently, PHA is not well commercialised as compared to fuel-based plastics and products. The main hurdles are the high cost of production and relatively poor characteristics. Still, researchers are searching for the solution to this problem as PHA offers an eco-friendly and sustainable alternative to petrochemical-based products and has a promising future (Wang and Chen 2017).

6.5.5.2 Nanocellulose

In the last few years, remarkable development has been noticed in nanotechnology, especially in nanocellulose production. Nanocellulose produced from lignocellulosic waste is a potential alternative for obtaining various value-added products that can meet the demand of the market and environmental issues (Jaiswal et al. 2021). According to various literature, lignocellulosic biomass like rice husks, wheat straw, cotton, sugarcane bagasse, flax fibres, wood bark, softwood pulp, corncob, hardwood, etc. can be used for the production of nanocellulose (Michelin et al. 2020).

Currently, acid hydrolysis is the most regular method for the production of nanocellulose. However, nowadays production of nanocellulose using enzymatic hydrolysis is gaining significant importance as toxic residues are not produced. Moreover, during enzymatic hydrolysis, mild conditions are used, which makes it a low energy-intensive process (Karim et al. 2017). The process of nanocellulose production by enzymatic hydrolysis contains several steps. The first or pretreatment step consists of delignification where lignin is removed using various mechanical processes (chipping and milling) and chemical processes (alkaline pretreatment and bleaching pretreatment). The second step is enzymatic hydrolysis which is generally carried out at the pH range from 4 to 7 and temperature range from 45 to 50 °C. The last step includes homogenisation, where the enzymatically treated material is homogenised by washing or mechanical homogenisation (Ribeiro et al. 2019).

de Aguiar et al. performed enzymatic hydrolysis of sugarcane bagasse and straw at 50 °C and 200 rpm. The cellulose nanocrystals (CNC) produced by both bagasse and straw showed a crystallinity index of approximately 70% and high thermal stability (de Aguiar et al. 2020). In another study, Yarbrough et al. (2017) reported that the synergistic effect of two or more enzymes shows a better effect than an individual enzyme. They demonstrated that the *Caldicellulosiruptor bescii* with multifunctional enzymes is better in cellulose and nanocellulose production than the classical system of “free enzyme” produced by *Trichoderma reesei*.

The application of only one technique is not as effective as the combination of two or more techniques. For example., high-quality nanocellulose is produced using a coupled ball milling process and enzymatic hydrolysis, which can be further improved when combined with any other technique (Teo and Wahab 2020). Zhang et al. (2020) designed a new approach using poplar wood as lignocellulosic biomass to produce nanocellulose. They used steam explosion and delignification for the pretreatment of poplar wood. Further, the enzymatic hydrolysis was performed using cellulase enzyme followed by ultrasonic treatment. The optimum condition determined by them for enzymatic hydrolysis was 200 U/g at 50°C for 12h, giving approximately 13.2% yield of nanocellulose. The crystallinity of the composite produced in this study was 61.98% which was higher than the crystallinity of poplar cellulose, and the structure of the composite was not damaged during the preparation steps. Squinca et al. (2020) performed enzymatic hydrolysis using a cellulolytic enzyme complex with the high specific activity of endoglucanase produced by the fungus *Aspergillus niger*. They pretreated the cellulose pulp of eucalyptus by ball milling, followed by enzymatic hydrolysis and sonication, which yielded 24.6% of cellulose nanocrystals (CNCs) by the enzymatic hydrolysis of 96 h. CNC's length, diameter, and crystallinity were 294.0 nm, 24.0 nm, and 78.3%, respectively.

Apart from nanocellulose isolation, cellulases can also be used for the pretreatment of lignocellulosic waste and other pretreatment techniques. Zeng et al. (2020) used endocellulase for enzymatic pretreatment of the bleached pulp of softwood kraft before wet ball milling. Further, they used mechanical grinding for the production of cellulose nanofibrils (CNF).

Nanocelluloses have a wide range of applications in different industries it can be used as material for food packaging in food industries, electronic displays in the electronic industry, paper and coating material in the paper and pulp industry, a supporting material in the medical and tissue industry, absorbent material in the water treatment industry, etc. (Zaki et al. 2021). The enzymatic hydrolysis is a time-consuming process for the production of nanocellulose. However, it has gained the attention of companies and researchers as it has shown better saccharification efficiency and penetration. Despite the challenges, enzymatic hydrolysis for nanocellulose production has great potential because of its unique characteristic and eco-friendly nature (Teo and Wahab 2020).

6.6 Role of Cellulase in a Circular Economy

The application of cellulases for the efficient valorisation of agro-industrial waste has tremendous potential for generating biofuels and biochemicals with low carbon and water footprints that can be recycled back to the earth within the scope of a circular economy (Astolfi et al. 2019). This conceptualises the 3Rs of a circular economic system. In situ resource utilisation, enzyme recycling, and sequential zero-waste biorefinery approaches are commercially viable solutions for sustainable development.

6.6.1 Valorisation via Carbon-Neutral Technologies

Fossil-based resources are now being replaced by alternative renewable feedstocks for the synthesis of cellulases and bioconversion for biofuels, commercially important chemicals, and biomaterials to envisage a decarbonisation system (Adsul et al. 2020). Millions of tonnes of lignocellulosic waste are generated per annum globally. Their valorisation in an economical and eco-friendly manner forms the core of a bio-based circular economy (Sheldon 2020). In the current scenario, the entire focus lies in the thoughtful conversion of the so-called wastes into valuable products such as reducing sugars, biochemicals, and biofuels, primarily regulated by cellulase enzymes.

6.6.2 Life Cycle Assessment of Cellulase-Based Biorefinery

The environmental and economic effects of a process analysed by the life cycle assessment (LCA) technique include all inputs and outputs of material and energy flow at different life cycle stages (Russell et al. 2005; Kumar and Verma 2021c). LCA technology in the assessment of cellulase production and utilisation is limited by rigid system boundaries, data accuracy and availability, variations in statistical techniques, variations in product utility, its selectivity, and local environmental conditions (Borrion et al. 2012). System boundaries of the cellulase manufacturing process focus on the greenhouse gas emissions related to the cradle-to-gate activities for cellulase production (Fig. 6.3). In a case study on cellulase production from corn feedstock, Aspen-Plus and GREET 1.8c.25 were used for estimation of emissions and financial matrices. 258 g CO_2 eq. L^{-1} of bioethanol was estimated for onsite production and 403 g CO_2 eq. L^{-1} for offsite production. The cost estimation was made on the basis of bioethanol plant size and cellulase loading. An additional input like return on investment is used for offsite data. The final production cost was 0.46 USD gal^{-1} of bioethanol for cellulase for on-location production (Hong et al. 2013).

Cellulase production from coffee husk was assessed on the basis of data taken from EcoInvent v3.4 (SimaPro v8.5 software) database. The results showed that the downstream process significantly impacts the environment and economic value (Catalán et al. 2019). In another study, an integrated ethanol production process using spruce loggings was compared to an offsite production scenario. The greenhouse gas emissions were lower in the onsite process as compared with that of the offsite process. The ethanol selling rate was 0.568 euro per litre for the integrated cases and 0.581 euro per litre for the off-location case (Olofsson et al. 2017).

6.6.3 Increased Circularity via Onsite Application

The change in the substrate from enzyme production to hydrolysis and offsite enzyme application often alters the enzymatic efficiency. Researchers have found that the microorganisms grown on various carbon sources under different physicochemical environments produce different isoforms of cellulase, which show behavioural diversity while interacting with the same substrate (Siqueira et al.

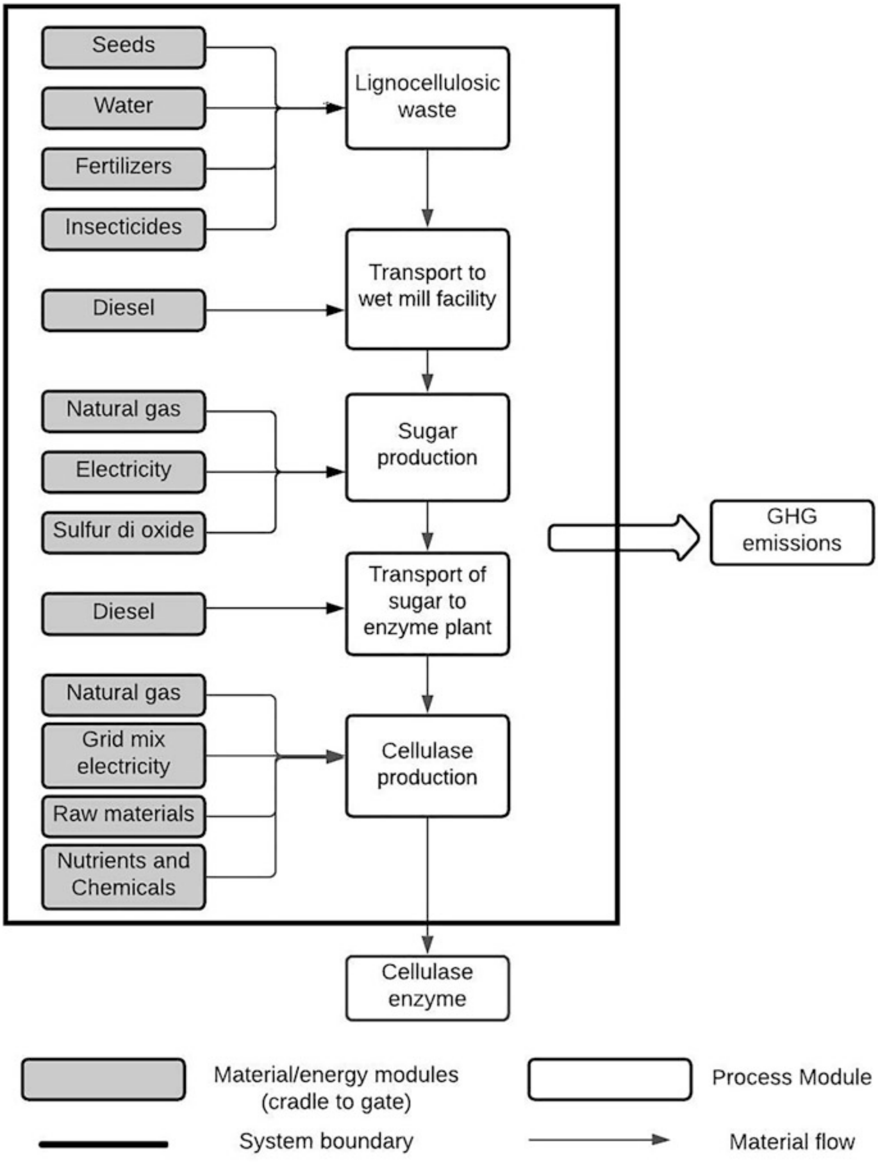

Fig. 6.3 System boundaries for cellulase application in biorefinery

2020; Zhao et al. 2018). The techno-economic feasibility was assessed for the onsite and offsite cellulase synthesis and utilisation for ethanol generation using corn stover as feedstock. The biomass channelised from the ethanol production stream improved the value of onsite cellulase production (Kazi et al. 2010). The comparative routes for onsite, offsite, and integrated biorefinery are shown in Fig. 6.4.

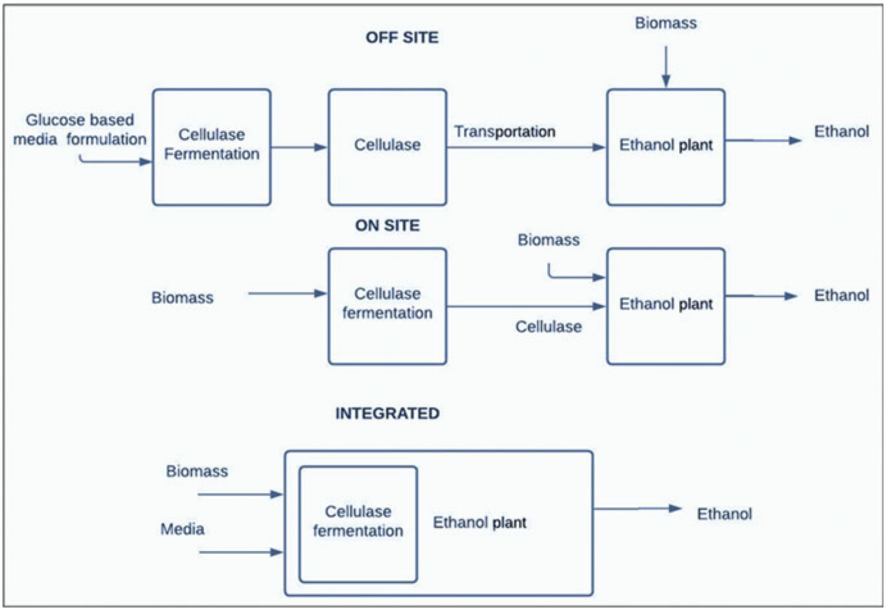

Fig. 6.4 Comparison of offsite, onsite, and integrated biorefinery

Novozyme introduced Cellic CTec3 based on the economic bioconversion of pretreated lignocellulosic substrate (Sun et al. 2015). The techno-economic model for the corn-based ethanol industry revealed the significance of onsite cellulase production for biorefinery. The use of pure glucose, priced $580/t as a carbon source, covers over 50% of cellulases' production cost, which is commercially not feasible (Humbird et al. 2011). Working on a low-cost substrate, non-sophisticated downstream processes, less storage, and transport makes onsite enzyme production eco-friendly and contributes to a circular economy.

6.6.4 Challenges and Perspectives

The circular economic sustainability is challenged by two major threats. These are the lignocellulose biorefinery supply chain and the resistant structure of lignin, which restrict the access of cellulose by cellulases (Garlapati et al. 2020). The last issue significantly affects the cellulose crystallinity and the efficacy of cellulases. Low-cost, energy-efficient pretreatment strategies can resolve the lignin problem. The energy recovery process needs to be accompanied by soil replenishment (Battaglia et al. 2021). In this context, it is essential to re-conceptualise the enzymatic reduction of agricultural lignocellulosic waste for obtaining value-added products through sustainable utilisations. The integrated lignocellulosic biorefinery leads to the circular economic framework through the endorsement of niche markets, consumer-oriented value generation, and reduction of transportation through supply chain modifications of lignocellulosic feedstocks (Sarsaiya et al. 2019). The ultimate benefits would be a cleaner environment and economic profitability.

6.7 Conclusion

Cellulase plays an important role as it is responsible for the hydrolysis of cellulose into simple sugars, which can be further used as a carbon source for microbial fermentation. Nowadays, valorisation of lignocellulosic waste has gained the attention of researchers, and efforts are made to make this process industrially and commercially feasible as it is eco-friendly and has great potential and a promising future. Cellulases are produced at a large scale using cellulolytic microorganisms either by SSF or SmF. However, industries prefer SmF over SSF as it is easy to monitor and operate. The commonly reported microorganisms for cellulase production are *T. reesei, S. argenteolus, B. licheniformis, Candida cylindracea, Aspergillus oryzae,* etc. Cellulases are a powerful tool for the bioconversion of agro-residues, food, paper, and textile industry waste into beneficial products like surfactants, furfurals, aromatics, phenols, ethanol, butanol, lactic acid, succinic acid, gluconic acid, citric acid, etc. Recently, the use of cellulase is extensively explored for the production of microbial polymers such as nanocellulose, polyhydroxyalkanoates, polyhydroxy butyrate, xanthan, and pullan.

The major challenge behind the use of lignocellulosic biomass in biorefineries is the cost of production. Many strategies have been developed to reduce the cost such as the utilisation of immobilisation techniques for the reusability of cellulase, onsite cellulase production, use of enzyme cocktails instead of a single enzyme, combination of two or more techniques for the pretreatment step, and use of low-cost substrates. Despite many challenges, great progress has been made in the direction of using lignocellulosic biomass as it is a potential renewable alternative for fossil-based resources. Also, advanced tools such as techno-economical analysis (TEA) and life cycle assessment analysis (LCA) provide insight into actual benefits associated with enzyme-based conversion processes over chemical processes. These assessments promise an optimised circular economy approach for maximum fulfilment of societal needs and minimum impact on the environment and ecosystem.

Competing Interests There is no conflict of interest.

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Chapter 7
Technical Criteria for Converting Biomass to High Liquid Bio-Oil Yields

Naval Koralkar and Praveen Kumar Ghodke

Abstract Rising energy demands and depletion of fossil fuels have led the research community to investigate alternative fuel sources. Green and renewable biofuels have evolved to substitute for a non-renewable energy source. Biomass can be utilized as a raw material for producing low-carbon fuels. Although biomass-based fuels can replace fossil fuels, direct use is limited due to the low quality of the fuels and expensive process costs. An unrivaled solution to this problem is an integrated biorefinery concept involving generating hydrocarbon-grade fuels and valuable chemicals from pyrolysis-derived bio-oil. The chapter examines recent breakthroughs in bio-oil up-gradation processes and moisture removal techniques and bio-oil recovery of valuable compounds. One of the widely used and well-developed techniques for producing bio-oil is the fast pyrolysis of biomass. The catalytic cracking process has been identified as a viable technology for converting bio-crude to liquid fuel in bio-oil upgrading. The chapter examines recent trends and advances in the fast pyrolysis technique to improve overall profitability of the process. Critical analysis of the potential and existing techniques and necessary future steps are essential for adopting these methods industrially and in a feasible manner.

Keywords Pyrolysis · Upgraded fuel · Green fuel · Biomass

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
https://doi.org/10.1007/978-981-19-4312-6_7

Abbreviations

CHNS-O	Analyzer
CO_2	Carbon dioxide
DSC	Differential scanning calorimetry
SEM	Scanning electron microscope; Py-GC/MS- Pyrolysis-gas chromatography/mass spectrometry
FTIR	Fourier transforms infrared spectroscopic analyzer
NMR	Nuclear magnetic resonance spectroscopy
NO_x	Nitrogen oxides
SO_2	Sulfur dioxide (SO_2)
TGA	Thermogravimetric analysis analyzer
XRD	X-ray diffraction analyzer

7.1 Introduction

Biomass is a promising eco-friendly alternative renewable energy source in today's energy landscape. The present global energy supply is primarily dependent on fossil fuels such as oil, natural gas, and coal, with limited reservoirs (Smith et al. 2018; Goswami et al. 2021a). Thus, it has become necessary to evaluate an alternative long-term energy source that can meet the demands of the growing global population and the increasing per capita energy consumption. Also, the evidence of increasing global warming due to greenhouse emissions has raised concern for most developed and developing countries. All these concerns have increased the importance of research for fossil-free alternatives.

Biomass is a renewable energy source that is widely available (Sarkar and Praveen 2017; Agrawal and Verma 2022). Due to environmental concerns and rising energy demands worldwide. Biomass utilization in mainstream energy usage attracts much attention. Biomass is composed of hemicellulose (20–35 wt.%), cellulose (30–50 wt.%), and lignin (15–35 wt.%) (Cheng et al. 2016; Kumar et al. 2020). Apart from carbon-based components, biomass also contains a small amount of nitrogen, sulfur, and inorganic composition ash. As a result, when compared to conventional fossil fuels, biofuel burning produces fewer toxic gas pollutants such as nitrogen oxides (NO_x), sulfur dioxide (SO_2), and soot. Furthermore, biomass fuel combustion can produce zero or negative carbon dioxide (CO_2). emissions since CO_2 generated from bio-oil combustion can be recycled back into the plant through photosynthesis (Debalina et al. 2017; Goswami et al. 2020a, 2021b).

Different routes are available by which biomass can be converted into biofuel. These include thermal, biological, and physical processes. Among the different available processes, pyrolysis has emerged as a promising technology for producing liquid fuel products due to its storage, transport, and versatile applications such as combustion engines, boilers, and turbines. Managing solid biomass and waste is a complex and cost-intensive task that encourages pyrolysis research. However, it is still in its early stages of development and faces various technological and economic challenges to compete with existing fossil fuel-based technologies (Tang et al. 2020; Goswami et al. 2020b). An extensive investigation of the production of bio-liquids and other products using different biomass species has been carried out in the past.

The quality bio-oil production from different biomass is challenging and requires the application of advanced technologies such as catalytic pyrolysis. Thermochemical conversion techniques can efficiently and economically transform biomass into energy-rich compounds used in various applications (Mandapati and Ghodke 2021). Different routes are available for converting biomass into usable fuel. These technologies include thermochemical conversion of biomass via combustion, pyrolysis, and gasification. The disadvantage of the gasification process is that the produced synthesis gas needs to be utilized at the place of production as it becomes economically inviable or costly for storage and transportation through pipelines (Mandapati and Ghodke 2020).

The chapter discusses the different routes of pyrolysis and its technical specifications and the advances in the pyrolysis technology used for biomass conversion. The chapter covers a detailed description of the pyrolysis technique, its technical specifications, and the technology involved. Pyrolysis has emerged as an essential technology in turning biomass into solid, liquid, and gaseous fuels. A yield of around 60–65% bio-oil production has been reported in literature through the pyrolysis process utilizing a fluidized bed reactor.

7.2 Pyrolysis

Pyrolysis is the process in which both thermal and chemicals effects the conversion of organic materials in an oxygen-depleted atmosphere such as nitrogen. It is an endothermic reaction (Basile et al. 2015). The term pyrolysis was derived from two Greek words: pyro, which means fire, and lysis, which denotes degradation into essential components. During pyrolysis, components of biomass begin to decompose at 350 °C–550 °C due to rapid heating and progress to 700 °C–800 °C, resulting in the generation of a variety of products such as liquids, solids, and gases (Das et al. 2015). Biochar and bio-oil are the solid carbon-rich product and the volatile fraction of pyrolysis that is partly condensed to a liquid fraction product, respectively. The pyrolysis process produces hydrogen, carbon dioxide, methane, and carbon monoxide, among other gases (Moorthy Rajendran et al. 2020). These products are intriguing because they could be used as alternative energy sources. Pyrolysis has emerged as a critical method in converting biomass into solid, liquid, and gaseous fuels. The literature reported a yield of roughly 60–65 wt.% bio-oil generation through the fast pyrolysis process using a catalytic fluidized bed reactor. However, pyrolysis-produced bio-oil has numerous unfavorable qualities that directly use bio-oil as an engine fuel challenge. Thus, bio-oil is enhanced by the hydrotreating or catalytic cracking process to make it compatible as a drop-in fuel molecule (Shihadeh and Hochgreb 2000).

7.2.1 Different Routes of Pyrolysis

Pyrolysis processes may work efficiently under a variety of conditions. Thus, there are various pyrolysis processes, such as fast, slow, flash, intermediate, ultra-flash, vacuum, and catalytic pyrolysis (Wei et al. 2021). Especially, vacuum pyrolysis occurs at negative or low pressures, whereas another pyrolysis of biomass occurs at atmospheric or controlled positive pressure (Chintala et al. 2018). The ideal primary fuel for the pyrolysis process is waste material, such as forest debris, woody biomass, and agricultural waste. Longer residence times and high temperatures increase biomass conversion to gas. Pyrolysis conditions can be varied depending on the desired product type (Bridgwater 2012; Dhyani and Bhaskar 2017). Several different modes of biomass pyrolysis depending on conditions, such as heating rate and residence time of biomass, are being actively developed (Hu and Gholizadeh 2019; Kiliç et al. 2014; Adelawon et al. 2021; Dhyani and Bhaskar 2017). However, the most generally used classification of pyrolysis processes is slow, fast, and flash pyrolysis.

7.2.1.1 Slow Pyrolysis

Slow pyrolysis or conventional pyrolysis has been used to convert diverse feedstock biomasses into charcoal or biochar at slow heating rates for a lengthy residence time, around 5–30 min, and at temperatures below 300 °C since the beginning of the pyrolysis process (Ahmad et al. 2014). Feedstocks, wheat straw, pinewood, dried algae, and green garbage were employed. This procedure can also make bio-oil or liquid fuels. Slow pyrolysis is typically carried out at atmospheric pressure. The heat required for the process is provided from an external source, usually produced from partial combustion or combustion of the produced gases or biomass feedstock (Ghodke and Mandapati 2019). The process results in the development of vapor phase components that continue to react, resulting in the formation of charcoal and other liquid products. Slow pyrolysis produces roughly 35 wt.% biochar, 30 wt.% bio-oil, and 35 wt.% gaseous products. However, due to technological restrictions such as cracking of the primary product due to high residence time (Demirbaş 2005; Jahirul et al. 2012), bio-oil is produced through slow pyrolysis is not suitable for direct use as a liquid fuel.

7.2.1.2 Intermediate Pyrolysis

Intermediate pyrolysis is a type of pyrolysis that occurs halfway between fast and slow pyrolysis. It has an excellent product distribution and may be employed in the coproduction of biochar, bio-oil, and gas (Meng et al. 2019). Intermediate pyrolysis is flexible to diverse materials and has good product distribution. The product is a two-phase separable bio-oil, high quality, and biochar compared to other pyrolysis categories (Bridgwater 2003; Kumar et al. 2021). Researchers have also discovered that it has easily distinguishable liquid phases, with the organic phase exhibiting biodiesel-like qualities. The organic phase can be combined with up to 50 wt.% (Xiong et al. 2009). Its aqueous phase, which comprises C2–C6 sugars, hydroxy acids, oligomers, and water-soluble phenols, is also effective in manufacturing biogas and ethanol. The process has the advantage of requiring less bio-oil upgrading than quick pyrolysis oil and allowing for complete usage of all products. Because of the extensive interaction with steam, intermediate pyrolysis can treat high moisture content feedstock, and when this happens, the biochar takes on the properties of activated carbon (Gao et al. 2020).

7.2.1.3 Fast Pyrolysis

Fast pyrolysis is the rapid thermal degradation of biomass at more excellent heating rates, such as 1000 °C min^{-1}. Fast pyrolysis has a short vapor residence time of less than 2 s (Bhattacharya et al. 2009). Bio-oil is the main product of rapid pyrolysis. However, the amount of product created depends on the feedstock composition, ranging from 60% to 75% oily products, and 10–20 wt.% gaseous (CH_4, CO, CO_2, H_2, and light hydrocarbons), and 15–30 wt.% solids products. Rapid heating and quenching produce bio-oil, and the high reaction rates reduce char formation and favor the generation of either gas or liquid products. Higher temperatures, heating rate, short vapor residence time, rapid cooling of vapors for high bio-oil production, and precise control of reaction temperature are the essential characteristics of the fast pyrolysis process (Collins and Ghodke 2018). Furthermore, a fast pyrolysis process requires reducing the water content of feedstock and reducing the particle size to less than 2 mm. In fast pyrolysis, rapid and systematic separation of solids (char), rapid gas removal, and cooling pyrolysis product favor the formation of bio-oil or liquid products (Ponnam et al. 2021). This liquid product can be readily and inexpensively transported and stored, decoupling solid biomass handling from consumption (Malode et al. 2021).

7.2.1.4 Flash Pyrolysis

Ultra-fast pyrolysis is another name for the process. Flash pyrolysis is a thermal breakdown of large molecules into smaller molecules that occurs in an inert

Table 7.1 Summary of the classification of the pyrolysis method

Method	Residence time	Temperature (°C)	Heating rate (°C/s)	Major bioproducts
Slow pyrolysis	5–30 min	400–500	10	Char, bio-oil (tar), gases
Ultra-fast/flash pyrolysis	<0.5 s	750–1000	>500	Bio-oil and gases
Fast pyrolysis	0.5–2 s	500–650	100	Char, good bio-oil, gases

atmosphere such as nitrogen at a rapid heating rate of 1000–10,000 °C per minute and residence time is less than 1 s. An excellent feed particle size (2 mm) is required to perform this procedure at an optimal rate. The degradation of biomass produces a significant amount of coke and aerosol vapors during flash pyrolysis. A dark brown liquid (bio-oil) is produced after cooling and condensation, with a heating value of half diesel. In contrast to prior procedures, this is a novel technology with well-regulated parameters that generate high liquid yields (Gandidi et al. 2018). Flash pyrolysis in fluidized bed reactors can produce a high liquid output of up to 75 wt.% bio-oil (Gómez et al. 2018). However, there are certain drawbacks to flash pyrolysis, such as low thermal stability, particles in the oil, and the oil's corrosiveness, which results in the generation of oils with high viscosity, density, low calorific value, and carbon residues (Huang et al. 2013). Table 7.1 depicts the summary of different pyrolysis technologies available and can be used to produce different bioproducts.

7.2.2 *Technical Specifications: Pretreatment, Characterization, and Mechanism*

7.2.2.1 Pretreatment

Pretreatment is an important stage in the biochemical and thermochemical conversion of biomass. It requires structural changes to overcome biomass's recalcitrance. Improved biomass features are necessary to increase the biomass's energy use efficiency (Wu et al. 2021; Bhardwaj and Verma 2021). The primary treatment process requires the heating of lignocellulosic biomass (cellulose, hemicellulose, and lignin) to convert into polymeric and aromatic constituents. In contrast, the heterogeneity in atoms and inorganic oxides element components of biomass act as catalysts, resulting in the generation of a biofuel product with different carbon structures and significant reforms that increase yield during the bioconversion process (Kim 2018; Kumar and Verma 2020a, b). Current pretreatment systems have two significant challenges: high costs and obtaining a processed product with essential component degradation. Past and ongoing research and development efforts have failed to meet these problems. Pretreatment treatments must be tailored to the type of biomass and how it will be utilized in bioconversion and biorefinery

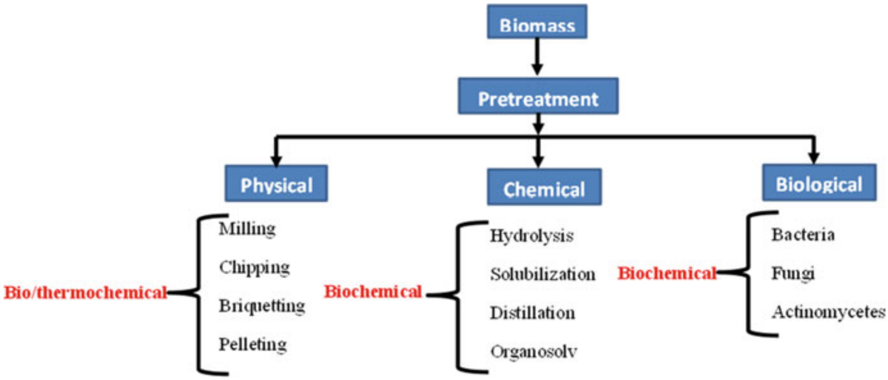

Fig. 7.1 Different pretreatments methods for biomass

processes. Figure 7.1 depicts the types and pretreatment processes required for biomass conversion technologies (physical, chemical, and biological). The subsections that follow go into the various types of preprocessing in greater depth.

Physical Treatment

Physical pretreatment of biomass aims to improve the surface area and pore size by reducing particle size through mechanical comminution. Physical processing reduces cellulose crystallinity and polymerization degree in lignocellulosic materials. Prior to both enzymatic and thermochemical biofuel production, this step is required. However, little is known about how physical preprocessing procedures function, particularly how biomass chemical content or bond structure are affected. The lignocellulosic biomass application determines the physical pretreatment technology to be undergone or utilized. Biochemical conversion of lignocellulosic biomass, for example, should undergo a reduction in particle size through milling, shredders, and cutters in order to improve biochemical digestibility. Milling of biomass is necessary before use in the thermochemical conversion process to reduce the size of biomass. Palletization, densification, and heat treatment torrefaction are the prior pretreatment process of thermochemical conversion technologies. Prior size reduction is essential in both biochemical and thermochemical conversion pathways to minimize mass and heat transfer constraints. Another physical pretreatment approach is chipping when employing waste wood biomass or agricultural residue as a feedstock in thermochemical conversion technologies. The thermochemical conversion technologies require feedstock with 50 mm or less diameter, feedstock with 50 mm or less is required.

Torrefaction, densification, and pelletization are examples of physical pretreatment procedures for biomass (Reckamp et al. 2014; Chi et al. 2021). These preprocessing procedures use heat to cause changes in the biomass, resulting in improved biomass characteristics. The physical pretreatment procedure has the drawback of removing the lignin content from lignocellulosic biomass materials, rendering the cellulose composition inaccessible. Another disadvantage is the high heat-energy requirements for pretreatment and not economically feasible commercial use. According to research findings, the process of removing lignin from lignocellulosic biomass materials can be led to an increase in the energy demand. Thus, thermal pretreatment treatment method could influence the total energy effectiveness/cost of a biorefinery process (Lewandowski et al. 2020).

Chemical Pretreatment

In chemical pretreatment methods, organic or inorganic chemical compounds are used to disrupt the chemical bonds of lignocellulosic biomass by interacting with the intrapolymer and interpolymer bond connections of the organic components are known as chemical pretreatment of biomass. Biomass, particularly lignocellulosic components, is considered recalcitrant because it is resistant to chemical breakdown. The structural diversity and complexity of biomass such as its crystalline nature and the degree of lignification, all contribute to its recalcitrance (Mai et al. 2014; Bhardwaj et al. 2020). In preliminary chemical pretreatment method, the chemical structural recalcitrance of the lignocellulosic nature of biomass is disrupted, resulting in cellulose crystalline phase reduction along with lignin breakdown. Before biochemical conversion, chemical preprocessing of biomass, particularly lignocellulosic biomass, is frequently employed to extract the biopolymeric constituents of the feedstock. Acids, alkalis, organic solvents, and ionic liquids are some of the chemicals that have been used to pretreat biomass chemically and have had a significant impact on its structure (Basak et al. 2020).

Biological Pretreatment

Biological preprocessing/pretreatment of the organic composition of biomass is always related to the activity of synthetic enzymes or enzymes produced from an organism that potentially can break down or depolymerize the hemicellulose, cellulose, and lignin components of biomass. The biological pretreatment method has many benefits over other physical/chemical pretreatment processes are particularly uses energy consumption and produces little or no toxic chemical. Biological pretreatment produces a high yield of required/valuable products. But major disadvantages are substrate and process reactions are very sensitive (Cao et al. 2013; Agrawal and Verma 2020). However, its significant drawbacks in biological pretreatment are that the method chosen was too slow and requires meticulous management of fungus growth conditions and the enormous amount of area required to complete the process (Kan et al. 2016). It was observed from the literature that the residence period or time required for biological activities in pretreatment was between 11 and 15 days. Moreover, because microorganisms consume the organic components of biomass, biological pretreatment operations have technological challenges and are seen as less economically appealing than other pretreatments (Robak and Balcerek 2018; Chintala et al. 2019). In the biological pretreatment of biomass, different fungi such as white-rot, brown-rot, and soft-rot fungi are used widely. Apart from fungi, actinomycetes and bacteria are used to pretreat the biomass. The fungi are notably applied to eliminate hemicellulose and lignin composition of biomass while causing minor damage to cellulose biomass. White-rot and brown-rot fungi have a wide degradation mechanism for gaining access and destroying the lignocellulosic biomass such as waste wood and agricultural residue. Their extraordinarily powerful metabolism or mechanism has been successfully employed in industrial commercial operations. White-rot and brown-rot fungi have been demonstrated to brighten hardwood kraft pulp, potentially lowering bleaching chemical costs and reducing the environmental effect of paper manufacturing operations (Phillips et al. 2017; Ghodke and Mandapati 2017; Bhardwaj et al. 2021).

Even though various preprocessing methods have been studied and more are in progress, evaluating pretreatment technologies is challenging. The primary reasons for challenging pretreatment techniques are upstream and downstream processing of biomass. Additionally, capital expenditure, waste treatment systems, and complicated chemical recycling (Shen 2015; Ghodke 2021).

The thermochemical conversion uses a variety of feedstocks, including wood waste, energy crops such as sweet sorghum, short rotation forestry, and agricultural residues. The critical technical parameters for thermochemical processing suitability are ash, moisture, and other physical characteristics. The two most essential economic elements are cost, including collecting, production, transportation, and availability. Competing uses such as pulp and combustion, board manufacture, recycling, and material recovery, rather than energy recovery, are also a concern.

7.2.3 Feedstock Drying

In most circumstances, pyrolysis necessitates a feedstock with a moisture level of less than 15 wt.% although there is a trade-off between moisture levels and conversion production efficiency. The moisture content essential for conversion differentiates between conversion plants. When biomass is delivered, the moisture level will be 50–60 wt.% range (Praveen et al. 2015).

Passive drying during summer storage can cut this by 30%. The moisture content of a silo can be reduced to as low as 12 wt.% with active silo drying. Drying can be done in various ways, including near-ambient solar drying, waste heat flows, and specially constructed dryers that operate at the location. Commercial dryers come in various shapes and sizes, but rotary kilns and shallow fluidized bed dryers are the most prevalent.

7.2.3.1 Characteristics of Feedstocks

Table 7.2 summarizes the essential physical features of biomass. Notably, the relatively low bulk density, high moisture content, and wide particle size range are notable traits.

7.2.3.2 Biomass Characterization

Biomass heterogeneity is still a natural feature. The biomass quality determines the possibility and viability of extracting products from it. The two conversion techniques such as biochemical and thermochemical conversions are primarily applied to recover commercially valuable products from biomass. The attributes of biomass also affect the conversion route chosen. Thus, characterization is required to effectively understand the underlying physicochemical properties of biomass. Depending on its characteristics, one can evaluate its suitability for bioconversion. The physical properties are critical for the efficient use of biomass in biofuel production methods (Dutta et al. 2015).

However, the fundamental organic components of biomass influence its features, which vary based on the source of biomass composition, biomass source, species, soil condition, climatic condition, and other factors. Depending on the end-use of biomass, proximate and final analyses are routinely determined and reported using a variety of analytical processes. The data is crucial for assessing biomass's diverse application potential, notably its energy production potential when third-generation biomass is used as a biofuel in thermochemical conversion operations (Sharma et al. 2020). Among the characteristics analysis techniques used in physicochemical characterization investigations involving organic composition are the following:

- XRD- X-ray diffraction analyzer
- FTIR- Fourier transforms infrared spectroscopic analyzer
- TGA- Thermogravimetric analysis analyzer
- NMR- Nuclear magnetic resonance spectroscopy
- CHNS-O analyzer
- DSC-Differential scanning calorimetry
- SEM-Scanning electron microscope
- Py-GC/MS- Pyrolysis-gas chromatography/mass spectrometry

Table 7.2 Essential physical features of biomass

Feedstocks	Forestry residues	Poplar tree	Waste wood	MSW	Straw
Moisture content (%)	20–50	10–40	5–30	20–30	5–25
Density (kg/m^3)	350	450	350	450	250

7.3 Future Prospects

The replacement of fossil fuels with biomass resources on a wide scale is a hot topic not just for energy generation but also for manufacturing chemicals, bioproducts, and materials. Moreover, and since biomass is extensively accessible, commercial products/biofuels from lignocellulosic materials can be produced in most geographic locations. Biomass characteristics determine the economic viability and effectiveness of the value-added product production, the primary treatment method used. However, biomass heterogeneity, high capital and operating costs associated with bioconversion, and the mechanisms underlying the biomass conversion process are all issues with using biomass for heat, chemical products, and fuels generation. As a result, efforts should be made at all levels to build more user-friendly and cost-effective technologies to stimulate the broad use of biomass and attract investment in this field. Furthermore, because ideal biomass pretreatment conditions are rarely published, nothing is known about them.

7.4 Summary

Biomass preprocessing and characterization is critical in determining that biomass materials are utilized effectively in biofuel production. An improved comprehension is required of the origins of biomass and its recalcitrance. Further the impact of primary treatment to maximize the different biofuel production pathways. It requires an assessment of biomass using cutting-edge analytical techniques capable of providing knowledge. Based on the features of the pyrolysis products, criteria for assessing the feasibility of biomass for a pyrolysis conversion process to produce solid, liquid, and gaseous fuels are developed. The applicability of various biomass for pyrolytic transformation is investigated using this technique. It is discovered that various biomass is suitable for diverse applications such as combustion of fuel, liquefaction, gasification, and the production of char adsorbents depending on the chemical composition of biomass.

Conflict of Interest All the authors declare that they have no competing interests.

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Chapter 8
Biomass Pyrolysis and its Multiple Applications

Shivangi Pathak, Anil Kumar Sakhiya, and Priyanka Kaushal

Abstract In the twenty-first century, the growing demands of a modernized and growing population have led to the rapid expansion of agricultural and industrial sectors around the world. This expansion leads to produce a massive amount of biomass materials and various organic and inorganic pollutants. Biochar has promising potential in tackling such global concerns and can serve as a low-cost adsorbent for accomplishing sustainable development goals (SDGs). Biochar, a carbon-rich solid product, can be obtained by slow pyrolysis of biomass under an oxygen-limited atmosphere. Produced biochar can be used as an adsorbent to remove organic and in-organic pollutants from groundwater and industrial wastewater. However, biochar has a lower surface area and limited surface functional groups, which results in lower adsorption capacity. Hence, activation is required. Apart from adsorbent biochar is also used as a soil additive to sequestrate carbon to mitigate climate change and enhance its fertility and water retention capability hence lowering the frequency of irrigation in the field. In this chapter, the fundamentals of slow pyrolysis, its process parameters, product yield distribution, and various application of biochar will be discussed in detail.

Keywords Pyrolysis · Biochar · Activation · Adsorbent · Soil amendment

Abbreviations

ACB	*Araucaria columnaris* bark
BSA	Biochar soil amendment
CEC	Cation exchange capacity
DCFC	Direct carbon fuel cell
DFT	Density functional theory

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
https://doi.org/10.1007/978-981-19-4312-6_8

dw	dry weight basis
fw	Fresh weight basis
GRSB	Granular Rice Straw biochar
JPB	Jujube pit biochar
MB	Methylene blue
MBC	Magnetically modified rice husk biochar
OM	Organic matter
PAHs	Polycyclic aromatic hydrocarbons
PBB	Powdered bamboo biochar
PRSB	Powdered Rice Straw biochar
RE	Removal efficiency
RO	Reverse osmosis
SA	Sulfonamides
SPS	Spent *P. ostreatus* substrate
SSS	Spent shiitake substrate
TC	Tetracycline
TPH	Total petroleum hydrocarbons
WHC	Water holding capacity

8.1 Introduction

The world's food, water, and energy demand are increasing rapidly as the global population increases. Large amounts of biomass waste (crop residues, forest residues, organic) are generated daily due to high living standards and economic development. Globally, the approximately 140 Gigaton biomass waste generated and managing such a huge amount of waste is a great challenge. Most of the biomass waste is discarded and open burning in the field, which negatively impacts the environment (Tripathi et al. 2019; Goswami et al. 2020a; Agrawal and Verma 2022). The conversion of biomass waste to biochar through pyrolysis is a feasible solution and creates value addition in society.

Biochar is a "carbon-rich solid product" formed by pyrolyzing biomass at high temperatures (300–600 °C) in an inert environment (Sakhiya et al. 2020; Goswami et al. 2020b, 2021). Biochar can be used for a variety of energy and environmental purposes, including clean solid fuel, fuel cells, catalysts, soil amendments, composting additives, groundwater and wastewater purification, air purification, carbon sequestration, hydrogen storage, etc. (Dillon and Heben 2001; Sakhiya et al. 2021a, b; Baghel et al. 2022). The pyrolysis product yield distribution is influenced by a variety of factors, including pyrolysis temperature, heating rate, residence time, and particle size. Presently, biochar is used as an economical adsorbent for removing organic (PAHs, pesticides, dye, surfactants, pharmaceutical) and inorganic (heavy metals such as As, Ni, Pb, Zn, and Cu) contaminants from groundwater and wastewater (Cha et al. 2016). Moreover, biochar has a good water holding capacity and nutrient retention capacity, improving agriculture sustainability and product yield. Biochar produced from agricultural waste and used in the soil can return the nutrients and develop a circular economy (Zhou et al. 2021).

However, there are certain limitations to using biochar as an adsorbent and other environmental application due to cation exchange capacity, limited surface functional groups, low porosity, and surface area. The activation is a process that improves the physicochemical properties of biochar using different activation agents and heating in the temperature range of 500–900 °C. According to the report "Global Activated Carbon Market Forecast & Opportunities 2017," demand for activated carbon is predicted to grow at a rate of higher than 10% per year for the next half-decade, reaching a market value of 3 billion dollars by 2025 (Park et al. 2013). The sustainable utilization of biomass to produce bioenergy and activated charcoal would not only assist in alleviating the environmental issues due to coal mining but also cuts down the price of producing efficient sorbents.

This chapter describes the biochar production through the pyrolysis, types of pyrolysis process, parameters influencing the pyrolysis. Activation of biochar via physical and chemical activation is also discussed in detail. Additionally, biochar has a wide array of uses such as solid fuel, catalyst, the adsorbent in water purification, additives in composting, and hydrogen storage were described in detail.

8.2 Pyrolysis

Pyrolysis is a thermochemical conversion technology in which biomass is thermally heated at elevated temperature and produced three different products: biochar, bio-oil, and gas. In addition to its efficacy, pyrolysis produces multi-products compared to other thermochemical conversion processes (Tripathi et al. 2016).

8.2.1 Physics of Pyrolysis

In the pyrolysis process, organic material is thermally decomposed under an oxygen-limited environment. It's a particularly complicated process with a lot of various reactions in the reacting zone. Biomass contains three major constitutes, including hemicellulose, cellulose, and lignin (Kumar and Verma 2021a, b). The heating of biomass, biomolecules of hemicellulose, and cellulose break down in the form of volatile matter and produce bio-oil by condensation. The heating of biomass under an oxygen-limited environment allows a rise in temperature greater than its limit thermal stability and produces a more stable solid product called biochar.

The pyrolysis process mainly consists of two steps, i.e., primary and secondary pyrolysis. During primary pyrolysis, heat causes biomass molecules to cleave and devolatilize, forming numerous functional groups such as hydroxyl, carboxyl, and carbonyl. The process of devolatilization takes place by dehydration of biomass, followed by decarboxylation and dehydrogenation. Secondary pyrolysis begins after the completion of the primary pyrolysis process in which heavy hydrocarbon breakdown into condensable (bio-oil) and non-condensable gases (CO, CO_2, H_2, and CH_4). The cracking of heavy hydrocarbon compounds can be presented by the following reaction (Tripathi et al. 2016):

$$\begin{aligned}(C_6H_6O_6)_n \rightarrow\ & (H_2 + CO + CH_4 + \ldots + C_5H_{12}) \\ & + (H_2O + CH_3OH + CH_3COOH + \ldots) + C \end{aligned} \tag{8.1}$$

Where the initial part of the products in the reaction represents the non-condensable gases, the later part represents the mixture of condensable gases, and the last part is the char yield.

8.2.2 Types of the Pyrolysis Process

The process parameters help in classifying the pyrolysis process into four categories: slow, fast, flash, and intermediate. Each type has its own set of benefits and drawbacks. The basic characteristics of each type of pyrolysis and the operating parameters are discussed in the following section. Table 8.1 represents the types of pyrolysis processes based on operating conditions.

8.2.2.1 Slow Pyrolysis

It is a conventional method and widely used to produce charcoal in history and characterized by a modest heating rate and a prolonged residence time. It is generally carried out from 400–600 °C to get higher biochar yield with a small amount of

Table 8.1 Operating conditions of types of pyrolysis processes

Operation condition	Slow	Fast	Flash	Intermediate
Temperature (°C)	550–950	850–1200	900–1300	400–650
Heating rate (°C/min)	0.1–1.0	10–200	>1000	1.0–10
Residence time (min)	300–500	0.5–10	<1	0.5–20
Particle size (mm)	5–50	<1	<0.5	1–5
Reference	Bahng et al. (2009), Demirbaş and Arin (2002)	Bahng et al. (2009), Demirbaş and Arin (2002)	Bahng et al. (2009), Demirbaş and Arin (2002)	Zhang et al. (2010), Kebelmann et al. (2013)

condensed bio-oil and non-condensable gases such as CO_2, CO, CH_4, and hydrocarbons (C_1–C_2) (Al Arni 2018). The slow pyrolysis is characterized by longer residence time (>60 min), lower heating rate (0.1–1.0 °C/min), a particle size of 5–50 mm, and performed at ambient pressure. The longer residence time provides an appropriate atmosphere and time to complete the secondary pyrolysis reaction. Additionally, a longer vapor residence time permits vapors formed during the secondary reaction to be evacuated, which results in higher biochar yield. Biomass with larger particle size, high lignin content, and lower ash content is best suited for the production of biochar (Demirbas 2004).

8.2.2.2 Fast Pyrolysis

Fast pyrolysis is mainly used to produce the bio-oil (yield >50%). Biochar and gas yields are overshadowed by bio-oil production. It has a high heating rate as compared to slow pyrolysis. Fast pyrolysis is mainly performed within the temperature of 850–1200 °C, with a heating rate ranging from 10–200 °C/min, the particle size of <1 mm, and residence time less than 10 s (Greenhalf et al. 2013). Different reactor designs are utilized for fast pyrolysis, including rotating cones, bubbling fluidized beds, circulating beds, ablative reactors, etc. The main objective of fast pyrolysis is to raise the temperature of the feedstock to a point where thermal cracking takes place while decreasing the exposure time, which promotes biochar formation. The bio-oil produced through fast pyrolysis is corrosive because of its low pH value. Moreover, bio-oil contains a high amount of water fraction, which lowers its heating value. As a result, before using bio-oil, it must be upgraded (Xu and Etcheverry 2008).

8.2.2.3 Flash Pyrolysis

Flash or rapid pyrolysis is a modified variant of fast pyrolysis and is characterized by a high heating rate, shorter residence time, and extreme reaction temperature. Rapid is carried out at a heating rate > 1000 °C/min and a short residence time of 1–10 s (Demirbaş and Arin 2002). Such an extreme condition is arranged in flash pyrolysis to obtain a high bio-oil yield with lower water fraction and biomass conversion efficiency of up to 70%. In flash pyrolysis, heat and mass transfer processes, chemical-reactions kinetics, and biomass transition phase behavior play a significant role in product yield distribution.

The most difficult aspect of implementing this pyrolysis on a large scale is designing a reactor in which the input biomass can be heated at an extreme heating rate for a short residence time. A major issue is the stability and quality of the bio-oil as it is heavily influenced by the presence of biochar in the product. The presence of biochar in bio-oil leads to catalysis of the polymerization reaction, resulting in a higher viscosity of bio-oil (Tripathi et al. 2016).

8.2.2.4 Intermediate Pyrolysis

Intermediate pyrolysis is usually carried out to achieve the balance of product yield between fast pyrolysis and slow pyrolysis. It has a decent product yield distribution, and therefore, it can be used in the co-production of biochar, bio-oil, and gas. The process conditions of this pyrolysis lie between fast and slow pyrolysis. The pyrolysis is carried out in the temperature range of 400–650 °C with a heating rate of 1–10 °C/min and residence time of 15–20 min. The advantages of the conditions in intermediate pyrolysis are that they prevent the development of high molecular tar compounds with excellent quality bio-oil and generate dry biochar which is appropriate for soil amendment and bio-energy production (Kazawadi et al. 2021). The bio-oil produced through this pyrolysis can be used in engines and boilers directly because it does not have a high amount of reactive tar. This is a significant benefit of intermediate pyrolysis over fast pyrolysis (Mahmood et al. 2013).

8.3 Effects of Process Parameters

8.3.1 Process Temperature

Temperature is the most crucial element to control the reaction process, and it directly influences the biochar physicochemical properties and yield. The increment in pyrolysis temperature negatively impacts biochar yield because it facilitates the thermal cracking of heavy hydrocarbon compounds leading to a rise in liquid and gas yield (Ahmad et al. 2014). Biochar developed in the primary pyrolysis reaction takes part in the secondary reactions and enhances the bio-oil and gas yield at the expense of biochar. Hence, a lower pyrolysis temperature is suitable for higher biochar yield. Moreover, biochar has a graphene-like structure when it is produced above the 300 °C temperature. Graphene holds a flat-polyaromatic and monolayer carbon structure, high electrical conductivity, and stability index. Additionally, biochar produced at higher temperatures enhances physicochemical properties such as pH, surface functional groups, and BET surface area (Wu et al. 2012). Biochar produced at higher temperatures can also have high aromaticity and recalcitrant carbon fractions in biochar which improves the stability.

8.3.2 Heating Rate

In biomass pyrolysis, the heating rate affects the product yield and physicochemical properties to some extent. The pyrolysis process is mainly classified based on the heating rates. The process with a lower heating rate can minimize the secondary pyrolysis reaction and hence, it confirms that no thermal cracking arises, resulting in higher biochar yield. In contrast, higher heating rates promote the fragmentation of feedstock and increased the bio-oil and gas yield by restraining the possibility of char formation. The higher heating rate also enhances the depolymerization of lignocellulosic constitutes into primary volatile compounds, which reduces the biochar yield (Tripathi et al. 2016).

Dilek Angin performed the pyrolysis of safflower seed press cake for biochar production by altering the heating rates (10–50 °C/min) (Angin 2013). It was noticed that as the heating rate increased the biochar yield decreased. Similar results were observed in the literature (Ateş et al. 2004; Huang et al. 2017; Zhao et al. 2018).

8.3.3 Residence Time

Residence time has a crucial part in the minimalism of the product yield distribution, product properties, reaction mechanism, and product quality. The biochar production can be carried out at various scales of residence time ranging from a few minutes to several days. Low temperature combined with longer solid residence time is suitable for char production (Cha et al. 2016). The higher residence time supports the depolymerization of lignocellulose composition by offering them adequate reaction time. In contrast, lower residence time in the pyrolysis process minimizes the depolymerization reaction, which results in lower biochar yield (Park et al. 2008).

Residence time influences the char yield and the characteristic and physicochemical properties of biochar such as surface area, micro- and macropore development, and surface functional groups. It was reported that longer residence time in biomass pyrolysis enlarged the pore size (Tay et al. 2009). Pyrolysis temperature, particle size, heating rate, and other variables frequently govern the influence of holding time. This makes it difficult to give a clear picture of the role of residence time in the development of biochar.

8.3.4 Particle Size

Particle size is also one of the essential factors in the biomass pyrolysis process as it controls the reaction rate and heat transfer rate. The heat transfer rate of input feedstock decreased from the outer surface to the core of the material by increasing the particle size, which results in higher biochar yield (Encinar et al. 2000). Additionally, when particle size increases, the vapor released during the thermal breakdown of feedstock travels a greater distance inside the biochar layer, which triggers secondary pyrolysis and leads to an increase in biochar yield.

Hong et al. (2020) studied the effect of temperature and particle size on biochar yield using various agriculture waste. The biochar yield increased with increasing the particle size (Hong et al. 2020). Demirbas also studied the influence of particle size on char yield through pyrolysis of agriculture waste. It was observed that char yield improved from 19.3 to 35.7% for olive husk and 5.6–16.7% for corncob by rising particle size from 0.5 mm to 2.2 mm (Ayhan Demirbas 2004).

8.4 Biochar Activation

8.4.1 Physical Activation

In physical activation, biochar produced thermochemically from biomass is processed with activities such as steam, CO_2, and air/O_2 at a temperature range of 700–900 °C. Biochar porosity increases in an oxidizing environment at an elevated temperature during the activation process. Activation increases the surface area and pore size of biochar, which improves its adsorption capacities. The oxidizing agents penetrate the biochar layers and gasify the carbon atoms, causing inaccessible pores to expand and open (Tripathi et al. 2016). Unlike air activation, steam and carbon interaction is an endothermic reaction, making it simpler to curb (Demirbas 2009). Activation temperature, degree of activation, biomass feedstock, and activation agent strongly controls the physical activation. The generic trendline observed in the literature shows that with the increase in process temperature and time, porosity growth enhances. Moreover, this leads to an increase in pore size distribution. Using the air as an activation agent shifts the reaction in the direction of combustion because of the synergistic effect of air and biochar. An unregulated reaction can cause excessive ash formation and reduced activated carbon yield (Dawson et al. 2003). Tables 8.2 and 8.3 show the mechanism of the activation agent and the effect of the activation agent on biochar BET surface area, respectively.

Table 8.2 The mechanism of activation agent on biochar BET surface area

Oxidizing agent	Chemical reaction	Process	Reference
Steam/ H_2O	$C + H_2O \rightarrow C(O) + H_2$ $2C + H_2 \rightarrow 2C(H)$	Chemisorption	Ahmed et al. (2016), Belaroui et al. (2014), Mendoza-Carrasco et al. (2016)
CO_2	$C + CO_2 \rightarrow C(O) + CO$ $C(O) \rightarrow CO$ $C + CO_2 \rightarrow 2CO$	Carbon gasification by carbon dioxide	Aworn et al. (2008), Betancur et al. (2009)
Air/O_2	$C + O_2 \rightarrow CO_2$	Carbon gasification by oxygen	Jung et al. (2015), Singh et al. (2008), Xiao and Pignatello (2016)

Table 8.3 Effect of activation agent on the BET surface area of biochar

Feedstock	Activation agent	Activation temperature (°C)	Activation time (h)	BET surface area (m^2/g)	Reference
White wood (Spruce)	Steam	750	2.46	643	Azargohar and Dalai (2008)
Populus nigra wood	Steam	800	1	322	Shim et al. (2015)
Mixed hardwood	CO_2	800	–	730	Contescu et al. (2018)
Rice husk	Steam	700	0.75	236.7	Mayakaduwa et al. (2017)
Aspen wood	CO_2	800	3.6	910	Veksha et al. (2015)
Poplar	Air	250	0.5	570	Suliman et al. (2016)
Waste rubber	Air	500	0.08	240	Heras et al. (2009)

8.4.2 Chemical Activation

The biochar is doped with a different chemical agent to improve its physicochemical characteristics including surface area, pore volume, and fictional groups. The functional group, pore volume, and the surface area are changed according to the impregnation ratio of the chemical agent. The chemical activation of biochar generally takes place within the temperature range of 450–900 °C (Sakhiya et al. 2020). This activation of biochar is broadly classified into two categories: single-step and multi-step chemical activation. The chemical activation mechanism is ambiguous in comparison to physical activation. Mainly two types of reactions occurred on the surface of biochar during the chemical activation, i.e., dehydration and oxidation. The main advantages of chemical activation in comparison to physical activation are greater carbon yield, low temperature, high surface area, high porosity structure, and high efficiency. Chemical agents also suppress tar formation. Over a long period, the corrosion and depletion of equipment take place due to the corrosive nature of chemical agents, which is the major limitation of chemical activation. Even at high temperature, the corrosion increases and more rapidly harm the equipment. After chemical completion of activation, washing of biochar is mandatory which makes the process costlier as compared to physical activation.

There are different types of chemical activation methods available in the literature according to the desired application. If oxidation of surface functional group required acidic chemical agents were used (nitric, hydrochloric, phosphoric acids, hydrogen peroxide). Similarly, if basic modification is required NaOH and KOH agents are used for activation. Different modifications of biochar such as sulfonation, amination, and impregnation of various metals ($FeCl_3$, $ZnCl_2$, MgO, CaO, ZnO, etc.) were also used (Sajjadi et al. 2019). Among the above listed chemical agents, the

KOH is more suitable for activation due to lower process temperature, higher surface area (up to 3000 m^2/g), high product yield, and superior microporous structure (Li et al. 2020). The CH_3COOK is a non-toxic chemical agent and can be used for biochar activation. Sakhiya et al. (2021b) studied the comparative study of steam and CH_3COOK-activated biochar for heavy metal adsorption. Results indicated that CH_3COOK-activated biochar had a higher surface area and adsorption capacity in comparison to the steam-activated biochar (Sakhiya et al. 2021b).

8.5 Biochar Applications

Biochar, a low-cost carbonaceous material has a stable carbon matrix capable of retaining materials such as water, air, organic compounds, and metals. Biochar has specific thermal and electrical properties that are still being investigated. With so many different characteristics, biochar is an efficient, eco-friendly, cost-effective alternative with a wide range of applications (Schmidt and Wilson 2014). Figure 8.1 shows the various applications where biochar can be used as a substantial alternative.

8.5.1 Biochar as an Absorbent

Biochar has emerged as a cost-effective alternative to other carbonaceous materials for removing various inorganic and organic pollutants from gaseous, aqueous, and solid phases, including heavy metals, aromatic dyes, polycyclic aromatic hydrocarbons (PAHs), phenols, and antibiotics (Oliveira et al. 2017).

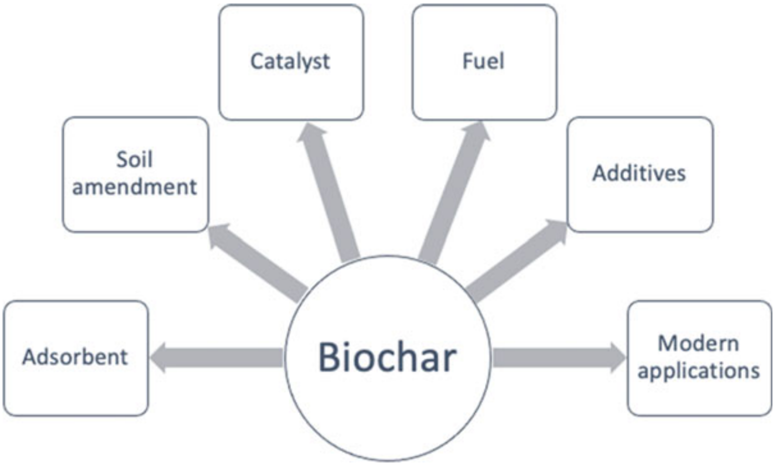

Fig. 8.1 Various applications of biochar

8.5.1.1 Biochar for Wastewater Treatment

Large volumes of wastewater effluent containing hazardous chemicals are generated by industries and are routinely deposited into adjoining environmental water sources, either directly or indirectly. Therefore, effluents must be treated before discharge to remove contaminants in order to safeguard the aquatic ecosystem and human health (Singh et al. 2020a, b). The global population is rising by 80 million citizens each year, causing a need for safe drinking water of around 64 billion cubic meters; the world must focus on creating methods for a safe water supply (Alam et al. 2014).

Some traditional wastewater treatment techniques necessitate the use of dangerous chemicals, which are both expensive and harmful to the environment (Khin et al. 2012). These processes often affect the environment by producing toxic and non-eco-friendly end products with considerable initial and ongoing capital costs (Singh et al. 2020a, b). The most used wastewater treatment processes are adsorption, reverse osmosis (RO), and membrane filtering. These processes have drawbacks such as membrane deformation, high operational costs, complex instrument handling, the development of undesirable sludge, and other disposal issues. As a result, an alternative, improved, substantial, and cost-efficient wastewater treatment technique is required.

Economically and environmentally sustainable wastewater remediation setups are based on biomass's highly efficient and ecologically sustainable materials. Biochar has specific characteristics such as high porosity, large surface area, and holding water for a longer time making it a suitable substitute for wastewater treatment (Yargicoglu et al. 2015). This section of the chapter emphasizes biochar's potential to remove undesired and hazardous species such as organic contaminants and heavy metals from wastewater. Figure 8.2 demonstrates the adsorption mechanism of heavy metals and organic compounds onto biochar's surface.

Biochar for Heavy Metal Removal

Heavy metals in wastewater have the ability to cause damage to the environment. Even at minor concentrations, long-term exposure to heavy metals can cause major health concerns. (Ahmed et al. 2016; Sakhiya et al. 2022). According to recent research, biochar generated from plant wastes and animal manure can effectively absorb heavy metals from waste and drinking water (Dai et al. 2017; Higashikawa et al. 2016; Tan et al. 2016; Zhou et al. 2017).

The functional groups such as OH and −COOH on the surface of biochar show a strong affinity towards heavy metals. The π conjugate aromatic structure of biochar allows it to change negative charge in π-orbital, resulting in losing electrons of a functional group more efficiently, and adsorption becomes more significant (Wang et al. 2018). Samsuri et al. (2014) showed that the polarity index, functional groups

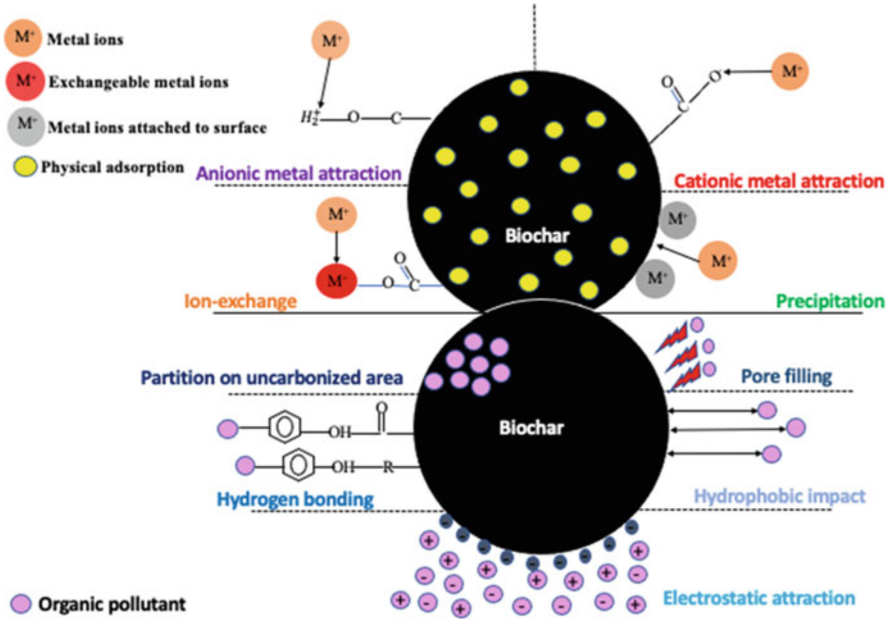

Fig. 8.2 Adsorption mechanism of organic pollutants and heavy metals onto biochar

containing oxygen or O/C molar ratio has an important role in the heavy metal adsorption process (Samsuri et al. 2014).

Arsenic is found in both wastewater and drinking water and is highly toxic. Van Vinh et al. (2015) impregnated $Zn(NO_3)_2$ over biochar, and the results revealed an increase in adsorption capacity of As^{3+} from 5.7 to 7.0 mg/g (Van Vinh et al. 2015). Furthermore, fresh and dehydrated banana peels biochar was used to remove Pb^{2+} from wastewater, removal efficiencies obtained were of 359 mg/g and 193 mg/g, respectively (Zhou et al. 2017). Higashikawa et al. (2016) studied the effect of pyrolysis temperature on Cd^{2+} adsorption using a mixture of biochar derived from rice husk, sugarcane straw, chicken manure, and sawdust. Rising the pyrolysis temperature from 350 to 650 °C increases the percentage of Cd^{2+} removed (Higashikawa et al. 2016).

Removal of Organic Pollutants

Organic contaminants are widespread in wastewater. Dyes, phenols, PAHs, and antibiotics have recently gained high attention due to their complex aromatic structure, high toxicity, and biodegradable resistances in the environment.

Globally, the textile sector is estimated to be worth $1 trillion, accounting for approximately 7% of total global exports and engaging roughly 35 million people (Desore and Narula 2018). The water pollution caused by the textile industry has a significant impact on the environment. According to the literature, biochar application can be an economical and environment-friendly solution to remove dyes from the aqueous solutions with more than 80% efficiency (Srivatsav et al. 2020). Various operational factors (such as temperature, solution's pH, biochar dosage, and concentration of dye) have a critical role in altering the adsorption of dye using biochar (Chu et al. 2020; Mahmoud et al. 2020; Park et al. 2019). Experiments were conducted to determine the threshold pH values, and the findings revealed that biochar could withstand pH levels as low as 2 and as high as 11. Despite this, removal efficiencies were higher than 80% (Srivatsav et al. 2020). Fan et al. (2017) used BC prepared from municipal sludge to extract methylene blue (MB), accurately represented by a pseudo-second-order model, and had a removal efficiency of up to 100% (Fan et al. 2017).

Furthermore, after three cycles, the clearance rate of MB has remained at 60%. The adsorption capacity increased with increasing pH throughout the adsorption phase is attributed to electrostatic interaction. Furthermore, Si–O–Si on BC can offer adsorption sites and interact with MB's functional group containing nitrogen. Moreover, MB can create a hydrogen bond with BC's hydrogen. Kelm et al. (2019) studied the performance of biochar derived from wood residues for adsorption of Indosol Black NF1200 dye and results indicated that at low pH values, biochar could be an efficient adsorbent for azo dyes removal from textile industries (Kelm et al. 2019).

Phenols are being widely used at an industrial scale, which leads to the release of phenolic pollutants in industrial wastewater (Mohammadi et al. 2015). PAHs are also released from various industries and are toxic, carcinogenic, mutagenic, and persistent. Phenols and PAHs have a complex aromatic structure, making them biodegradation resistant (Busca et al. 2008), thus emerging the need to remove these pollutants before moving into the aquatic system. Biochar is used to remove PAHs and phenols from aqueous solutions due to its high adsorptive ability. Various factors such as surface area, adsorbent and adsorbate concentrations, pore-volume, and size affect the adsorption of phenols and PAHs on biochar.

Recently, Chandola et al. (2021) conducted a study for removing phenols from aqueous solutions using biochar produced at different temperatures from *Araucaria columnaris* bark (ACB), 100% phenol removal was achieved with the biochar produced at a temperature of 500 °C (Chandola et al. 2021). A study showed that 57% of PAHs dissolved in sewage sludge can be removed using biochar (Oleszczuk et al. 2012). A review by Lamichhane et al. (2016) stated that more than 98% adsorption capacity could be achieved using biochar as adsorbent for PAHs removal (Lamichhane et al. 2016).

Antibiotic contamination and the emergence of antimicrobial-resistant microorganisms are significant environmental concerns across the world. Given the rising use of antibiotics, reducing their presence in the environment is critical (Krasucka et al. 2021).

Peng et al. (2016) studied the use of biochar for the adsorption of seven antibiotics in an environmental concentration of aqueous solutions. A significant amount of antibiotics were removed, and the adsorption energy increased significantly using the density functional theory (DFT) as the number of rings increased, showing the relevance of π–π interactions in the adsorption process (Peng et al. 2016). Peiris et al. (2017) studied the removal of Sulfonamides (SA) and Tetracycline (TC) using biochar and investigated the adsorption mechanism in detail. Electron donor–acceptor interactions of electron-withdrawing compounds with surface aromatic rings are the most common adsorption mechanism (Peiris et al. 2017). Fan et al. (2017) pyrolyzed rice straw at different temperatures to examine if BC could remove common antibiotics like TC. Due to its wide specific surface area and porosity, BC produced at a higher temperature showed a maximum adsorption capacity of 50.72 mg/g (Fan et al. 2017). Table 8.4 shows literature on biochar applications for removing heavy metals, PAHs, phenols, dyes, antibiotic pollutants.

8.5.1.2 Biochar for Air Purification

When gaseous chemical pollutants are released into the atmosphere, they cause serious human health and environmental threats; hence, we need to prevent their emissions. Fabric filters, electrostatic precipitators, and activated carbon injections are the few techniques used to reduce the emission of toxic gaseous contaminants in the environment (Yang et al. 2018). The high maintenance and installation costs of these techniques limit their application on a large scale. According to recent research, biochar can also remediate gaseous pollutants (Bamdad et al. 2018). Biochar derived from palm kernel, eucalyptus wood, cotton stalk, and pine efficiently removed CO_2 with adsorption capacity ranging from 3.22 mmol/g to 7.32 mmol/g (Chatterjee et al. 2018; Heidari et al. 2014; Nasri et al. 2014; Zhang et al. 2014). Similarly, the H_2S removal efficiency of more than 95% was achieved using biochar derived from various feedstocks (Bhandari et al. 2014; Das et al. 2019; Sun et al. 2017). Alkali medium is favorable for achieving high H_2S adsorption. The interaction with biochar's surface functional groups COOH and OH is responsible for H_2S adsorption (Shang et al. 2013). Table 8.5 shows the various recent studies which used biochar for removing toxic gaseous contaminants removal.

Biochar is also used as an adsorbent for the remediation of pollutants from soil. Since it is a very vast application, it has been reviewed in detail in the next section.

8.5.2 Biochar as a Soil Amendment

Various studies have recommended biochar as an efficient soil additive in agricultural soils. Biochar application improves soil aggregate stability and enhances its capacity to hold water for a more extended period by improving its pore characteristics, surface area, particle, and bulk density. The kind of soil and its texture also plays an important role. Biochar amendment effects are more noticeable in soil having high sand-sized particles than in soil rich in clay (Blanco-Canqui 2017; Kavitha et al. 2018).

Table 8.4 Biochar produced from various feedstocks is used to remove heavy metals and organic pollutants

Biochar feedstock	Pyrolysis temperature (°C)	Pollutants	Residence time (h)	Adsorption temperature (K)	R.E^{a}/Q_{max}^{b}	Reference
Long-root Eichhornia crassipes	500	Pb(II) Zn(II) Cu(II) Cd(II)	4	298	39.09 mg/g 45.40 mg/g 48.20 mg/g 44.04 mg/g	Li et al. (2018)
Spent *P. ostreatus* substrate (SPS), spent **shiitake** substrate (SSS)	700	Pb(II)	2	298 ± 0.5	326 mg/g	Wu et al. (2019)
Sesame straw	700	Cd, Cr, Cu, Pb, Zn	4	298	8 6 mg/g 65 mg/g 55 mg/g 102 mg/g 34 mg/g	Park et al. (2016)
Mixed municipal discarded materials	300	Cu(II)	12	303	4–5 mg/g	Hoslett et al. (2019)
Chicken manure	700	NAP	2	298	84.3%	Liu et al. (2021a, b)
Jujube pit biochar (JPB)	800	Pb(II)	2	298	137.1 mg/g	Gao et al. (2020)
Wheat straw	600	NAP	1	298	69.6 mg/g	Jiang et al. (2014)
Soya bean straw	700	NAP	3	298	25.66 mg/g	Hu et al. (2019)
Magnetically modified rice husk biochar (MBC)	500	PHE	2	298	97.6 mg/g	Wei Guo et al. (2018)
Excess sludge	700	PHE PYR	1.5	298	87.32 mg/g 80.88 mg/g	Guo et al. (2017)
Rice straw	550	Naphthenic acid	2	298	8.6617 mg/g	Singh et al. (2020a, b)

(continued)

Table 8.4 (continued)

Biochar feedstock	Pyrolysis temperature (°C)	Pollutants	Residence time (h)	Adsorption temperature (K)	R.E[a]/Q_{max}[b]	Reference
Pine fruit shell	550	Phenols	1	298	99%	Mohammed et al. (2018)
Pine chips	300	Acetaminophen and naproxen	0.25	298	94.1% and 97.7%	Jung et al. (2015)
Alternanthera philoxeroides	600	Ibuprofen	1	298	97%	Du et al. (2021)
Soybean dreg	600	Methylene blue	1	318	1273.51 mg/g	Ying et al. (2021)
Palm Kernel shell	350	Crystal violet	0.33	298	24.45 mg/g	Kyi et al. (2020)
Poplar wood	750	Trichloroethylene	0.25	298	98%	Puppa et al. (2020)

[a] *R.E* Removal efficiency

[b] Q_{max} Maximum adsorption capacity

Table 8.5 Literature of gaseous pollutants removed by biochar

Feedstock	Preparation mechanism	Pollutant	Removal rate	Reference
Hickory chips	By simply ball milling of pristine biochar with ammonium hydroxide, N-doped biochar was prepared.	CO_2	N-doped biochar resulted in 31.6–55.2% higher adsorption than the corresponding pristine biochar	Xiaoyun Xu et al. (2019)
Waste wood/ brominated flame retarded	Brominated biochar was prepared using one-step pyrolysis at 600 °C and biomass to plastic ratio 1:1 (mass basis)	Elementary mercury	40% removal efficiency was achieved	Xu et al. (2018)
Black spruce and white birch residues	Activated biochar was prepared using KOH, CO_2, and superheated steam	SO_2	The highest adsorption capacity of 76.9 mg/g was obtained using steam-activated white birch biochar.	Braghiroli et al. (2019)
Biomass	Biochar was produced by pyrolysis at 550 °C under an inert (N_2) environment at 12–15 min residence time.	Gaseous ozone	The removal efficiency obtained was 55 ppbv	Zhou et al. (2018)
Neem	Biochar was prepared through a moderate pyrolysis N_2 environment	Toluene	Adsorption capacity obtained was 65.5 mg/g	Kumar et al. (2020a)
Pinecone	Biochar was prepared at 500 °C with 5 °C/min N_2 flow for 90 min Activation was done using hydrogen peroxide impregnation	Formaldehyde	The removal efficiency obtained was 89%	Yi et al. (2018)

Biochar addition to soil affects its physicochemical parameters such as surface area, tensile strength, pH, cation exchange capacity (CEC), and water-holding capacity, which have a direct impact on plant growth (Chan et al. 2008; Lehmann and Rondon 2006; Zong et al. 2014). Various studies showed that biochar addition improves plant growth by facilitating the nitrogen (N), phosphorus (P), and potassium (K) biochemical cycle (Chan et al. 2008; Gul and Whalen 2016) and influencing soil microbial activities. The elements such as carbon (C), hydrogen (H), sodium (Na), calcium (Ca), magnesium (Mg), N, P, and K present in biochar (Zhang et al. 2015) supply nutrients to plants for sustainable growth. Biochar decomposes slowly in soil due to its long residence life of about 3000 years. Yuan and Xu showed that factors such as biochar's alkalinity, functional groups present on its surface, and strong pH buffering capacity help to regulate soil acidity (Yuan and Xu 2011).

Table 8.6 Biochar application as a soil amendment

Biochar feedstock	Contaminant	R.E. (%)	Reference
Rice straw	Cd	87.1	Tang et al. (2020)
Clover	TPH	18.6	Abbaspour et al. (2020)
Rice straw	PAHs	40–58.84	Zhang et al. (2020)
Poplar wood	Cu, Cd, Pb, and Zn	72.8	Chen et al. (2020)
Wheat straw	TPH PAHs	45.83 30.34	Han et al. (2016)
Rice straw	TPH	84.8	Qin et al. (2013)

R.E. Removal efficiency, *TPH* total petroleum hydrocarbons

Biochar amendment improves the nutrient cycle of a plant. A review by Tesfaye et al. (2021) showed a significant impact of biochar soil amendment (BSA) on plant P uptake and soil available P by 55% and 65%, respectively (Tesfaye et al. 2021). Scheifele et al. (2017) reported an increase in nodule dry matter and biological nitrogen fixation (BNF) by 1.8 and 1.2 folds, respectively, in soybean plants with the amendment of maize and wood biochar (Scheifele et al. 2017).

Biochar having a large surface area and pore volume has been an excellent means to remove heavy metals present in polluted soil (Ahmad et al. 2018). The soil amendment using biochar improves soil pore fraction, which provides more space for microorganisms to grow, and N, P, Ca, and K present in biochar provides nutrients for plant growth (Sakhiya et al. 2020). On the other hand, Warnock et al. (2007) examined the effect of BSA on microorganisms present in the soil. BSA results in a reduction in overall microbial biomass (Warnock et al. 2007). Few recent studies of remediations of various contaminants from soil using biochar have been mentioned in Table 8.6.

8.5.3 Biochar as a Catalyst

Biochar having high surface area and specific surface functional groups can be prepared by functionalization or activation. Biochar has plenty of potentials to be utilized as a flexible catalyst or catalytic assist in various chemical processes because of its unique chemical structure. Biochar can be utilized as a catalyst in biogas upgrading, biodiesel production, improved syngas production, biomass conversion to chemicals and biofuels, de-NO_x processes, and microbial fuel cell electrodes (Cao et al. 2017; Lee et al. 2017). The biochar properties are enhanced by activation or functionalization procedure for being used as a catalyst. The biochar's physico-chemical characteristics, mainly its specific surface area, pore-volume, and pore size distribution, can be enhanced to various degrees depending on the activation techniques used (Cao et al. 2017). According to a study by Do Minh et al. (2020), the electrical and chemical configuration of biochar, when correctly controlled, makes it a great photo-, electro-, and chemo-catalyst that might even be used in modern applications. Biochar can be used in combined catalysis with other phases due to its unique characteristics of semiconductivity (Do Minh et al. 2020).

Zhu et al. (2015) prepared chemically and physically activated biochar from rice husk. The evaluation of the biochar characteristics indicated that it could be employed as catalytic support. In methane catalysis, the activated biochar-assisted Ru (Ru/ABC) catalyst excelled or was equivalent to the standard AC-assisted Ru catalyst. Under the optimum reaction conditions, 98% of CH_4 selectivity was achieved and 100% CO conversion (Zhu et al. 2015).

8.5.4 Biochar as an Alternative to Fuel

Biomass has enormous potential as a fuel source and a source of both thermal and electrical energy. Because of the limited reserves of conventional energy resources, lignocellulosic biomass is becoming the central focus of the modern period, which does not need any energy storage systems (Kumar et al. 2020b, c). Biochar is typically high in carbon and can be a pollution-free solid biofuel (Kane et al. 2016).

The high moisture content, bulkiness, low energy density, hygroscopic nature, and high transportation cost in various cases are certain drawbacks of raw biomass when utilized as a fuel (Abdullah and Wu 2009; Tsai et al. 2007), making it unsuitable for a variety of industrial applications. On the other hand, because of their biodegradability, environmental friendliness, and long-term viability, these organic materials have emerged as a leading contender for biofuels and bioenergy production. Pyrolyzing biomass at high temperatures to various value-added and energy-rich products is a preferable solution. Biochar, which has entirely different characteristics than the respective feedstock, has the potential to make significant and long-term improvements in guaranteeing a future supply of green energy and turning bioenergy into a carbon-negative sector (Kwapinski et al. 2010). Many studies have been carried out on producing biochar from various agro-residues for being used in fuel applications. Biochar's heating value (16–35 MJ/kg) is equivalent to, or nearly twice the raw biomass and many low-grade coals heating value for any given feedstock (Mullen et al. 2010; Sukiran et al. 2011). Around three billion people worldwide rely on conventional stoves, for example, three stone and open fires, to meet their cooking needs. These cookstoves emit hazardous fumes and are responsible for four million fatalities per year (Sakhiya et al. 2020). Biochar-fired cookstoves can minimize carbon and few other hazardous gas emissions in cookstoves when used for heat and cooking (Birzer et al. 2014). Compared to an open cooking fire, biochar stoves lowered particulate matter emissions by 92% and carbon monoxide emissions by 87% in laboratory tests (Schultz 2013).

8.5.5 Biochar as an Additive

8.5.5.1 Biochar Used as an Additive in the Construction Sector

In recent years, the spread of industry and urbanization has heightened the need for concrete for building purposes. The building industry, especially the cement industry, has been identified as one of the significant contributors to CO_2 emissions, accounting for around 7% of all GHG emitted into the atmosphere (Andrew 2018; Benhelal et al. 2013; Gupta et al. 2018). As a result, rising importance for developing greener solutions to decrease the company's carbon footprint and raw material usage (Miller et al. 2018). Several researchers have utilized biochar as an eco-friendly filler in cement manufacture and cement-based construction products to reduce carbon emissions. Biochar has poor heat conductivity, excellent chemical stability, low flammability, and conductivity, making it a suitable candidate for construction material and a filler in cement mortar products (Gupta and Kua 2017). Suarez-Riera et al. (2020) utilized biochar microparticles as a filler and a replacement for cement powder in cement paste and mortar composites. The results indicated that 2 wt% biochar fragments are adequate to improve the strength and resilience of cement and mortar mixtures. When used instead of cement, mechanical properties equivalent to the reference samples were achieved (Suarez-Riera et al. 2020). Another research uses biochar made from wood, food waste, and rice as a carbon-sequestering additive in mortar, attaining comparable mechanical strength results by adding 1–2 wt% biochar to the control mix.

Gupta and Kua (2019) also discovered that adding finer biochar particles at the start guarantees an increment in early strength and water tightness when utilized in cement mortar fusions. It was reported that timber waste biochar can be utilized as a filler material in concrete structures to improve strength and moisture resistance (Gupta and Kua 2019).

Poor thermal conductivity, directly impacted by the availability of broad arrays of pores on biochar, depends mainly on the process temperature and biochar's feedstock (Brewer et al. 2014). Extraction of oxygen functional group from the biochar's surface reduces the energy sites, forming the biochar to cause less hazardous reactions when blended with concrete mixes (Cross and Sohi 2013).

8.5.5.2 Biochar as an Additive in Composting

The swift development of humans and lifestyle changes have caused high waste creation. Furthermore, the animal farm business is expanding, posing its own set of problems. Biochar production involves transforming biodegradable carbon (biomass) into aromatic carbon (biochar), which is less degradable. Therefore, along with waste management, biochar production has an additional quirk of being an atmospheric carbon sequestration technique. Composting also promotes a more orderly breakdown of organic waste materials biologically and physicochemically.

An integrated technique employing biochar in composting reduces ecological concern throughout the waste treatment process by decreasing harmful chemical leaching and emission (e.g., heavy metals, H_2S, NH_3) as well as pathogen levels (Antonangelo et al. 2021).

Biochar has several advantages as a compost addition, including boosting composting and humification performance, promoting microbiological activities, lowering GHG and NH_4 emissions, and immobilizing heavy metals and organic contaminants (Guo et al. 2020). Various studies showed that biochar helps reduce nitrogen losses (Awasthi et al. 2018), as compounds like NH_3 and NH_4 are adsorbed by biochar (Janczak et al. 2017). The temperature goes up quicker in the course of the composting process in the presence of biochar, and the thermophilic phase lasts longer. When biochar is added at the beginning of the composting process, it enhances the water holding capacity (WHC), assuring that most composts have the required moisture content of 50–60% w/w. The carbon to nitrogen (C/N) ratios of various feedstock-derived biochar and composts vary, which has a direct impact on the rate of organic matter (OM) breakdown (Godlewska et al. 2017). Biochar has a high specific surface area (SSA) and a highly porous structure, providing nutrients for soil microorganisms to grow. Various functional groups on the biochar surface result in high cation exchange capacity (CEC), which acts as an electron carrier, making it easier to transfer and transport electrons (Antonangelo et al. 2019). Biochar application rates to compost have ranged from 5 to 10% (mass basis) to 50% or more (Jindo et al. 2012). A dose of more than 20–30% biochar (mass basis) is not encouraged since an excessive quantity of biochar compared to the composting material might obstruct biodegradation. Biochar has been proven to speed up the composting process when used in sufficient amounts, primarily by enhancing the consistency and structure of the mix and boosting microbial activity in the composting mixture. This enhanced activity results in higher temperatures and shorter compost development time (Camps and Tomlinson 2015). Table 8.7 shows the impact of biochar addition to compost in various other studies.

8.5.6 Other Modern Applications

Besides the above-discussed applications, biochar can be used in energy storage gadgets such as supercapacitors, lithium, and sodium-ion batteries etc. Biochar is used as electrode material in supercapacitors. Biochar activation was done to increase its specific surface area, resulting in an increased capacitive performance of biochar (Tan et al. 2017). For supercapacitor fabrication, Jin et al. (2014) prepared biochar from corn stover using microwave-assisted slow pyrolysis coupled with KOH activation. At a current density of 0.1 Ag^{-1}, the biochar had a specific capacitance of 246 F g^{-1} (Jin et al. 2014). Biochar is a carbon-rich material, highly porous and conductive, which makes it a suitable material to be used for sulfur-carbon (S/C) cathode composite for lithium-sulfur (Li-S) batteries (Vivekanandhan 2018). The activation process enhances biochar characteristics such as surface area,

Table 8.7 Impact of biochar on composting

Biochar feedstock	Scale	Biochar dosage	Compost material	Impact on the composting process	Reference
Corn biochar		1% w/w	Corn waste compost, corn biochar (1:1)	Shoot concentration, N, P, and K availability increased by 16, 38, and 15%, respectively, after biochar + compost addition over control soil	Liu et al. (2021a, b)
Powder and granular rice straw and bamboo biochar	Lab	10% (fw[a])	Pig manure, wheat straw (10:1)	• When compared to GRSB,[b] PRSB,[c] and PBB,[d] GBB had the lowest CH_4 and N_2O emissions • GBB had the highest cumulative NH_3 emissions (957 mg/kg)	He et al. (2019)
PRSB (500 °C)	Field	10% (dw[e])	Pig, dry chicken manure, rice straw (10:10:1 fw)	• The GWP achieved from biochar treatment was 19.8% lower than that obtained from the control treatment • Biochar reduces energy consumption in turning piles and has the potential to enhance the oxygen supply	He et al. (2017)
Rice hull biochar	Lab	20% fw	Chicken manure, hardwood sawdust, and rice hull biochar (7:1:2)	• BM drastically reduces N_2O and CO_2 emissions by 27% and 35%, respectively • Biochar amendment in chicken manure compost reduces soil N_2O emissions significantly by controlling soil organic stabilizing and functional group activities	Yuan et al. (2017)
Bamboo biochar	Pilot	3% w/w	Pig manure, wood chips, and sawdust (3:2)	• The addition of biochar lowers the NO_2-N concentration and also reduces the NO_2 emissions from pig manure composting	Wang et al. (2013)

(continued)

Table 8.7 (continued)

Biochar feedstock	Scale	Biochar dosage	Compost material	Impact on the composting process	Reference
				• Manure has lower moisture content and higher pH • The addition of biochar significantly changed the number of denitrifying bacteria	
Broad-leaved tree konara oak biochar	2% v/v	Field	Poultry manure, apple pomace, rice husk, oak bark (2:5:2:1)	• Biochar increased the amount of carbon collected by humic substance extraction by 10% and decreased the amount of water-soluble carbon by 30% • Phosphate, urease, and polyphenol oxidase activities improved by 30–40% due to biochar blending despite lower biomass	Jindo et al. (2012)
Eucalyptus grandis biochar	50%	Pilot	Biochar, coffee husk, and sawdust (1:1 fw)	Biochar amendment in poultry manure reduces the loss of nitrogen. This enrichment allows process optimization through odor emission and nitrogen loss reduction via nutrient balancing	Dias et al. (2010)

[a] *fw* fresh weight basis
[b] *GRSB* Granular Rice Straw biochar
[c] *PRSB* Powdered Rice Straw biochar
[d] *PBB* Powdered bamboo biochar
[e] *dw* dry weight basis

carbon content, surface functional groups, porosity, and pore volume, which improves metal encapsulation. Sajib et al. (2017) used KOH-activated biochar derived from canola meal as cathode composite. At the 0.05 °C rate (83.75 mA/g), the biochar cathode composite showed a high initial discharge capacity of 1507 mAh/g (Sajib 2017). Further, biochar is gaining a huge interest for fuel cell applications. Biochar can be used as a fuel in the electrolyte, as the chemical energy accumulated in biochar is a source for electricity generation, in direct carbon fuel cell

Table 8.8 Biochar applications in energy storage devices

Feedstock	Energy storage device	Biochar role	Reference
Fish scale	Supercapacitor	Electrolytes	Senthil and Lee (2021)
Walnut shell	Supercapacitor	Electrodes	Xiaoyang Xu et al. (2017)
Coconut shell	Supercapacitor	Electrodes	Jain and Tripathi (2014)
Cornstalks	Li-ion battery	Anode	Shengbin Wang et al. (2015)
Ginkgo leaves	Li-ion battery	Anode	Ou et al. (2016)
Pinecone	Sodium-ion battery	Anode	Zhang et al. (2017)
Sepals of palmyra palm fruit	Sodium-ion battery	Anode	Damodar et al. (2019)
Cherry petals	Sodium-ion battery	Anode	Zhu et al. (2018)
Banana peel	Li-S battery	cathode	Yang et al. (2016)
Almond shell	Li-S battery	cathode	Benítez et al. (2018)

(DCFC) (Huggins et al. 2016). Table 8.8 shows the application of biochar in various energy storage devices.

Altogether, enhancing biochar's physical and chemical properties through activation has many applications, such as energy storage devices. Utilizing biochar is a sustainable approach; therefore, we can expect exponential growth in its usage in the coming years.

8.6 Conclusion

The world's population is increasing at an alarming rate (approx. 80 million people annually), leading to the increased demand for food, energy, safe water supply, etc. Agricultural production has been increased around 50% in the last two decades, resulting in the generation of a massive amount of biomass waste daily. The majority of biomass waste is thrown or burned openly in the field, which has a severe influence on the ecology and public health. Biochar is a cost-effective and sustainable option to address the above-mentioned problems. This chapter reviewed different types of pyrolysis processes for biochar production and the factors affecting the biomass pyrolysis process.

The chapter also discussed the different biochar applications such as adsorbent in water purification, air purification, soil amendment, additives in composting and construction sector, an alternative to fuel, catalyst in various processes such as syngas production, biogas upgradation, and biodiesel production. Moreover, there are certain modern applications including, electrodes and electrolytes in supercapacitors, anode, cathode composites in lithium and sodium-ion batteries, and hydrogen storage. The application of biochar is highly dependent on its physicochemical characteristics such as porosity, specific surface area, and surface functional groups. These properties of biochar are enhanced using various types of activation processes: physical and chemical. Worldwide biochar gets attention due to its desired physicochemical properties which can be useful in different types of applications to generate the circular economy.

Conflict of Interest Statement The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this chapter.

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Chapter 9
Recent Advances in Direct Catalytic Thermochemical Gasification of Biomass to Biofuels

Rupesh S. and Deepanraj

Abstract Biomass gasification is the sub-stoichiometric thermochemical transmutation of biomass into gaseous biofuel. The gasification products mainly consist of syngas, tar, and char. In general, conversion of tar to useful fuel constituents is energy intensive as it requires a higher process temperature (>800 °C) due to the higher activation energy requirement for cracking. Catalyst takes a crucial position in biomass gasification by increasing the quality and yield of gaseous biofuel at the expense of undesirable tar and char, at a lower process temperature at a faster rate. Among the different catalysts, commercial Ni-dolomite combinations exhibit remarkable tar reforming capability of 89–99% by mutually mitigating the deactivation of nickel and CH_4 reformation insensitivity of dolomite. In this view, Ni-dolomite combinations can economically nourish producer gas through simultaneous tar reformation and CO_2 sorption. Recent practices and future scopes for catalytic performance enhancement through new catalyst configurations and novel technologies are also discussed.

Keywords Biomass gasification · Gasifier · Tar reforming · Catalysts · Deactivation

Abbreviations

ASH	Ash
ATR	Autothermal reforming
d_{af}	Dry ash free
ER	Equivalence ratio
FC	Fixed carbon

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
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FT	Fischer–Tropsch
GR	Gasifying ratio
GT	Gas turbine
M	Moisture
ms	Milliseconds
MTG	Methanol-to-gasoline
Nm^3	Normal cubic meter
PAH	Polycyclic aromatic
SBR	Steam to biomass ratio
VM	Volatile matter
WGS	Water gas shift

9.1 Introduction

Environmental sustainability and fossil fuel utilization are two inevitably conflicting requirements for the better being of mankind. Complete reliance on conventional energy sources, to meet the global energy demand, leads to both an energy crunch and adverse environmental issues due to the surplus emission of greenhouse gases like carbon dioxide (Goswami et al. 2020, Goswami et al. 2022). The estimated rise in world energy demand for 2021 is 4.6%, with an associated increase of 33 billion tonnes of carbon dioxide emission. Thus, depleting nature of conventional energy sources and their unfavorable environmental impacts encouraged energy extraction from replenishable energy sources. Consequently, in 2020, the global utilization and electricity generation from renewable resources is raised by 2% and 3%, respectively. Moreover, an 8% improvement in renewable energy to electricity conversion is targeted in 2021 to attain an output of 8300 TWh (Rupesh et al. 2021). Among the renewable energy sources, biomass is the highest energy distributer, approximating 15% of primary global energy consumption. However, the practical applicability of biomass can be ensured by tackling its low energy density through sustainable and eco-friendly energy conversion routes. Among the feasible bio-chemical, physiochemical, and thermochemical conversion methods, thermochemical means (pyrolysis, combustion, and gasification) are attractive because of their faster and continuous conversion. In thermochemical conversion, biomass gasification is a potential and practically feasible pathway to extract and concentrate energy embedded in biomass. In gasification, biomass is transmuted to gaseous fuels and upgraded chemical products in sub-stoichiometric conditions, without leaving any net adverse impact on the environment. The gaseous fuel obtained from gasification is mainly a mixture of hydrogen and carbon monoxide, turned into synthesis gas or syngas, which can also serve as a chemical feedstock for synthesizing other liquid fuels and value-added chemicals. In biomass gasification, the extent of biomass conversion and, the quality and quantity of the fuel generated are significantly influenced by the reactor, operating parameters, and presence of catalysts. This chapter deals with various aspects of biomass gasification and the role of catalysts in augmenting the quality and yield of syngas.

9.2 Biomass Gasification

Biomass is non-fossilized, renewable, and biodegradable organic matter derived from animals, plants, or microorganisms. Major biomass sources consist of terrestrial and aquatic biomasses, agricultural, municipal, and solid waste, and forest residue (Sikarwar and Zhao 2017; Kumar and Verma 2021a, b). Especially, non-edible fibrous plant derivatives composed of lignin, cellulose, and hemicellulose, known as lingo-cellulosic biomass, threaten proper waste management or lead to adverse environmental impacts on direct combustion. This can be properly addressed by converting them to energy through appropriate energy conversion routes (Bridgwater 2003; Bhardwaj et al. 2021a, b; Bhardwaj and Verma 2021). Biomass gasification is the sub-stoichiometric thermochemical transmutation of biomass to gaseous fuel and upgraded chemical products. During gasification, biomass is subjected to thermal decomposition followed by chemical reactions with the participation of a medium, known as a gasifying agent, in a reactor termed as gasifier. Basically, gasification is a four-stage process comprising drying, pyrolysis, partial oxidation, and reduction. The steps in gasification are mentioned in Table 9.1.

The gasification product's yield firmly relies on the biomass, gasifying medium, reactor configuration, and process parameters. In general, the gasification products comprise a non-condensable gaseous mixture mainly consisting of H_2, CO, CO_2, CH_4, known as producer gas, condensable higher hydrocarbon species collectively termed as tar, and solid constituents such as char and ash. The overall biomass gasification process can be represented as:

Table 9.1 Different steps in biomass gasification (Sansaniwal et al. 2017)

Name	Temperature range (°C)	Process
Drying	100–150	The moisture content in biomass (5–35 wt.%) is transformed into steam
Pyrolysis	150–700	Thermal dissociation of biomass structural constituents such as lignin, cellulose, and hemicellulose into condensable and non-condensable volatiles and char
Partial oxidation	700–1500	Sub-stoichiometric combustion or oxidation of pyrolysis products that release heat to drive the other three endothermic steps
Reduction	800–1100	The various condensable and non-condensable gases, char, and gasifying agents chemically interact to yield gaseous constituents of producer gas

$$\text{Biomass} + \text{Gasifying agent} + \text{Heat} \rightarrow H_2 + CO + CO_2 + CH_4 + H_2O + \text{Tar} + \text{Char} \tag{9.1}$$

9.2.1 Gasification Chemistry

The biomass gasification chemistry is too intricate with numerous reactions and is not yet completely explored (Pfeifer and Hofbauer 2008). The main homogenous and heterogeneous chemical reactions in gasification are listed in Table 9.2. The

Table 9.2 Main gasification reactions (Basu 2010; Valderrama Rios et al. 2018;Silva et al. 2019)

S. No.	Reaction name	Stoichiometry	Enthalpy of reaction (kJ/mol)
1	Drying	Wet Biomass + Heat → Dry Biomass + H_2O	–
2	Pyrolysis	Dry Biomass + Heat → Gas + Tar + Char	–
Oxidation reactions			
3	Char oxidation	$C + O_2 \rightarrow CO_2$	−394
4	Partial char oxidation	$C + 0.5O_2 \rightarrow CO$	−111
5	Hydrogen oxidation	$H_2 + 0.5O_2 \rightarrow H_2$	−242
6	Carbon monoxide oxidation	$CO + 0.5O_2 \rightarrow CO_2$	−283
7	Methane oxidation	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	−520
8	Tar partial combustion	$C_mH_n + (0.5m + 0.25n) O_2 \rightarrow mCO + 0.5nH_2O$	–
Reduction reactions			
9	Boudouard	$C + CO_2 \leftrightarrow 2CO$	+172
10	Hydrogasification	$C + 2H_2 \leftrightarrow CH_4$	−74.8
11	Char steam reforming (Water gas reaction)	$C + H_2O \leftrightarrow CO + H_2$	+131
12	Water gas shift (WGS) reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	−41.2
14	Methanation reactions	$2CO + 2H_2 \rightarrow CH_4 + CO_2$	−247
15		$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	−206
16		$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	−165
Tar decomposition reactions			
17	Thermal cracking	$C_mH_n \rightarrow aC_{m-x}H_{n-y} + bH_2$	–
18		$C_mH_n \rightarrow 0.25C_{m-x}H_{n-y} + 0.25(4n - m) H_2O$	–
19	Steam reforming	$C_nH_m + nH_2O \rightarrow \left[n + \frac{m}{2}\right]H_2 + nCO$	–
20	Dry reforming	$C_nH_m + nCO_2 \rightarrow \frac{m}{2}H_2 + 2nCO$	–
21	Hydrogenation	$C_nH_m + 2(n - 0.25m)H_2 \rightarrow nCH_4$	–
22	Carbon formation	$C_nH_m \rightarrow nC + 0.25mH_2$	–

reactions can be classified as drying, devolatilization or pyrolysis, oxidation, reduction, and tar reforming reactions. The extent of involvement of each reaction in the process relies on biomass composition, type of gasifying medium, reactor design, and process parameters. Overall, gasification is an endothermic process; is termed autothermal if the heat required is supplied by the combustion reactions, within the reactor, or allothermal if supplied externally.

9.3 Gasifying Agents

The role of gasifying medium or agent is pivotal in the yield and quality of gasification products. Air, steam, air-steam (both air and steam), oxygen, and steam-oxygen (both steam and oxygen) are the mainly used gasifying agents in biomass gasification. A comparison of the merits and limitations of air, steam, and oxygen as gasifying agents is listed in Table 9.3. In general, the quantity of gasifying agent used is referred to using non-dimensional terms defined with respect to the quantity of biomass used. Equivalence ratio (ER), steam to biomass ratio (SBR), and gasifying ratio (GR) are the non-dimensional terms, respectively, used for air, steam, and steam-oxygen mixture.

$$\text{Equivalence ratio (ER)} = \frac{\text{Actual air} - \text{fuel ratio}}{\text{Stoichiometric air} - \text{fuel ratio}} \tag{9.2}$$

$$\text{Steam to biomass ratio (SBR)} = \frac{\text{Mass of steam}}{\text{Mass of biomass}} \tag{9.3}$$

$$\text{Gasifying ratio (GR)} = \frac{\text{Mass of (steam + oxygen)}}{\text{Mass of biomass}} \tag{9.4}$$

Table 9.3 Comparison of different gasifying agents (Sansaniwal et al. 2017)

Agent	Merits	Demerits
Air	• No external heat is required as heat for gasification is obtained from partial combustion. • Economical	• Low calorific value due to N_2 dilution • Can be used only for direct burning applications
Oxygen	• The gasifying medium can enable partial oxidation, so no external heat is required. • H_2, CO, and CH_4 enriched producer gas with minimum tar and no N_2 dilution • Better carbon conversion	• Comparatively, expensive handling is required • Safety issues
Steam	• Producer gas enriched with H_2 • A higher H/C ratio of producer gas is suitable for the synthesis of liquid fuels	• Higher tar content • Energy-intensive as external heat is required to enable gasification

Table 9.4 Influence of gasifying medium on gas composition

Medium	Gas composition (vol.%)					Gas yield (Nm^3/kg_{daf})
	H_2	CO	CO_2	CH_4	N_2	
Air	5–16.3	9.9–22.4	9.0–19.4	2.2–6.2	42–62	3.7–61.9
Steam	38–56	17–32	13–17	7–12	0	60–95
Steam and oxygen	13.8–31.7	42.5–52	14.4–36.3	6–7.5	0	2.2–46

Air gasification is autothermal as the heat input for gasification is derived from partial oxidation of biomass. But the quality of the producer gas obtained is low as it is diluted with N_2 contained in the air. Consequently, the heating value of the producer gas from air gasification is limited to 4–7 MJ/Nm^3. Self-sustained gasification with H_2, CO, and CH_4 (without N_2) enriched producer gas enables the achievement of a superior calorific value of 12–28 MJ/Nm^3 in oxygen gasification. On the other hand, the use of steam results in producer gas with a higher H/C fraction having a calorific value (lower heating value) of 10–18 MJ/N m^3 (Basu 2010). Combinations of different gasifying agents are used to merge their advantages to improve the producer gas characteristics. Gas yield and composition using different gasifying agents are depicted in Table 9.4.

9.4 Types of Gasifiers

The gasifier, the reactor in which gasification takes place, has a vital impact on the quantity and quality of producer gas generated. The design, construction, and operation of gasifiers differ depending on the biomass attributes (moisture content, ash content, size, shape, etc.), quality, and yield of syngas to suit various downstream applications. The reactor is generally classified into fixed bed, fluidized bed, entrained flow, and plasma gasifiers.

9.4.1 Fixed Bed Gasifier

9.4.1.1 Updraft Gasifier

In an updraft gasifier, the gasifying agent supplied from the bottom reacts with the descending biomass loaded from the top to generate producer gas rising through the bed. The reactor is termed updraft, due to the upward flow of gas, whereas the opposing gas flow relative to biomass in the reactor signifies its alternate name countercurrent gasifier (Loha et al. 2018). In updraft gasifiers, biomass is sequentially subjected to drying, pyrolysis, reduction, and partial oxidation in the respective

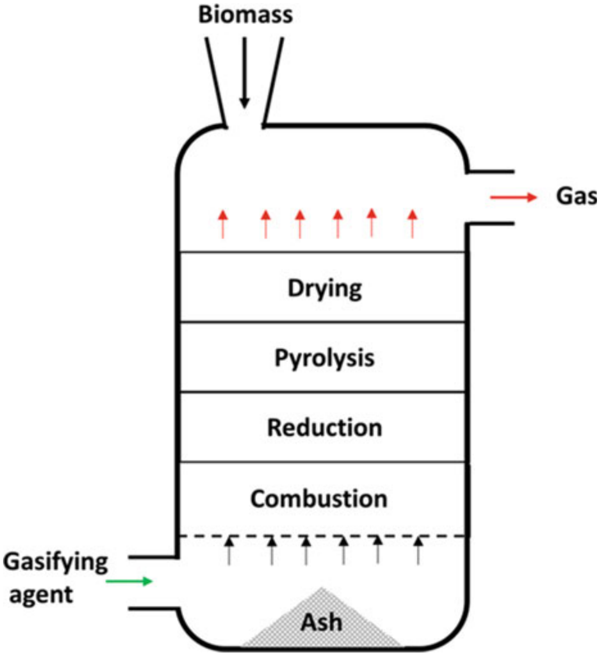


Fig. 9.1 Updraft gasifier

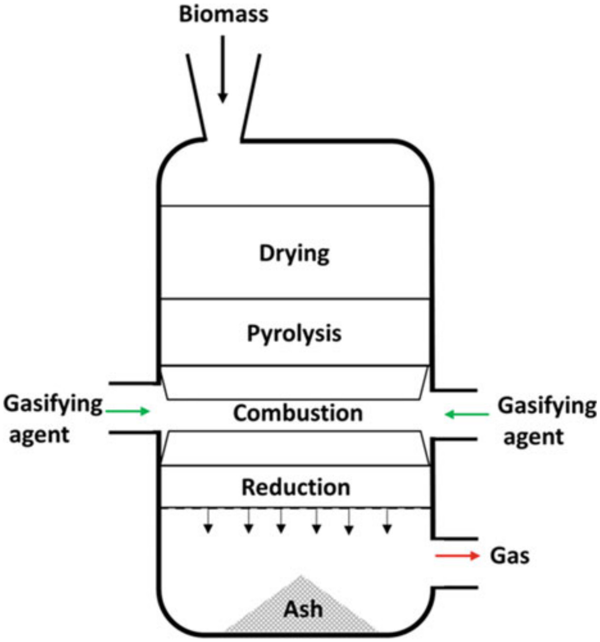
distinct zones to generate producer gas as shown in Fig. 9.1 (Ren et al. 2019). Generally, in the oxidation zone, the ash is melted at 1200 °C.

The flow of raw gas generated through a relatively low-temperature pyrolysis zone laden the producer gas with uncracked tar precursors, resulting in lower syngas yield with higher tar content. During this process, after passing through the fuel bed, the hot gases leave at a lower temperature range of 200–400 °C (Basu 2010; Surisetty et al. 2012). As the gas flows from a high-temperature oxidation zone to low-temperature pyrolysis and drying zones, the heat content in it can be utilized for drying and pyrolysis, thereby achieving improved thermal efficiency. Thus, updraft reactors can accommodate feedstock with higher moisture content (up to 60% by weight) and are well suited for downstream applications that can accommodate producer gas with high tar content, low dust at high flame temperature (Sansaniwal et al. 2017).

9.4.1.2 Downdraft Gasifier

In this gasifier, both biomass loaded from the top and gas generated move parallelly downward and hence the name downdraft gasifier. Due to this unidirectional movement of biomass and producer gas, this reactor is also known as a co-current gasifier (Sansaniwal et al. 2017). The tar concentration in the producer gas is relatively low due to the gas flowing from the low-temperature drying zone to the high-temperature

Fig. 9.2 Downdraft gasifier



combustion zone and thereby cracking the tar formed from the pyrolysis more effectively (Bermudez and Fidalgo 2016).

Thus, producer gas passing through the high-temperature (900–1000 °C) zones aids in the partial combustion of tar and leaves the gasifier at 700 °C (Basu 2010; Devi et al. 2020). However, pyrolytic gas combustion to support endothermic reactions lowers the heating values of produced gas (Ruiz et al. 2013). Moreover, incompetence in accommodating biomass with high moisture (<25%) and ash (<6%) content limits its usage (Surisetty et al. 2012). But producer gas with low particulate and tar content makes it appropriate for small-scale power generation. The schematic of the downdraft gasifier is shown in Fig. 9.2.

9.4.1.3 Crossdraft Gasifier

These gasifiers are named so due to the mutually perpendicular flow directions of biomass and producer gas with respect to the reactor, as shown in Fig. 9.3. Here feedstock is introduced from the top, while the entry of gasifying agent and exit of producer gas takes place from diametrically opposite sides of the gasifier respectively side (Devi et al. 2020).

The fuel is subjected to drying, devolatilization, and gasification as it descends the reactor. The high-velocity gasifying agent directly fed to the oxidation zone reacts with char to generate a very high temperature (<1500 °C). As gasifying agent enters through the oxidation zone and the generated producer gas leaves through the

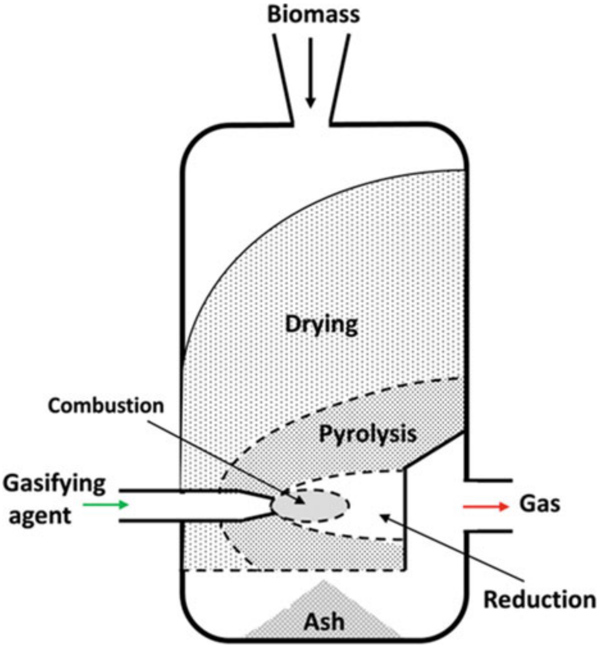


Fig. 9.3 Crossdraft gasifier

reduction zone, pyrolysis, drying, and ash disposal zones act like separate zones thereby restricting the fuel type (Loha et al. 2018). Moreover, the high temperature of exit gas results in higher CO_2 and lower H_2 and CH_4 concentrations, respectively, limiting its practical usage. Even though, this type of gasifier offers a quick response against load, better producer gas flexibility, easy and quick start-up, its incapability to handle biomass with high moisture (<20%), ash content (<1%), volatiles, and lower particle size further limits its application (Sansaniwal et al. 2017). Also, product gases leaving the gasifier at 900–1250 °C lower the energy efficiency by up to 75%, along with slagging issues (Basu 2010; Bermudez and Fidalgo 2016).

9.4.2 *Fluidized Bed Gasifier*

A fluid-like behavior of both the bed material and biomass particle is experienced in this gasifier. The bed made up of fine particles like silica sand, dolomite, etc. acts as fluid suspension when acted up by the fluidizing media like air, steam, oxygen, or their combination. The entire bed is supported over a plate provided with a large number of holes, known as distributed plate, through which a uniform distribution of gasifying medium at sufficient velocity is provided. In these gasifiers, fluidizing medium is maintained at a minimum velocity, minimum fluidization velocity, to ensure proper fluidization of bed material. The random movement of bed particles in a fluidized bed promotes proper mixing, thereby achieving better heat and mass transfer (Sansaniwal et al. 2017). The higher heat and mass transfer associated with fluidized beds ensure better temperature uniformity, syngas quality, cold gas efficiency, and fuel flexibility, making it the most promising reactor (Ren et al. 2019).

Moreover, the vigorous mixing in the bed leads to non-distinguishable reaction zones with overlapping gasification stages leading to homogeneous product gas. Furthermore, around 95% carbon conversion efficiency and excellent scaling up suitability enhance the adequacy of fluidized bed gasifiers. Fluidized bed gasifiers of capacity ranging from 5 to 50 MW are widely used in small- to medium-scale applications (Devi et al. 2020). The main two variants of fluidized bed gasifiers are as follows.

9.4.2.1 Bubbling Fluidized Bed Gasifier

The schematic of the bubbling fluidized bed gasifier is depicted in Fig. 9.4. This is the most extensively used variant owing to its flexibility to adapt parameters like capacity, temperature, feedstock, etc. The fluidized medium like oxygen, air, or steam is forced through the plenum over the inert bed made up of fine sand or alumina particles with minimum fluidization velocity to counterbalance the weight of the solid particles (Ren et al. 2019; Devi et al. 2020). On further increasing the gas velocity, the bed material got suspended in upward flowing gas forming the fluidized

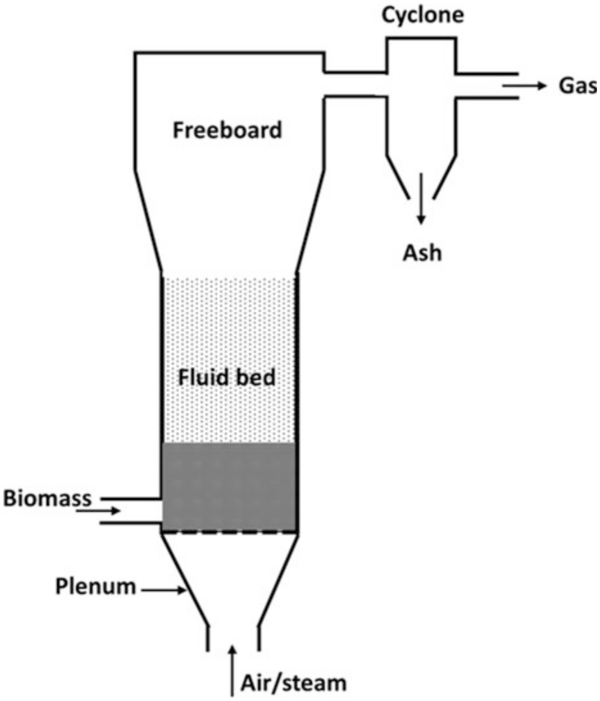


Fig. 9.4 Bubbling fluidized gasifier

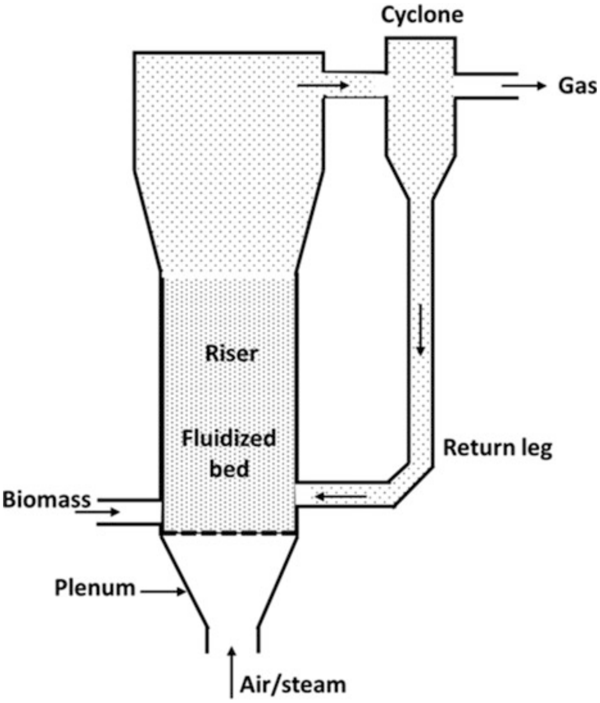
bed. At this point, the weight of the bed particles is counterbalanced by the drag force between solid particles and fluid, resulting in a pressure drop. On further increasing the velocity, the bubble formation starts in small sizes, grows bigger, and moves through the bed. These bubbles set the particles in motion by withdrawing particles from their surrounding as they move up. While reaching the free surface of the bed, these bubbles are subjected to bursting, letting the gas free board. The rapid, random, and repeated movement of solid particles maintain a uniform temperature distribution with minimum particles escaping the gasifier along with the gas. A cyclone separates solid particles from the producer gas such as escaped bed materials, char, and ash, thereby providing particle-free producer gas. (Sansaniwal et al. 2017; Loha et al. 2018).

Usually, for bubbling fluidized bed gasifiers, fluidization velocity is maintained in the range of 1–3 m/s to guarantee the suspension of solid particles. In a bubbling fluidized bed, maximum syngas content is achieved above 1200 °C, and maximum H_2 or methane is obtained below 1000 °C (Devi et al. 2020) and can process medium-sized feedstock (Silva et al. 2019). High heat exchange and reaction rates due to compact construction, high ash content with a low melting point, proper adaptation to moisture and ash content, and other fuel characteristics are the significant merits of using the same. The main setbacks of the gasifier include melting of ash, bed agglomeration, poor solid conversion due to back mixing, high tar, and dust content, and high temperature of producer gas. Nevertheless, these reactors are apt for medium capacity applications greater than 5 MW (Surisetty et al. 2012; Bermudez and Fidalgo 2016).

9.4.2.2 Circulating Fluidized Bed Gasifier

This reactor mainly comprises a riser, cyclone, and a return leg as in Fig. 9.5. The biomass introduced through the side of the reactor mixes with the hotbed. Here, the fluidization velocity is well above that of the bubbling bed beyond the bubbling bed in the range of 5–10 m/s (Ren et al. 2019). In this velocity range, the solid particles are spread over the entire riser region, the majority being entrapped by the gas (Basu 2010). The raw producer gas exiting the reactor is supplied to a cyclone where the gas and solid particles are segregated. These segregated char and bed material is fed back to the reactor bed through the return leg, thus forming a loop of circulating solids (Surisetty et al. 2012). This, a solid circulation loop with enhanced gas velocity is established by maintaining suitable pressure differences across the reactor. Thus, enhanced heat and mass transfer characteristics, compared to that of the bubbling type, can be achieved by increasing the residence time through particle recycling (Loha et al. 2018; Ren et al. 2019). Besides high cost and erosion, these reactors are well suited for scale-up applications up to 100 MW.

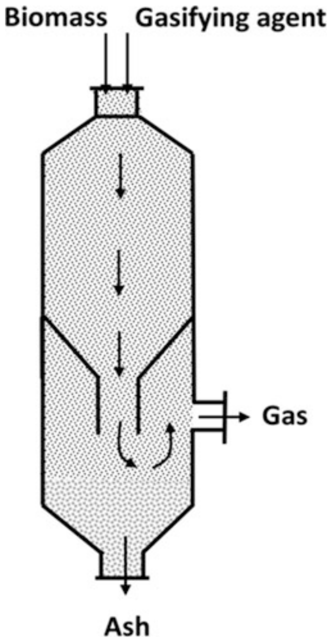
Fig. 9.5 Circulating fluidized gasifier



9.4.3 Entrained Flow Gasifier

This gasifier establishes a co-current flow of very fine biomass particles and gasifying agents introduced at the top of the reactor as in Fig. 9.6. Here, gasifying agents like oxygen, air, or their combinations are used at velocities higher than 10 m/s. The gasifying agents entrap fine biomass particles along with the flow to form a thick cloud within the gasifier. The very low retention of biomass inside the gasifier demands high operating temperatures in the range of 1200–1500 °C. The extreme turbulent flow thus existing in the reactor causes the rapid conversion of fuel and high throughput (Loha et al. 2018). The higher operating temperature provides high-quality producer gas with low tar content (Silva et al. 2019). Even though entrained flow gasifier has fuel flexibility, the oxygen consumption is reduced by biomass with less ash and moisture content. Apart from the cost incurred in sizing the biomass, these reactors are preferred for large-scale operations with applicability greater than 100 MW (Ruiz et al. 2013).

Fig. 9.6 Entrained flow gasifier



9.4.4 Plasma Gasifier

This gasifier is mainly designed for municipal solid waste management. In a plasma gasifier, the crucial part plasma torch is placed towards the bottom of the gasifier as in Fig. 9.7. The biomass is introduced to the plasma zone from the top of the gasifier and reacts with the ionized gasifying agent introduced next to the plasma torch. An electric discharge is experienced when the temperature within the gasifier reaches 10,000 °C, causing degradation of matter at an atomic level. Thus, the fuel breaks down into its constituent elements converting all organic ingredients into gaseous fuel (Ren et al. 2019). The resulting gas is taken out from the top of the gasifier and the residue is melted and is removed as slag (Loha et al. 2018).

Any toxic or poisonous solid waste can be gasified through a plasma gasifier without any prior segregation or treatment. Using these gasifiers, waste reduction can be attained on large scale with leach-resistant inert slag as the by-product, used as a building material. But the overall energy production from plasma gasification is low even at high-energy consumption and capital cost. Moreover, the rapid reaction with fewer syngas contaminants makes it suitable for large-scale applications like municipal or hospital waste gasification (Munir et al. 2019). A comparison between various characteristics of gasifiers is as in Table 9.5.

Fig. 9.7 Plasma gasifier

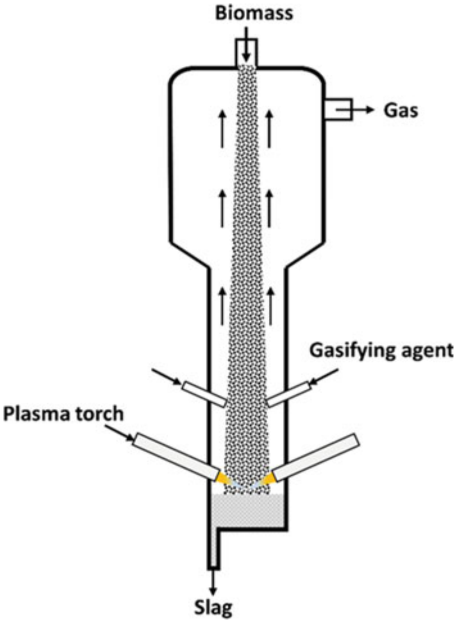


Table 9.5 Comparison of gasifiers (Moustakas et al. 2005; Fabry et al. 2013; Gabbar et al. 2020; Kuo et al. 2020)

Gasifier	Feed size (mm)	Temperature (°C)	Cold gas efficiency (%)	Tar (g/N m^3)	Output (MW)	Capacity
Fixed bed or moving bed gasifiers						
Updraft	5–100	200–700	80	30–150	1–10	Small
Downdraft	20–100	700	80	0.015–3	0.01–1	Small
Crossdraft	5–20	1250	80	0.01–0.1	< 10	Medium
Fluidized bed gasifiers						
Bubbling	10	800–900	89	1–3	< 25	Medium
Circulating	0.18–0.23	800–900	89	< 5	60	Medium
Entrained and Plasma gasifiers						
Entrained	< 0.075	1200–1500	80	~ 0	> 100	Large
Plasma	25–200	1200–5000	38.3–47	<0.01	12–100	Large

9.5 Tar

Tar is a dark, viscous, and sticky liquid with a boiling point of 150 °C, formed by condensation of volatiles at the low-temperature zones of the gasification system. It is the most undesirable product of gasification as it leads to coking, clogging, and corrosion in end-use devices like turbines, engines, heat exchangers, pipelines, and other contact surfaces when condensed. It also reduces the syngas heating value and gasification efficiency, thereby increasing maintenance and process cost (Rakesh and

Dasappa 2018). In actual practice, the constituents of tar are enormously diverse in the chemical constitution and are generally differentiated as a group of organic formulations with a molecular weight greater than that of C_6H_6 (Maniatis and Beenackers 2000).

9.5.1 Composition

The typical composition of tar from biomass is depicted in Fig. 9.8.

Tar can be classified into four tar groups based on the presence of aromatic rings in the constituents. The details of different forms of tar for a residence time of 300 ms are as follows: (Evans and Milne 1997)

- Primary group: consists of cellulose, hemicellulose, and lignin-derived compounds comprise syringols, acids, phenols, aldehydes, sugars, etc. They are initiated at 500 °C and gradually decomposed mainly to secondary tar between 500 and 800 °C.
- Secondary group: Generated between 500 and 800 °C by the decomposition of primary tar to phenols and olefins. Beyond 800 °C they decompose to tertiary tar.
- Tertiary group: More than 90% of tertiary tar is observed in the temperature range of 500–800 °C. Aromatics derived from methyl groups such as methyl acenaphthylene along with indene, methylnaphthalene, and toluene form this group.
- Condensed tertiary: They are poly-cyclic aromatic hydrocarbons (PAHs) lacking substituents for hydrogen-like C_6H_6, $C_{10}H_8$, $C_{12}H_8$, $C_{14}H_{10}$, $C_{16}H_{10}$, etc.

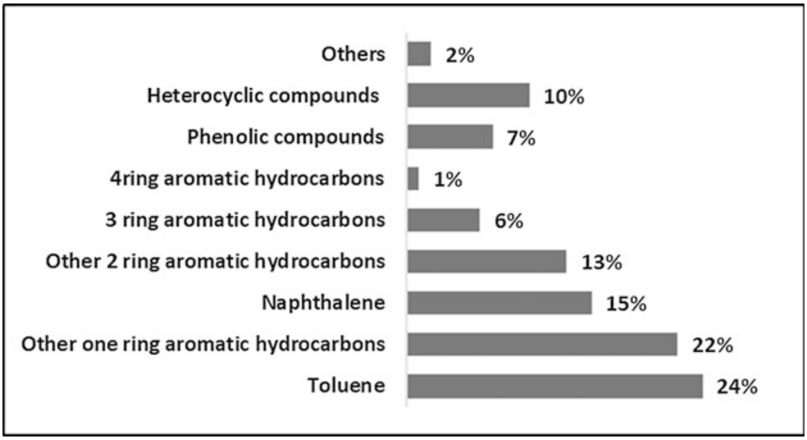


Fig. 9.8 Composition of tar (Devi et al. 2005a; Anis and Zainal 2011; Guan et al. 2016)

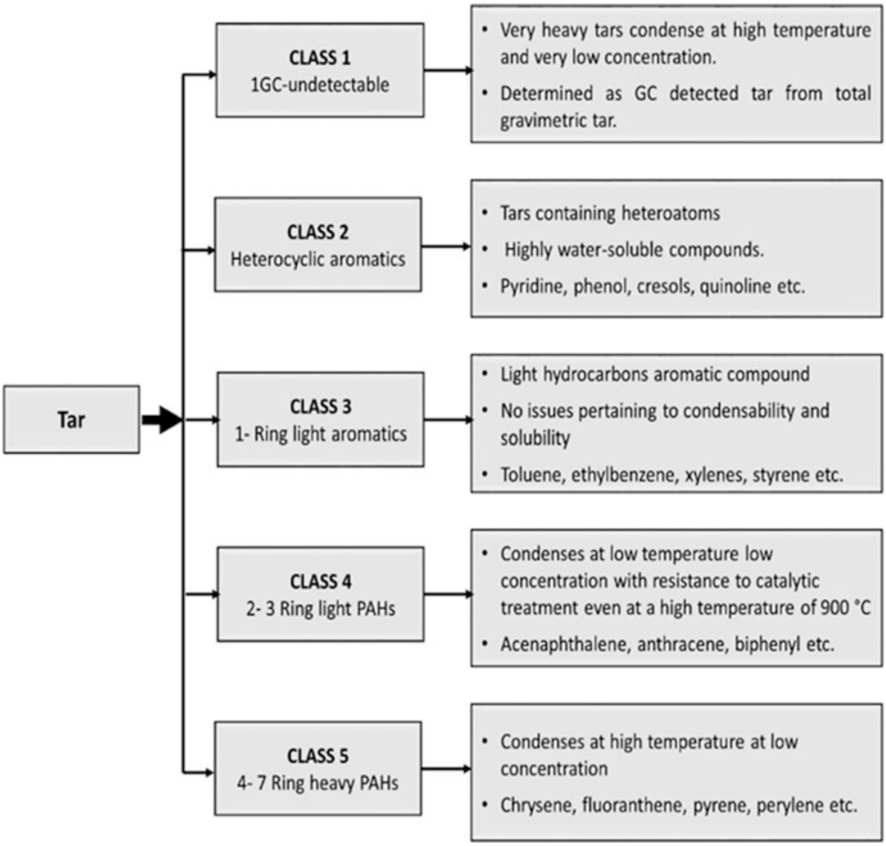


Fig. 9.9 Classification of tar is based on condensability and solubility (Devi et al. 2005c; Anis and Zainal 2011)

Information regarding condensability and solubility of tar constituents is very critical as it predicts the tar fouling and tar removal strategies. Based on this, tar can be classified into five distinct classes, as given in Fig. 9.9.

9.5.2 *Effects of Operating Conditions on Tar Yield*

Apart from the reactor design, operating conditions such as temperature, pressure, gasifying agent, and residence time have a significant role in the yield and conversion of tar during biomass gasification. Temperature is the most vital parameter that determines the yield and composition of tar by driving tar decomposition reactions. In general, an overall quantity of tar and char decreases with an increase in temperature. The yield of oxygen comprising tar species, such as C_6H_6O (phenol), C_7H_8O

(cresol), and C_8H_6O (benzofuran) decreases with temperature, mainly below 800 °C. The formation of aromatic formulations without substituents such as benzene and naphthalene are promoted with temperature. Moreover, the production of substituted 1 and 2 and 3 and 4 ring aromatics decreases and increases, respectively, with temperature (Devi et al. 2003). The total reduction in tar yield with complete eradication of phenols accompanied by a decrease in poly-cyclic aromatic hydrocarbons is reported with an increase in pressure between 8 and 21.4 bar (Knight 2000). The choice of gasifying agent significantly influences the tar formation. It is reported that tar yield is lowest for air and highest for steam with respective values of 2–20 and 30–80 g/Nm^3 (Basu 2010). Injection of steam reduces the process temperature whereas the addition of air or oxygen can increase process temperature and reduce tar formation at the expense of heating value, by promoting the oxidation of volatiles. A 50% tar reduction was reported by Narváez et al. (1996) at 800 °C when ER is increased from 0.2 to 0.45. Apart from all the operating conditions discussed, residence time has a consequential role in tar yield. A tar reduction of 75% is achieved by varying residence time from 1 to 5 s due to the increase in the duration of tar exposure with a gasifying agent.

9.5.3 Application Limits

As tar can cause operational issues, the quantity of tar content in producer gas determines the potential end-users of the gas. The acceptable tar content in producer gas for different applications is depicted in Table 9.6.

From Sect. 9.3, it is clear that the tar yield with different gasification agents is appreciably high compared to the permissible limit of tar content for different applications. Furthermore, tar constituents are stable carcinogens with adverse environmental impacts (Guan et al. 2016). In view of the same, it is inevitable to reduce the tar content to suit the gas for different applications and to safeguard the health and environment.

Table 9.6 The permissible limit of tar content in producer gas for different applications (Fabry et al. 2013; Valderrama Rios et al. 2018)

Application	Tar content (mg/Nm^3)
Direct combustion	No limit
Compressors	50–500
I C engines	Less than 100
Gas turbine	Less than 5
Fuel cells	Less than 1
Methanol synthesis	Less than 0.1
Fischer–Tropsch synthesis	Less than 0.1

9.6 Effect of Key Operating Parameters on Gasification

The product distribution and conversion efficiency of biomass gasification mainly depend on the operating parameters and gasifier design. This section is dedicated to the various key operating parameters and their influence on biomass gasification.

9.6.1 Biomass/Feedstock

The primary factor that influences the gasification performance and product gas composition is the type of biomass used for gasification. A preliminary comparison of the gasification performance of different feedstock can be done from their structural, chemical, and gross constitution. Structurally, lignocellulosic biomass is composed of lignin (20–30%), cellulose (33–51%), and hemicellulose (19–34%) (Van Maris et al. 2006). Biomass with higher hemicellulose and cellulose contributes to more gas yield whereas, lignin, being a cementing agent, is considered the possible source of tar (Valderrama Rios et al. 2018). So, biomass with a higher value for the ratio of the sum of cellulose and hemicellulose to lignin is preferred for biomass gasification. The composition of biomass in weight percentage of elements such as C, H, O, N, and S plus moisture and ash content can be determined by performing ultimate analysis. The elemental composition thus obtained can be used to estimate the stoichiometric air requirement and higher heating value of the feedstock (Rupesh et al. 2020). Feedstock with higher oxygen content is reported to yield syngas with lower calorific values (Rupesh et al. 2015). On the other hand, the gross composition of biomass in terms of fixed carbon (FC), volatile matter (VM), moisture (M), and ash (ASH) obtained from the proximate analysis can also serve as an indication of gasification performance. Feedstock with higher moisture content demands additional heat to vaporize the moisture, leading to lower operating temperatures. Even though biomass with the moisture content of less than 35% is acceptable, that in 10–15% is the most suitable (Kaushal and Tyagi 2012). On the other hand, biomass with higher ash content reduces gas yield and demands more ash handling.

Feedstock particle size and density also significantly influence the gasification process. Smaller particle size possesses a larger surface area, which in turn leads to enhanced heat and mass transfer. Thus, biomass with smaller particle size leads to better carbon conversion, H_2 yield, and lower tar content in the producer gas at the expense of energy spend for sizing the biomass (for particle size <1 mm) (De Lasa et al. 2011; Chan et al. 2019). Moreover, biomass with lower density exhibit invariable temperature throughout the biomass particle leading to homogenous gas generation. Whereas, the existence of temperature gradient in denser feedstock leads to non-homogeneous gas yield (Kirubakaran et al. 2009). Thus, it is clear that the physical and chemical properties of biomass have a predominant role in gasification and hence feedstock characterization is the most important prerequisite for any gasification study.

9.6.2 Temperature

Being an endothermic process, temperature has a vital role in determining the char conversion, tar content, gas yield, and producer gas constituents. Increasing temperature up to 600 °C favors tar yield, due to enhanced devolatilization of biomass, and decreases thereafter (Fagbemi et al. 2001). When the temperature is increased from 700 to 850 °C, tar yield is found to be decreased (Narváez et al. 1996). This is due to the combined influence of enhanced tar cracking and tar reformation reactions at higher temperatures. Consequently, H_2 and CO concentrations were increased and that of CO_2 was decreased. Similarly, an increase in temperature from 700 to 900 °C increases carbon conversion and gas yield, respectively, by 18.5% and 76.9%, with a corresponding reduction of 7.3% in gas calorific value (Lv et al. 2004). The higher char conversion at higher temperatures is mainly promoted by endothermic Boudouard and char steam reforming reactions. The hydrogen concentration in producer gas increased with temperature to a maximum of 45% at 950 °C and decreased thereafter. The decrease in H_2 concentration beyond 950 °C (at higher temperatures) is attributed to the promotion of WGS reaction in the reverse direction justified by Le Chatelier's principle (Gai et al. 2016; Niu et al. 2017). The influence of temperature on calorific value depends on whether the process is autothermal or allothermal. In the former, the calorific value degrades with temperature as higher temperature demands enhanced combustion, leading to a reduction in H_2 and CO, and consequent increase in CO_2 and N_2 (Wu et al. 2009). On the other side, being energy-intensive, indirect heating or allothermal operation can alleviate the problem economically if heat is supplied from an external renewable source. Apart from the merits of high-temperature gasification, elevated temperature promotes the melting of biomass ash with alkali metals and leads to agglomeration, sintering, corrosion, and clinkering (Wang et al. 2008). Also, higher operating temperature demands higher equipment costs and advanced operational strategies.

9.6.3 Pressure

Based on the operating pressure, gasifiers can be distinguished as atmospheric and pressurized gasifiers. Gasification at elevated pressure can decrease the yield of char by promoting char conversion. Mixed observations were made by researchers regarding the effect of pressure on tar yield. A decrease in syngas tar content in pressurized biomass gasification was reported by Wang et al. (2008). On the contrary, an experimental investigation of fluidized bed gasifiers by Mayerhofer et al. (2012) reported an increase in tar content when pressure is increased in the range of 0.1–0.25 MPa. Higher second law efficiencies of pressurized gasification with feeble variation in syngas calorific value and yield were identified by Motta et al. (2018). However, pressurized gasification is preferred for downstream applications that demand high-pressure syngas such as engines and turbines. An increase in overall turbine efficiency by 52.17% is observed when gasification pressure is increased from 1.013 to 4 bar (Fryda et al. 2008). However, pressurized reactors are preferred only to industrial-scale gasification units owing to their operational complexities and cost.

9.6.4 Residence Time

The quantity and configuration of tar generated during gasification are significantly affected by residence time, the mean time for which feedstock particles are retained inside the gasifier. An increase in residence time reduces oxygen-containing compounds as well as compounds with one and two aromatic rings, with a corresponding increase in compounds with three and four aromatic rings. An increase in residence time increases the extent of completion of all reactions, especially for heterogeneous reactions with a limited rate like char gasification (Martin-Sanchez et al. 2017). Thus, an increase in residence time promotes char conversion and improves syngas yield with lower tar content. However, the initial increase in the yield of gas constituents, such as H_2, CO, and CH_4, got stabilized beyond a specific residence time, with insignificant temporal change thereafter, as the reactions approach completion (Guan et al. 2016). Based on the design, fixed bed gasifiers can have more residence time whereas, in a fluidized bed reactor it is decided by the minimum fluidization velocity (Agu et al. 2019). A smaller biomass particle size is preferred for reactors such as entrained gasifiers with a lesser residence time of the order of 1–2 s to ensure the entire gasification within the stipulated residence (Zou et al. 2018). So, an appropriate residence time should be selected to balance the gas yield with gasification efficiency and downstream application requirements (Cao et al. 2020). This can be achieved with the proper design of reactors and forced draft units (blower or fan) associated with the same.

9.6.5 Equivalence Ratio

Equivalence ratio (ER) is the dimensionless representation of actual air supplied to gasification, compared to the corresponding stoichiometric requirement, given by Eq. (9.2). ER is the parameter that significantly influences the producer gas quality, especially in autothermal air and air-steam gasification. In an autothermal reactor, a supply of sufficient air is required to maintain the required gasifier temperature through partial oxidation of feedstock. Hence, smaller ER values lead to lower gasification temperature (Lv et al. 2004), leading to lower conversion efficiency and gasification performance degradation, as discussed in Sect. 9.6.2. On the other hand, higher ER leads to the oxidation of char and tar to CO_2 instead of converting them to combustible constituents such as H_2, CO, CH_4, and other lighter hydrocarbons. Thus, the shifting of the process from gasification to complete combustion adversely affects the producer's gas calorific value (Mansaray et al. 1999). Moreover, the N_2 contained in the supplied air dilutes the producer gas, thereby, significantly reducing its energy content. So, for better gasification performance, an optimum ER ranging between 0.2 and 0.4 should be maintained based on the other performance parameters (Narváez et al. 1996). Lv et al. (2004) varied ER from 0.19 to 0.27 in air-steam biomass gasification to analyze the influence of ER on producer gas calorific value and yield. During the initial variation of ER from 0.19 to 0.23, the lower calorific value and gas yield is increased in the ranges of 8.82–8.84 MJ/Nm^3, and 2.13 to 2.37 Nm^3/kg, respectively. On the further increase of ER, from 0.23 to 0.27, calorific value and gas yield is decreased to 7.3 MJ/Nm^3 and 1.9 Nm^3/kg, respectively. This is attributed to enhanced oxidation of combustible constituents such as H_2, CO, and CH_4, and consequent increase in CO_2 composition.

Thus, an ER of 0.23 is proposed as the optimum value for biomass gasification. Similar studies were carried out by other researchers to explore the effect of ER on the gasification process. Parallel observations were made for syngas calorific value with tar reduction by Narváez et al. (1996) when ER is varied from 0.25 to 0.45. An ER of 0.26 is identified as the optimum value for maximizing hydrogen concentration in the syngas. In another comparable work, Skoulou et al. (2008) observed the shifting of CO enhancement to CO degradation when ER is increased from 0.2 to 0.4. An ER corresponding to 0.2 is revealed as the optimal value for maximum H_2 yield. So in biomass gasification, an ER has to be selected to convert feedstock to fuel gas rather than feed stock to flue gas.

9.6.6 Steam to Biomass Ratio

Steam to biomass ratio (SBR) (defined in Eq. 9.3) is the predominant parameter that governs H_2 yield in biomass gasification. It is the dimensionless representation of quantitative steam addition with respect to that of the biomass. H_2 and CO_2 concentration in producer gas increase with steam addition and that of CO and hydrocarbons decreases. The enhancement of H_2 and CO_2 concentration is mainly because of the WGS reaction and steam reforming of tar. With the availability of excess steam, the CO formed is in turn consumed in the water gas shift reaction for the further improvement of H_2 and CO_2 concentration (Lv et al. 2004). Apart from the advantage of higher H_2 concentration, an increase in incombustible CO_2 with steam addition leads to inferior gas quality and greenhouse gas emissions. Moreover, steam generation is energy-intensive (requires external heat addition) and steam injection reduces the gasification temperature, adversely affecting the gasification performance. Thus, an optimum SBR value should be maintained for higher gasification efficiency with low carbon emission. Several studies reported the influence of SBR on producer gas attributes and tar yield. Tar content in the gas is reduced with an increase in steam addition (Mayerhofer et al. 2012; Song et al. 2012). A decrease in tar yield by 55.8% with lower aromaticity is reported when SBR is increased from 0.49 to 2.66 (Qin et al. 2015). Excessive SBR in the range of 0.35–4.04 reported a reduction in gas yield, calorific value, and carbon conversion due to a drop in gasification temperature (Lv et al. 2004). In steam biomass gasification, H_2 concentration is increased by 20% with an increase in SBR from 0 to 0.5, the variation in concentration being insignificant beyond an SBR of 0.5 (Cao et al. 2020). The addition of an oxidant in the form of air or oxygen with steam makes the process autothermal, with required gasification temperature, with a compromise in H_2 and CO concentration (Gil et al. 1997). The higher CO_2 concentration associated with steam addition can be reduced by using CO_2 sorbents like CaO. CaO sequestrates CO_2 to form solid $CaCO_3$ through a carbonation reaction, given by Eq. (9.5), thereby improving H_2 concentration in the producer gas (Rupesh et al. 2016).

$$\mathrm{CaO} + \mathrm{CO_2} \rightarrow \mathrm{CaCO_3} \tag{9.5}$$

These operating parameters take a pivotal role in the design, development, and performance prediction of gasification systems. Further improvement in gas quality, yield, and H_2 concentration can be achieved by using different catalysts to enhance steam reforming of char and tar.

9.7 Need for Catalytic Biomass Gasification

As mentioned in Sect. 9.5, tar is an undesirable and unavoidable by-product of thermochemical biomass conversion, which significantly reduces the heating value of synthesis gas. It can be commercially converted to non-condensable and simpler combustible constituents by two methods (1) thermal cracking and (2) catalytic cracking. Thermal cracking is the splitting of complex hydrocarbon tar molecules into simpler ones by heating the product gas above 1100 °C. This additional heat required is either supplied from an external source or internally generated by providing more oxidizer, making the process energy-intensive and reducing the syngas quality, respectively. On the other hand, catalytic cracking (hot syngas cleaning) is the process of simultaneous cleaning and quality upgradation of raw gas in the presence of a catalyst (Basu 2010). The cleaning and quality improvement are mainly due to compositional upgradation of the gas achieved by reforming higher hydrocarbons (tar) to simpler gaseous constituents like hydrogen and carbon monoxide (Sutton et al. 2001). The presence of catalysts mainly reduces the activation energy of the tar cracking reactions, thereby achieving the reactions at lower temperatures. Generally, in catalytic cracking, the tar in the vapor phase is reformed to H_2 and CO using steam (Eq. 9.6), carbon dioxide (Eq. 9.7), or both. Catalysts can also enable the reforming of methane in the gas, using steam (Eq. 9.8) and carbon dioxide (Eq. 9.9), especially when the desired product is syngas (a mixture of H_2 and CO).

Steam reforming (tar)

$$C_nH_m + nH_2O \rightarrow \left[n + \frac{m}{2}\right] H_2 + nCO \tag{9.6}$$

Dry reforming (tar)

$$C_nH_m + nCO_2 \rightarrow \frac{m}{2} H_2 + 2nCO \tag{9.7}$$

Steam reforming (methane)

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{9.8}$$

Dry reforming (methane)

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{9.9}$$

Thus, catalytic gasification can upgrade the product gas quality and yield by transmuting undesirable tar to syngas constituents with lower energy expenditure. The different types of catalysts in biomass gasification and their characteristics will be discussed in Sect. 9.8.

9.8 Types of Catalysts

Catalysts of biomass gasification can be broadly classified based on their use and composition. Based on use, the catalyst can be identified as primary catalysts and downstream or secondary catalysts. Primary catalysts are either present in the reactor bed where biomass is added, or it is mixed with the biomass before feeding to the reactor, as in a fluidized bed gasifier. Thus, primary catalysts are mainly meant for promoting the gasification process and reducing tar. Whereas, secondary catalysts are mainly provided in a separate secondary reactor downstream of the reactor to promote reforming of tar and CH_4, thereby increasing syngas yield (Chan and Tanksale 2014a).

9.8.1 Natural Mineral Catalysts

Mineral catalysts are compounds that contain oxides of metals like aluminum, calcium, iron, magnesium, etc.

9.8.1.1 Dolomite

Dolomite ($MgCO_3{\cdot}CaCO_3$) is a cheap and easily available compound that serves as both a primary and secondary catalyst. Constitutionally distinct dolomites can exist based on their geographical origin. The comparative analysis of the catalytic activity of different dolomite variants was conducted by Narváez et al. (1996) and found that Norte and Seville variants, respectively, have the highest and lowest tar conversion of 95% and 77%. Higher syngas yield was obtained from variants with larger Fe_2O_3 content and pore size. This is due to the promotion of WGS reaction and tar cracking by the Fe content, and larger surface area contributed by the porous morphology of the catalyst. The porosity and reactivity of dolomite can be further improved by calcination above 900 °C, as the oxides formed can reduce tar by enhancing steam and dry CO_2 reforming reactions. The content of CaO and MgO in dolomite is an indirect measure of its tar cracking efficiency, the presence of MgO also retards the catalyst deactivation due to coking. The H_2 in the syngas is improved to 20–25% when dolomite is used in bed (Miyazawa et al. 2006). Calcined dolomite fails to reform methane even though it can achieve tar conversion completely. Apart from the tar reforming capability, fragmentation due to thermal shock, attrition, and elutriation limit the use of dolomite.

9.8.1.2 Limonite

It is a mineral in powdered form rich in FeOOH. The iron content in limonite (Fe_2O_3) improves its acceptance as a catalyst in gasification. On increasing the temperature to 673 K, raw limonite is reduced to Fe_2O_3, which exhibits high activity towards tar reforming (Li et al. 2007). This reduced limonite generates a maximum gas yield of 46.9 mmol/g. On further temperature rise, at 700 °C, H_2 rich gas yield of 74.1 mmol/g can be attained when steam is supplied. On the other hand, calcinated limonites under a steam environment, hinder carbon deposition and improve syngas production (Ren et al. 2019). But impurities in the form of talc mineral, dispersed in the limonite in powder form, limit its usage.

9.8.1.3 Olivine

Olivine ($(Mg, Fe)_2SiO_4$) is a non-porous silicate mineral containing magnesium and iron (Rapagnâ 2000; Corella et al. 2004; Devi et al. 2005a). Its outstanding mechanical strength, along with its non-toxic and attrition resistance, make it an excellent choice for bed material in fluidized bed gasifiers (Rapagnâ 2000; Pfeifer and Hofbauer 2008; Fredriksson et al. 2013). Apart from the limited tar reforming due to the non-porous structure, the presence of Fe and magnesite content imparts moderate catalytic activity to olivine (Devi et al. 2005a; Soomro et al. 2018). For an increase of temperature from 700 °C to 820 °C, the tar content is reduced approximately by a factor of 10 accompanied by a 1.5 times increase in the dry gas yield. Even though pure olivine is insensitive to methane reforming, olivine combined with nickel activates the same (Devi et al. 2005b). When used as in-bed catalysts, Ni-olivine combination can exhibit a tar reduction of 75% at 850 °C (Pfeifer and Hofbauer 2008). Deactivation of Ni-olivine catalyst at a high weight hourly space velocity of benzene can be mitigated by combining nickel with olivine powder and calcium aluminate cement to form nickel-modified olivine (Ni/MO) (Yang et al. 2019).

9.8.1.4 Calcite and Magnesite

Calcite ($CaCO_3$) and magnesite ($MgCO_3$) are naturally existing carbonates of calcium and magnesium. After calcination, calcined calcite (CaO) and magnesite (MgO) can be used as the catalyst for tar reduction. Delgado et al. (1997) made a comparative study of calcined dolomite, calcined magnesite, and calcite as the downstream catalyst for reforming raw producer gas from a fluidized bed gasifier. The catalytic reactivity, tar reduction capability, and gas yield were found to increase, respectively, for calcined dolomite, calcined magnesite, and calcined calcite. In steam naphthalene gasification, 75% carbon conversion is achieved with a mixture of CaO and MgO (in the ratio of 1:9), which is 25% and 17% higher than that with pure MgO and CaO, respectively (Alarcon et al. 2021).

9.8.2 Alkali Metal Catalysts

Alkali metals (Li, Na, K, Rb, etc.), alkali earth metals (Be, Mg, Ca, Ba, etc.), and alkali metal carbonates (K_2CO_3 and Na_2CO_3) together constitute the alkali metal catalysts (Dayton 2002). They exhibit dual catalytic function thereby capable of enhancing syngas yield and tar reforming. Alkali metal catalysts are considered to be the active catalytic components that promote char gasification, steam-tar reforming, hydrocarbon reforming, and water gas shift reactions; however, alkali earth metal has a predominant role in enhancing WGS reaction (Long et al. 2012). Bio-char that contains alkali earth metals formed during the steam-tar reforming can be used as a catalyst for ash treatment and value-added syngas production (Ren et al. 2019). The rate of biomass char gasification can be further increased by combining alkali carbonates with active metal-based catalysts (Baker and Mudge 1984). Complete elimination of tar and a higher yield of H_2-rich gas ($H_2/CO > 10$) can be obtained from biomasses like wood, sawdust, castor stalk, etc. with K_2CO_3 supported Al_2O_3 or SiO_2-Al_2O_3 catalysts (Mandal et al. 2019). The usage of alkali metals is constrained by particle agglomeration due to quick evaporation at elevated temperatures and catalytic activity loss. Moreover, the recovery difficulties and higher ash content make alkali metal catalysts less desirable for commercial use (Dayton 2002).

9.8.3 Metal-Based Catalysts

9.8.3.1 Ni-Based Catalysts

The higher effectiveness of nickel in tar reforming and quality improvement of syngas through methane reforming, water gas shift, and reversing ammonia makes it the most significant catalyst for biomass gasification (Guan et al. 2016). The capability of a nickel catalyst to reform methane makes it superior to naturally occurring mineral catalysts. Nickel catalysts can find its application as the primary catalyst in the gasifiers (in situ) and as a secondary catalyst in the downstream reactor (in post gasification). As a primary catalyst, nickel can perform both tar reforming and syngas cleaning, eliminating downstream reactor and extra heating (Chan and Tanksale 2014a). But in this case, the catalytic activity cannot be prolonged as a result of deactivation due to carbon formation, sulfur poisoning, and sintering (Baker and Mudge 1984). This can be addressed by using the same as a secondary catalyst in the downstream rector, thereby extending the spell of catalytic activity by minimizing coke formation. Further coke formation can be minimized by using catalytic support. Better dispersion of nickel with other supporting compounds enhances its catalytic activity. Generally, Ni is supported by Al_2O_3, olivine, ZrO_2, TiO_2, CeO_2, MgO, SiO, MgO, CaO, K_2O, and Fe_2O_3 to reduce carbon formation and these supported Ni catalysts are added with second metal additives for further improvement in stability and activity (Świerczyński et al. 2007).

The coke formation reactivity of steam reforming naphtha catalysts, UCI G90-C and ICI 46-1, with 15% Ni on alumina support, towards tar, is in the order benzene > toluene > anthracene > pyrene > naphthalene (Coll et al. 2001). For G-90B, a ceramic-supported 11% nickel catalyst, the methane reformation is tremendous methane above 700 °C. Moreover, at 800 °C, 86% of the benzene and 97% of the naphthalene reformation is achieved (Kinoshita et al. 1995).

9.8.3.2 Fe-Based Catalysts

Iron species show excellent activity towards tar conversion (Torres et al. 2007). Metallic iron (Fe^o) is the most active iron species metallic iron, FeO, Fe_2O_3, and Fe_3O_4 in toluene and benzene hydrogenation due to its C-C bond dissociation capability (Nordgreen et al. 2006). Whereas, oxides of Fe^3 and Fe^2 species exhibit the most catalytic reactivity in the steam phenol reforming (Richardson et al. 2012).

In addition to tar conversion, the reduced form of Fe_3O_4 further enhances the significance of Fe-based catalyst in biomass gasification by promoting WGS reactivity between 700 and 900 °C, (Newsome 1980). The performance similarity exhibited by 20 wt.% Fe with olivine to that with 3.9 wt.% Ni with olivine facilitates the possibility of replacing the usage of Ni with less toxic Fe in fluidized beds. Even though the Fe-olivine catalyst can prevent coking, it leads to a loss of about 5 wt.% of iron due to a drop in its reducible form, limiting its activity (Virginie et al. 2012). NH_3 decomposition is an added feature of Fe-based catalysts. Fe catalyst can accomplish a maximum NH_3 decomposition of 87% fixed bed secondary reactor at 900 °C (Hongrapipat et al. 2012).

9.8.3.3 Metal and Metal Oxide Catalysts

The catalytic activity of Ni-based catalyst can be improved by assisting it with noble metals such as Pt, Pd, Mn, Rh, and Ru, metal oxides (CaO, Al_2O_3, MgO, La_2O_3, CeO_2, TiO_2, etc.) or bimetal oxides (Ru/CeO_2, $n(CeZr)_xO_2$, etc.) (Ren et al. 2019). Compared to Rh, Ru, and Pd, Pt exhibits superior methane reforming in steam gasification due to its better alloying with Ni (Nishikawa et al. 2008). Noble metal-supported Ni inhibits sintering and maintains steady catalytic activity while alloying of Fe with Ni suppresses coke deposition. In general, Ni supported with metal oxides promotes steam reforming of tar, lifetime and overall catalytic activity conversion up to 99.95% and Al_2O_3-supported Ni/MgO catalyst can achieve a tar conversation of 99.95% in the range 720–760 °C (Ren et al. 2019, 2020). The activity order of metal oxide supports like MgO, CeO_2, ZrO_2, etc. is $Ni/CeO_2 - ZrO_2 > Ni/\gamma\text{-}Al_2O_3 > Ni/CeO_2 > Ni/ZrO_2$ (Ren et al. 2020). Further improvement in tar reforming can be attained by combining support material with another metal. A higher benzene conversion is attained at 850 °C, using bimetallic catalyst Ni/ZrO_2 with La, Sr, and Fe which in turn improves tar conversion. (Keller et al. 2016). Furthermore, a bimetallic $MgAl_2O_4$-supported IrNi catalyst exhibits superior stability during steam reforming of methane and tar due to a substantial reduction in coking and sintering (Dagle et al. 2016).

9.8.4 Zeolites

Zeolite, a crystalline aluminosilicate material occupying ions and water molecules within the cavities in its structural framework, comes under the category of fluid catalytic cracking catalysts, which have the potential to eliminate tar. Zeolites are acidic in nature with better hydro-thermal stability, good nitrogen, and sulfur resistance, low cost, and easy regeneration ability (Buchireddy et al. 2010). Zeolites usually find their application as supports to Ni-based or other metal-based catalysts in tar reforming. Among the different variants of zeolites like Zeolite Y, Zβ, ZSM5, ZY-5.2, the variants ZY-5.2 and Zeolite Y show better naphthalene conversion due to their acidic nature and larger pore size, respectively. But, nickel-supported zeolite (Ni/ZY-80) can attain a naphthalene conversion rate of 99% with prolonged activity (Kathiraser et al. 2016). Moreover, the addition of Fe or Ni in mesoporous SBA-15 catalyst improves the formation rates of H_2, CO, CO_2, and CH_4 whereas the addition of Ni in mesoporous MCM-41 can achieve the lowest coke deposit of 7 wt% of the catalyst, thereby, mitigating the major limitation of zeolite (Wu and Williams 2011a).

9.8.5 Activated Char Catalysts

Bio-char, a gasification residue concentrated with metals like K and Ca contributed from the base biomass feedstock, can act as a catalyst. These alkali or alkaline earth metals can promote WGS reaction and enhance tar reforming through H_2O absorption (Hu et al. 2015). Moreover, tar reforming contributed by some functional groups containing oxygen in the bio-char makes it a suitable catalyst for biomass gasification (Shen et al. 2015). Furthermore, the tar removal efficacy of bio-char can be improved up to 97% by incorporating it with Ni (Wang 2013). A better gas yield of nearly 90 mg per g of biomass and carbon balance of 98% is attained using Ni dispersed brown coal char at a lower temperature range of 400–550 °C (Li et al. 2010). Additionally, a more potent way of acquiring high-quality syngas is by combining char with Ni-Co catalyst, Ni-Co altering the quality and rate of syngas. (Yang et al. 2019).

9.9 Comparison of Different Catalysts

This segment deals with the comparison of different catalysts discussed in Sect. 9.8.

9.9.1 General Comparison

Initially, a general comparison of natural mineral, alkali metal-based, metal-based, zeolite, and char catalysts are incorporated, as in Table 9.7.

9.9.2 Comparison of Gas Yield and Tar Conversion

The tar reforming capability of a catalyst improves the yield and quality of syngas. The following section depicts the comparison of gas yield and tar conversion from different catalysts.

Table 9.7 General comparison of various catalysts

Classification	Catalyst	Merits	Demerits	References
Natural minerals	Dolomite	• Cheap, • Higher tar conversion rate	• No methane reformation • Fragmentation, attrition, and elutriation	(Gil et al. 1997; Zhou et al. 2009; Ren et al. 2019)
	Olivine	• Mechanical strength • Non-toxic • Attrition resistance	• Limited tar reformation • Insensitive to methane reforming	(Rapagnâ 2000; Devi et al. 2005a; Pfeifer and Hofbauer 2008)
	Limonite	• High tar reforming • Inhibit coke formation	• Presence of impurities	(Li et al. 2007, 2010)
Alkali metal-based	Alkali metal	• Enhances water gas shift reaction • Higher yield of H_2 rich gas	• Particle agglomeration • Higher ash content	(Dayton 2002; Long et al. 2012)
Metal-based	Ni-based	• Higher tar reforming • Ability to reform methane • Enhances water gas shift reaction • Can be used as both primary and secondary catalyst	• Coking, sulfur poisoning, sintering	(Baker and Mudge 1984; Guan et al. 2016)
	Metal and Metal oxide	• Ability to reform methane • Higher benzene conversion • Suppress coking and sintering	• Expensive • Deactivation due to sulfur poisoning	(Nishikawa et al. 2008; Ren et al. 2019)
Zeolite	Zeolite	• Better hydrothermal stability • Easy regeneration	• Intricacy in synthesis	(Buchireddy et al. 2010; Ren et al. 2019)
Char	Bio-char	• Ample availability • Obtained as a by-product of gasification • Promotes water gas shift reaction	• Susceptible to gasification	(Li et al. 2010; Yao et al. 2016)

Table 9.8 Comparison of natural mineral-based catalysts on gas yield

Catalyst	Reaction temperature (°C)	Gas yield (%)	References
Pt -Ni/dolomite	800	79.19	Chaiprasert and Vitidsant (2009)
Fe-Ni/dolomite	800	78.12	
Co-Ni/dolomite	800	49.53	
Ni/dolomite	770	69.1	Sato and Fujimoto (2007)
Natural dolomite	800	44.67	Islam (2020)
Calcined dolomite	800	61.33	
Natural olivine	800	36.60	
Calcined olivine	800	46.67	

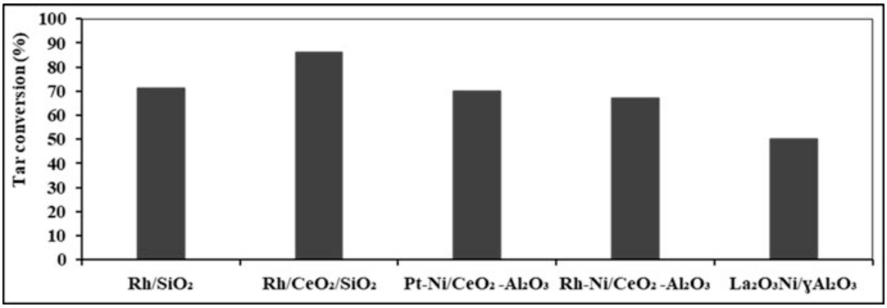


Fig. 9.10 Comparison of noble metal-based catalysts on tar conversion (Tomishige et al. 2004)

9.9.2.1 Natural Mineral-Based Catalysts

The comparison of natural mineral catalysts on gas yield is given in Table 9.8. It is clear that the tar reforming capability of both natural dolomite and natural olivine is improved when calcinated. Consequently, the gas yield is increased by 37.2% and 27.5%, respectively, for calcined dolomite and calcined olivine when compared with their natural form. Thus, the acceptance of calcined dolomite interns of gas yield is 31.4% more than that of calcined olivine. Moreover, the tar reforming as well as gas yield of dolomite can be augmented by combining it with metals like Ni, Fe, Pt, Co, etc. The addition of Fe and Pt with Ni/dolomite contributes comparable improvement in gas yield, with the former prompting coking and the latter being expensive.

9.9.2.2 Metal-Based Catalysts

The comparison of noble metal-based catalysts on tar conversion is represented in Fig. 9.10 CeO_2 has a vital role in enhancing tar conversion in a noble metal-based catalyst. Addition of CeO_2 in Rh/SiO_2 increased tar conversion by 21.12%. The tar

Table 9.9 Comparison of nickel-based catalysts on gas yield

Catalyst	Reaction temperature (°C)	Gas yield (%)	References
Ni/MgO	800	81	Xu et al. (2010)
NiO-MgO	800	47	Wang (2013)
NiO/MgO	850	51	Dong et al. (2017)
Ni-Mg-Al	800	52.9	Nahil et al. (2013)
Ni-Mg-Al-CaO	800	54	Nahil et al. (2013)
Ni-Mg-Al-Quartz	800	48.6	Nahil et al. (2013)
Ni/Al catalysts	650	77	Bimbela et al. (2013)
Ni/Al_2O_3	850	53	Wu and Williams (2011a)
Ni ZnAlOx	800	48	Ren et al. (2019)
Co-Ni/Al_2O_3	650	68	Nishikawa et al. (2008)
Ni–Ce/Al_2O_3	900	71	Fu et al. (2014)
Ni/CeO_2-Al_2O_3	650	82	Efika et al. (2012)
Ni/CeO_2–ZrO_2	800	70	Feng et al. (2017)
Pt-Ni/CeO_2-Al_2O_3	650	82	Efika et al. (2012)
Rh-Ni/CeO_2-Al_2O_3	650	83	Efika et al. (2012)
Ni/La_2O_3-αAl_2O_3	700	96	Remiro et al. (2013)
Ni- Fe K/dolomite	800	78.12	Chaiprasert and Vitidsant (2009)
Ni/MCM-41	800	51	Wu et al. (2013)

conversion capability of CeO_2/SiO_2 supported catalyst increases in the order Pd < Pt < Rh.

A significant variation in the reforming potential of catalysts can be achieved by combining different catalysts in various proportions and permutations. As the most effective tar reforming catalyst prone to easy deactivation, nickel is combined with other metal and mineral compounds to enhance its properties. The impact of various combinations with Ni catalyst is emphasized in Table 9.9.

The addition of magnesium to nickel improves the mechanical strength, attrition resistance, and porous structure of the catalyst considerably, with a modest reduction of 14% in gas yield (Sutton et al. 2001). The oxides of Mg improve the catalyst stability by increasing the metal dispersion of Ni and thereby evading the nickel aggregation. A substantial reduction in coke formation is detected with improved water absorptivity and OH surface mobility by adding magnesium (Wu and Williams 2011a). The compounds of Mg find its application as a CO_2 sorbent despite being used as primary and secondary catalysts (Arnold and Hill 2019). Dolomite is a potential mineral source that can practically incorporate Mg with Ni to form catalyst combinations with the aforementioned merits.

Aluminum and aluminum oxides are the most used catalytic support for Ni due to their excellent steam reforming reactions and initial catalytic activities amidst a wide range of impurities. Rapid deactivation faced by Al_2O_3 can be retarded by keeping the catalytic weight to biomass flow ratio higher than 0.65. While $NiAl_2O_3$ catalyst with 33% Ni shows high gas yield and tar reforming stability, Ni-Al catalyst with 28% Ni exhibits better H_2 production and reaction time (Wu and Williams 2011a). Further improvement in catalytic activities of Al can be achieved by supporting it with alkaline earth oxides, natural mineral catalysts, rare metal oxides, etc. An excellent tar conversion of more than 99% with higher gas quality can be attained by supporting Ni/Al with LaO_3 (Zhang et al. 2018a, b). The presence of Mg in Ni/Al improves the catalytic resistance to attrition and sintering. However, K has only a feeble effect on catalytic activity compared to Mg. Also, oxides of La and Co can significantly enhance the stability of the catalyst along with increased carbon conversion, reduced coke formation, and a higher syngas yield when used as Ni/Al support (Wu and Williams 2011b). A tremendous improvement in H_2 yield with higher tar conversion and coking resistance can be attained by adding Ce to Ni/Al catalysts (Nishikawa et al. 2008). Even if the addition of noble metals like Pt, Ru, Ir, etc., significantly contributes towards the stability of the nickel sites and reduction in coke formation, the effect of Pt is commendable over the others (Wu and Williams 2011a).

In general, the oxides of Zr and Si improve H_2 yield from gasification without appreciable tar reduction. However, there it with Ni catalyst inhibits coke formation. Similarly, Ca with Ni imparts increased H_2 yield, CO selectivity, and decreased CO_2 selectivity (Inaba et al. 2006). On the other hand, the presence of Fe in Ni catalyst improves the WSG reaction and hence the gas yield.

The addition of dolomite with Ni shows excellent catalytic activity and stability for tar reforming. Among the various Ni/dolomite variants, the catalyst with 15% Ni exhibits the optimum tar reforming (Srinakruang et al. 2006). The coking resistance of Ni/dolomite was found to be superior to Ni/Al_2O_3 and Ni/SiO_2 (Chaiprasert and Vitidsant 2009). In addition to choking resistance, the inhibition of sulfur poisoning makes Ni/dolomite unique among the other catalysts. Furthermore, MgO and CaO in calcined dolomite can act as potential CO_2 sorbent along with its excellent tar reformation.

The well-defined porous structure, significant surface area, and high thermal stability of zeolite improve the reforming and thermal cracking of hydrocarbons when used with Ni. Zeolite support in Ni catalyst reduces the tar content with the penalty of coke deposit. The coke formation owing to the acid nature of the catalyst can be inhibited by introducing metals like Ce, Mg, etc. (Wu and Williams 2011a).

A comparative assessment of commercial nickel catalysts on tar reforming is demonstrated in Table 9.10. In most commercial catalysts, the Ni O content is maintained below 25% to achieve better tar reforming. In addition to the oxides of Mg, Ca, Si, and K, Al_2O_3 has a prominent fraction in all commercial nickel catalysts. Along with the percentage fraction of the various constituents, reaction temperature also influences the tar conversion rate. The commercial catalysts experience good stability at a higher temperature which can be prolonged to around 60 h (Caballero et al. 1998). Moreover, the coke removal rate in this catalyst is higher than the coke formation rate at high temperatures. Furthermore, using steam or CO_2 gasification, deactivated catalysts can be regenerated with much ease (Wang 2013).

Table 9.10 Tar conversion of commercial nickel-based catalysts

Catalyst	Composition	Reaction temperature (°C)	Tar conversion (%)	Reference
BASF—G1-25/1	(25% NiO- 8% CaO-66%Al_2O_3-1% K_2O)	785–850	98–99	Chan and Tanksale (2014b)
BASF G1-50	(20% NiO- 11% MgO-16% CaO-32%Al_2O_3-7% K_2O – 32% $MgAl_2O_3$)	660–800	89–99	Corella et al. (2004)
Haldor Topsoe—R-67	(15% NiO-0.1% SiO_2-85% K_2O)	780–840	95–100	Corella et al. (2004)
ICI Katalco—46-1	(22% NiO-11% MgO-13% CaO-26% Al_2O_3- 16%SiO_2-7% K_2O)	700–875	73–100	Corella et al. (2004)
BASF—G1-25S	(12–15% NiO->70% Al_2O_3)	785	88–97	Caballero et al. (1998)
Haldor Topsoe—RKS-1	(15% NiO-85% K_2O)	785–800	92	Caballero et al. (1998)
Haldor Topsoe—R-67-7H	(15%NiO-85% $MgAl_2O_4$)	690–780	99	Mullen and Boateng (2008)
Sud Chemie—G-90LDP	(14% NiO-13% CaO-73%Al_2O_3)	850–900	99	Pfeifer and Hofbauer (2008)
Sud Chemie—G-90EW	(14% NiO- 10% CaO-65% Al_2O_3)	850–900	99	Pfeifer and Hofbauer (2008)
Sud Chemie—G-90B	14% NiO-6%CaO-76%Al_2O_3	650–900	99	Pfeifer and Hofbauer (2008

Pertaining to the aforementioned comparison, it can be presumed that Ni, the best tar reforming catalyst under dry and steam atmosphere owing to its excellent catalytic activity towards tar reduction at low cost, is the most accepted catalyst in biomass gasification. But, rapid catalytic activity loss due to carbon deposition confines its application in biomass gasification. Even though doping Ni catalysts with alkaline metals, noble metals or dolomite can influence its overall catalytic performance, agglomeration of alkali metals and sulfur poisoning of noble metals enables the coke resistant dolomite to the more suitable support for Ni catalysts. Thus in a nickel dolomite combination catalyst, the low methane reforming of dolomite and rapid coking of Ni are mutually resolved due to the superior methane conversion and coke resistance of Ni and dolomite, respectively. Additionally, the CaO content in dolomite acts as a sorbent for noncombustible CO_2 there by improving the syngas quality. So a combination of Ni and dolomite can perform as an excellent tar reformer and CO_2 sorbent. Owing to imparting ample value-addition to syngas, Ni/dolomite is supposed to be the better choice among the biomass gasifying catalysts, which can be in the mixed or impregnated form (Di Felice et al. 2009; Xu et al. 2010).

9.10 Catalytic and Deactivation Mechanisms

Catalysts enhance the quality of syngas from gasification by reforming higher hydrocarbons and CH_4 into high-valued gas constituents without contributing any pollutants (Gao et al. 2020). This is mainly achieved by reducing the activation energy of reforming reactions, thereby lowering the consumption of gasifying medium. The effectiveness of a catalyst rests on its structure, elemental constitution, reaction mechanism, deactivation resistance, and stability. The catalytic cracking mechanism for tar is a series of (Ren et al. 2019).

- Dissociation of hydrocarbons and CH_4, and absorption on the metal site.
- Dehydrogenation of hydrocarbons and CH_4.
- Oxidation of hydrocarbon through OH radicals derived from hydroxylation of water.
- Production of syngas, CH_4, and light hydrocarbons.

9.10.1 Catalytic Mechanism

Due to the inherent intricacy of tar, the tar cracking mechanism may be proposed by considering it from two perspectives (i) as real tar and (2) as a tar model represented by toluene.

9.10.1.1 Reforming Mechanism of Real Tar Using Char Catalyst

Due to the concurrent involvement of acid, alkali, homogeneous and heterogeneous reactions, and catalytic and deactivation effects, the tar cracking mechanism is relatively perplexed. Deposition, dehydrogenation with soot generation, and soot gasification are the main reaction routes involved in the tar cracking mechanism with char, where the alkali-alkaline earth metal variants (AAEM) in the char influence the soot generation rate. In the tar cracking reactions, no further aromatics are formed from benzene and naphthalene, whereas lighter aromatics are formed from alkyl-atomic compounds. The tar components adsorbed at the char active sites, undergo polymerization, and release gaseous product leaving soot.

The H/O/OH-free radicals formed from the dissociated steam and carbon dioxide are adsorbed on the char active sites to initiate tar reforming. The catalytic tar decomposition is further enhanced with additional free radicals from the electron

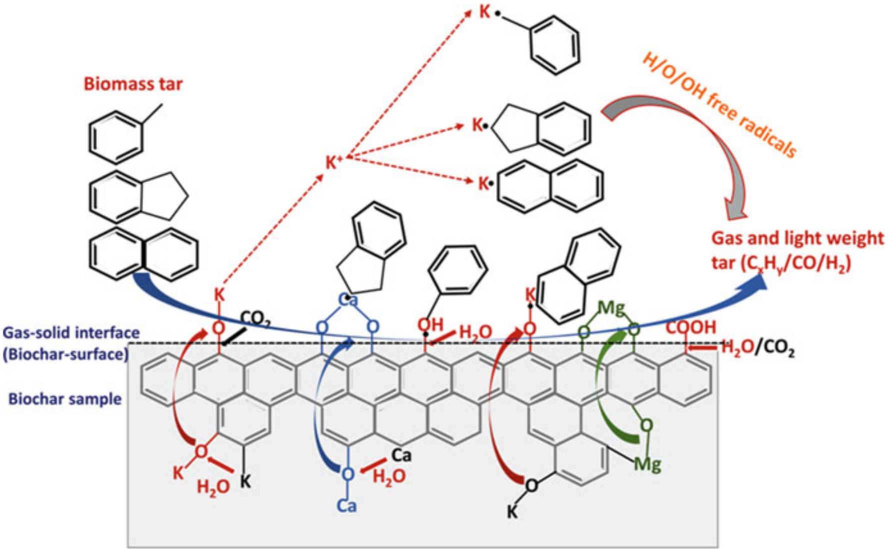


Fig. 9.11 Bio-char enabled tar cracking mechanism at 800 °C (Zeng et al. 2020)

pair shift towards small tar molecules, where H_2O and CO_2 dissociate the carbon bonds in smaller aromatic rings. The vacant sites resulting from this bond dissociation are again occupied by H/O/OH radicals, thus allowing many radicals into the char carbon structure. The AAEM species is bonded with the carbon element in the char through oxygen element forming AAEM-Oxygen bond (e.g., K-O bond shown). When tar is adsorbed, the AAEM-Oxygen bond is dissociated, due to the gasification reactions between H_2O, CO_2, and carbon, and the resulting AAEM species move to a solid-gas boundary, occupying the active sites on the fragmented tar. This AAEM species is further replaced by H/O/OH radicals thereby converting tar to lighter hydrocarbons and gas as shown in Fig. 9.11.

9.10.1.2 Steam Reforming Mechanism of Tar Model (Toluene)

In this section, the mechanism is discussed by representing biomass tar as toluene with LSNFO perovskite catalyst (Oemar et al. 2012). The mechanism is explained in three steps, namely (i) adsorption, (2) reaction, and (3) desorption as shown in Fig. 9.12. During adsorption, water present on the support site is dissociated to form adsorbed H and OH. This OH is then split to form adsorbed H and O, replacing the existing O in the support site. On the metal site, toluene (C_7H_8) is decomposed into adsorbed CH_2, and benzene (C_6H_6), followed by decomposition of benzene to C_2H_2. Subsequently, these CH_2 and C_2H_2 react with adsorbed oxygen on the support site to form CH_2O and C_2H_2O groups. The CH_2O gets further decomposed into CHO and H, and CHO is combined with available adsorbed oxygen to form H and

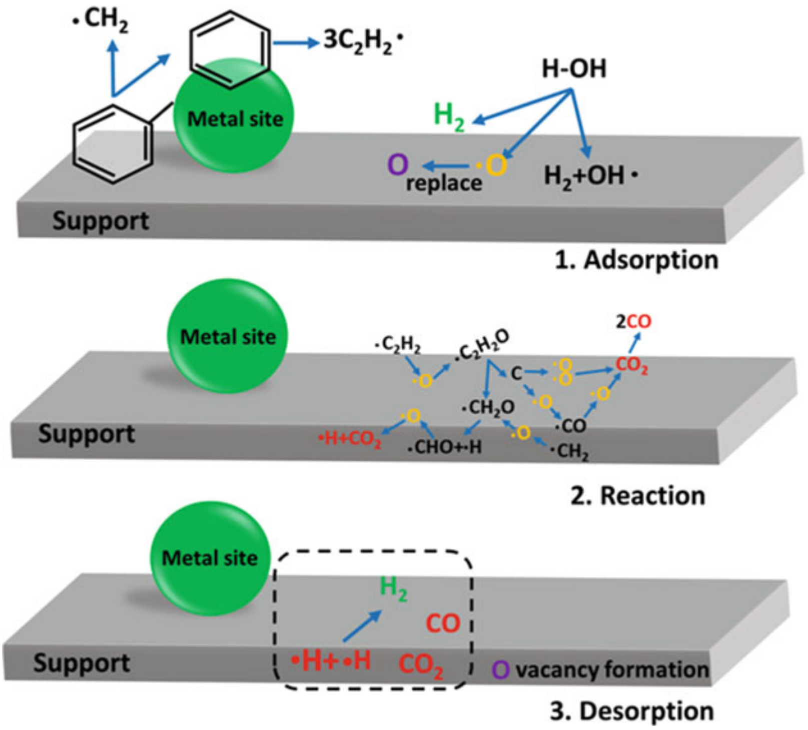


Fig. 9.12 Catalytic reforming mechanism of toluene

CO_2. The resulting free radicals of H combine to form hydrogen. On the other hand, C_2H_2O combines with the adsorbed oxygen to form CH_2O and C. Carbon further reacts with oxygen to form CO and CO_2. Finally, these resulting H_2, CO, and CO_2 desorb to form a support site for the gaseous phase.

9.10.2 Deactivation Mechanisms

Deactivation is the loss of catalytic activity over time due to usage. The loss associated with frequent replacement of catalysts can be minimized by using deactivation-resistant catalysts. Thus, a proper understanding of catalyst deactivation is inevitable in designing and developing deactivation inhabitant catalysts. The physical and chemical mechanism leading to the deactivation of tar cracking catalysts can be mainly classified into three, coking, sulfur poisoning, and sintering.

9.10.2.1 Coking or Coke Formation

It is the most common deactivation of catalyst encountered due to the deposition of coke or carbon on the active metal centers and/or pores on the catalyst, thereby reducing the catalytic activity by limiting the interaction between catalyst and reactants (Forzatti and Lietti 1999). Coking is due to the encapsulation of catalysts by carbonaceous deposits originating from the cracking or condensation of hydrocarbon or carbon monoxide and methane. The major reactions that promote coking are (Quitete and Souza 2017; Liu et al. 2019),

$$2CO \leftrightarrow C_{(s)} + CO_2 \tag{9.10}$$

$$CO + H_2 \leftrightarrow C_{(s)} + H_2O \tag{9.11}$$

$$CH_4 \leftrightarrow \ C_{(s)} + 2H_2 \tag{9.12}$$

$$C_nH_m \leftrightarrow nC_{(s)} + \left[\frac{m}{2}\right]H_2 \tag{9.13}$$

Amorphous and filamentous are the two variants of carbon deposition on catalysts. The formation of amorphous carbon leads to quick deactivation by encapsulating metal centers whereas, there is no rapid deactivation due to filamentous carbon unless a bulk deposit is formed, leading to reactor clogging (Tan et al. 2020). In general, calcined dolomite is deactivated by an amorphous variant but when calcined dolomite is loaded with Ni, filamentous carbon assumes deactivation.

The main factors that influence coking are the size of the active site, temperature, steam to carbon ratio (S/C) and tar composition. Size of metal particles that form the active site influence the deposition of carbon on the catalyst. Active metal sites with larger particle sizes are more vulnerable to carbon deposits. More carbon deposition was reported on Ni sites with bigger particle sizes when incorporated into MCN-41 mesoporous support (Wu et al. 2013). A similar observation is made when toluene is steam reformed with Fe-Ni/Palygorskite (Zou et al. 2018). An increase in temperature decreases coking, for instance, coking was completely absent beyond 750 °C (Islam 2020). S/C has a significant role in coking as the addition of steam enhances water gas shift reaction (2) and Boudouard reaction, thereby completely regenerating coked catalyst accompanied with improved gas quality (Quitete and Souza 2017). Improvement in hydrogen yield and reduction in carbon deposit was found in Ni/Al_2O_3 when steam to carbon ratio is increased (Cao et al. 2020). Tar composition determines the type of carbon formed on catalysts due to coking. Atomic carbon α-C, which readily reacts with steam, is formed by the reforming of phenol whereas, other forms of carbon β-C and γ-C, lesser reactive with steam, is resulted from naphthalene when Ni-Fe alloy combined with olivine is used as a catalyst for reforming (Meng et al. 2018). Also, filamentous and aromatic carbon is generated when the toluene benzene mixture and toluene naphthalene mixture is subjected to reforming in the presence of Ni catalyst.

Coking of a commercial catalyst can be depressed by selecting suitable catalytic composition and optimal operating conditions. Higher steam to hydrocarbon ratio and improved hydrogen partial pressure are used to restrain carbon-induced catalyst deactivation. The catalytic composition can also restrict coking as ions of alkali metals like potassium when integrated with catalyst catalyzes carbon deposit, thereby facilitating bed catalyst regeneration. Similarly, Pt/Al_2O_3 can be modified to $Pt\text{-}Re/Al_2O_3$ to attain prolonged aversion against coking.

9.10.2.2 Sintering

Sintering is a thermally initiated process leading to a reduction in active sites of supported and non-supported catalysts through surface modifications. Particle migration or coalescence and atomic migration are the sintering mechanisms for catalysts based on thermal diffusion of the catalyst constituents. In the former, two particles are transported along with the support, and their collision with each other leads to the formation of a bigger particle. Whereas, in atomic migration, a metal ion discharged by one particle is captured by another. For Ni, particle migration is predominant at temperatures less than 700 °C while at higher temperatures particle migration becomes more prevalent. Sintering reduces surface area and porosity and makes the active sites inaccessible for the reactants. The reverse of sintering, termed dispersion, is the phenomenon of reduction of particle growth due to O_2 and Cl_2 or both, due to the generation of oxides or chlorides of the metal followed by their splitting.

Sintering mainly depends on the temperature, atmosphere, carriers, promoters, and porosity (Bartholomew 2001; Morris and Bartholomew 2015). The sintering rate escalates exponentially with temperature notably in the presence of steam resulting in coarser and diverse particle sizes (Ochoa et al. 2018). Higher calcination and reaction temperatures favor thermal-driven metal growth and agglomeration. H_2 atmosphere promotes sintering in base metals whereas both O_2 and H_2 support the same in noble metal catalysts. Lower thermal stability and weak metal-carrier interaction promote the sintering mechanism. The thermal stability of metal with carrier improves in the order carbon $<$ silicon dioxide $<$ aluminum oxide. Unsupported CuO is subjected to sintering compared to supported CuO used for syngas reforming at 800 °C (Huang et al. 2013). Addition of promoters that increase (e.g., fluorine, lead, sulfur, oxides of barium, calcium) and decreases (oxygen, oxides of Ce, Ba, Ca) the metal mobility reduces sintering. The possibility of sintering impends when the pore size is comparable with that of metal crystallites. Thus, the tendency of catalyst sintering can be minimized by using thermally stable catalyst composition, avoiding metal-carrier interactions, proper choice of atmosphere and promoters.

9.10.2.3 Sulfur Poisoning

In general, poisoning is the degradation is catalytic activity resulting from firm chemical adsorption of impurities to the active metal sites from the feed stream. During thermochemical processing of biomass, the sulfur contained in the feedstock is converted to hydrogen sulfide which in turn converted to metal sulfide at the active metal sites. Consequently, the catalyst is deactivated as the active metal is encapsulated by inert metal sulfide, leading to deactivation due to sulfidation. Moreover, the lower thermal stability and better mobility of metal sulfides promote sintering. Especially, Ni-based catalysts are prone to this deactivation as hydrogen sulfide formed reacts with the Ni to form nickel sulfide.

$$\mathrm{Ni} + \mathrm{H_2S} \leftrightarrow \mathrm{NiS} + \mathrm{H_2} \tag{9.14}$$

The reaction is strongly influenced by temperature, above 900 °C nickel irreversibly combines with hydrogen sulfide, whereas at lower temperatures, sulfur forms only polysulfide that can be released easily in a sulfur-free environment (Hepola and Simell 1997). Adding oxygen or steam, or increasing temperature can successfully crack NiS formed, but the use of oxygen or steam leads to the formation of inert NiO or $NiSO_4$, an alternate source of deactivation (Li et al. 2007).

Apart from nickel, sulfur poisoning can also inhibit the reactivity of noble and transition metal-based catalysts. Sulfur poisoning reduced the activity of Rh–$LaCoO_3$ catalyst, used for tar reforming of syngas, due to the formation of Rh and Co sulfides (Ammendola et al. 2012). Deactivation of Co-based catalyst was also reported by Gao et al. (2020) due to inert cobalt sulfide formation

$$\mathrm{Co} + \mathrm{H_2S} \leftrightarrow \mathrm{CoS} + \mathrm{H_2} \tag{9.15}$$

Ammonia, potassium sulfate, potassium chloride, zinc chloride, and formulations of biomass-derived fly ash are the other compounds that can cause deactivation (Albertazzi et al. 2008). Normally, steps are taken to prevent or minimize sulfur poisoning as the poisoned catalyst is difficult to regenerate. One fundamental step to achieve the same is to subject the feed to suitable pretreatments like hydrodesulfurization or zinc oxide beds to remove sulfur compounds from the stream. Effective reduction of poisoning can be achieved by deploying guard beds ahead of the principal bed.

9.11 Products and Application of Biomass Gasification

Much focus is concentrated on the commercial application of biomass gasification to generate energy due to the renewability, carbon neutrality, and ample availability of biomass. Also, being the only renewable carbon source, biomass will be the future feedstock for chemical and transportation fuel production (Boerrigter and Rauch 2006). This section deals with the significant applications and products derived from biomass gasification.

9.11.1 Products

Biomass gasification can provide syngas (termed bio-syngas) as the primary product, which can be further processed to form secondary products such as electricity, chemicals (methanol, ammonia, etc.), liquid, and gaseous biofuels. Liquid biofuels like ethanol, gasoline, and diesel, and gaseous biofuels like methane and hydrogen are produced through direct conversion of syngas. These secondary products find application as industrial chemical feedstocks and energy conversion fuels (Demirbaş 2001; Arcoumanis et al. 2008).

9.11.1.1 Bio-syngas

Being the primary product, the syngas, a mixture of H and CO, mainly finds their application as a chemical and energy feedstock. Syngas is an essential precursor of methane, hydrogen, and valuable chemicals like ammonia, methanol, etc. The production of bio-syngas through steam reforming reaction results in bulk production of hydrogen followed by carbon monoxide, which further undergoes shift reaction to generate additional H_2 and CO_2. The H_2/CO ratio determines the formation of desired products like gasoline, methanol, etc. from syngas. Thus, syngas act as a carrier for power generation and an intermediate product for biofuel production. (Basu 2010; Molino et al. 2016).

9.11.1.2 Heat and Electricity Generation

The producer gas generated from gasification can be consumed in boilers and furnaces to generate heat, in ICE to produce small–medium scale electricity, and in GT to generate small–large scale electricity. In GT, the exhaust gas can be further recovered using a heat recovery steam generator and can be used to generate additional electricity (Bauen 2004).

9.11.1.3 Methanol

Methanol (CH_3OH), formed during the catalytic synthesis of syngas, acts as a potential transport and chemical industry feedstock. The primary use of methanol includes making formaldehyde, acetic acid, etc. and converting fats and oils to biodiesel through transesterification (Kumar et al. 2009). The catalytic conversion of syngas to methanol is carried out with Cu or Ni-Al-based catalysts. Steam reforming of methane leads to the production of methanol, which can in turn be converted to gasoline (Kumar et al. 2009).

$$CO + 2\,H_2 \;\rightarrow CH_3OH \tag{9.16}$$

9.11.1.4 Ammonia Synthesis

Ammonia (NH_3), synthesized from the combined effect of H_2 and N_2 on a catalytic bed, is widely used in fertilizers, disinfectants, refrigerants, etc. Iron catalysts with added promoters have a vital role in the synthesis of ammonia. The gas formed from biomass gasification is made to endure the shift reaction followed by a scrubbing and regeneration process before converting to NH_3 (Basu 2010).

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{9.17}$$

9.11.1.5 Ethanol

Ethanol (C_2H_6O) is a prominent biomass-derived transport fuel used in the transportation industry. It can be used as a single fuel or is used in spark-ignition engines along with gasoline. Ethanol is produced by the thermochemical conversion of syngas with Rh-based or Cu-based catalysts. But the energy loss occurring during the conversion of syngas to these liquid fuels inversely affects their overall energy conversion efficiency (Kumar et al. 2009; Basu 2010).

9.11.1.6 Gasoline

A hydrocarbon mixture that has a carbon number within the range of 5–11 constitutes gasoline. Using fixed and fluidized beds of zeolite catalysts, gasoline conversion from methanol is exercised through the methanol-to-gasoline (MTG) process. Gasoline is obtained by a double dehydration process with the production of dimethyl ether intermediate (Molino et al. 2016).

9.11.1.7 Diesel

A high-quality (Cetane number > 70) diesel oil, with a similar composition to petrodiesel (produced from petroleum), can be developed by employing the FT process. The diesel thus produced can be used in compression ignition engines along with petrodiesel (Molino et al. 2016).

9.11.1.8 Methane

Membrane technology can produce methane in which the compressed syngas is fed to some polymer permeation modules (Molino et al. 2016). The average operating temperature of FT synthesis is between 693 and 893 °C. The high temperature of FT also favors methane production, which can be further converted into H_2 through catalytic dehydrogenation (Huffman 2011).

9.11.1.9 Hydrogen

Hydrogen can be derived from syngas through catalyzed WGS reactions. Cr supported Fe-based catalysts, and Cu-based catalysts are usually used to enhance the shift reaction (Molino et al. 2016). In automobiles, H_2 is employed with zero-emission using fuel cells that can attain high efficiency of about 60%. Moreover, H_2 can be used to prepare chemicals and intermediate products like ammonia, methanol, etc. (Kumar et al. 2009).

9.11.2 Applications

The gasification process exercises the conversion of biomass feedstock to a suitable gaseous fuel product. The flexibility of this alternative energy conversion method to produce energy and a variety of fuels with fewer greenhouse emissions tremendously widens its possibilities (Winther et al. 2012). The significant areas of application of biomass gasification include boilers, gas turbines, internal combustion engines, and the synthesis of liquid transport fuels and useful chemicals (Kumar et al. 2009).

9.11.2.1 Boilers

In boilers, energy is harvested from syngas through direct combustion without causing any adverse environmental effects. Even though syngas finds ample applications in power plants, the low overall electric energy efficiency necessitates a cogeneration unit for heat reuse. Similarly, in power plants, biomass gasification products can be burned along with conventional fuels (co-combustion), limiting the weight percentage of the former in the range of 5–15 (Molino et al. 2016).

9.11.2.2 Gas Turbines

Syngas finds application in gas turbines (GT) with a relatively higher electrical conversion efficiency of 40% compared to conventional steam cycles. This improved conversion efficiency is attributed to the better combustion characteristics of gaseous fuels. An additional improvement in energy efficiency by up to 60% can be achieved using an additional energy recovery system, and GT is considered the most effective electrical-generation system (Jiang et al. 2016; Ren et al. 2020). However, a rapid turbine blade deterioration due to high-temperature flue gas demands a higher calorific value and appropriate cleaning methodologies.

9.11.2.3 Internal Combustion Engines

The biomass-derived syngas with high calorific value and fewer pollutants are required for the appropriate performance of internal combustion engines. Along with combustion, syngas is also employed for co-combustion with biogas achieving an overall energy conversion efficiency of 45%. But the fruitful application of syngas in engines demands modified fuel supply systems (Shah et al. 2010; Zhang et al. 2018a, b).

9.11.2.4 Fuel Cells

Yet another important application of syngas is its usage in high-energy fuel cells. In fuel cells, the electricity is generated through chemical energy conversion with an energy conversion efficiency greater than 40%. Moreover, direct feeding of fuel cells with syngas or with a mixture of H_2 and CH_4 adds flexibility (Molino et al. 2016). Furthermore, the noncombustible usage of syngas in high-temperature fuel cells makes the approach sustainable and eco-friendly (Pierobon et al. 2014).

9.11.2.5 Fischer–Tropsch Synthesis

Fischer–Tropsch (FT) synthesis is the catalytic transmutation of syngas to long-chain hydrocarbon. Catalytic support for the FT process is provided by iron, cobalt, and nickel-based metals (Basu 2010). The name of the process is coined as a portmanteau of the names of Franz Fischer and Hans Drops who developed the process in 1920. Hydrocarbons of varying molecular weight can be obtained by the reaction between H_2 and CO on feeding syngas to the FT reactor. A wide variety of oxygenated compounds with carbon number spanning from 1 to 35 (inclusive of gases and solid waxes) are produced from FT reactions in which hydrocarbons in the span C_5–C_{10} serves as synthetic fuels, and higher range hydrocarbons favor gasoline products. The standard operating temperature and pressure of FT reactions are between 200 to 350 °C and 20–300 atm.

$$(2x + 1)H_2 + xCO\ (\text{catalyst}) \rightarrow C_xH_{(2x+2)} + xH_2O \tag{9.18}$$

Where $C_xH_{(2x + 2)}$ indicates a hydrocarbon mixture spanning from methane to wax depending on the pressure, catalyst, and temperature maintained in the reaction.

9.12 Recent Advances and Future Perspectives of Catalytic Biomass Gasification

The previous section discussed various catalysts, their classification, mechanisms, and their effect on tar reforming and gas yield. This section deals with the recent trends and future scope in catalytic biomass gasification. Further improvement of catalytic performance through new catalyst configurations and novel technologies are discussed.

9.12.1 Recent Advances

One of the most recent advancements in catalytic biomass gasification is the reactive flash volatilization approach to improve the uneconomical options of fluidized bed gasifiers with a downstream catalytic reactor for tar cleaning or a downstream catalytic reformer with a pyrolysis reactor. A fixed bed gasifier with a significantly higher mass flow rate and carbon space velocity is used in reactive flash volatilization, making it cost-effective on a small scale (Colby et al. 2008). Reactive flash volatilization with Rh-based catalyst is appropriate for cellulose gasification and is a promising approach towards superior syngas production. But the high cost of Rh catalyst confines its application to bench-scale (Chan and Tanksale 2014b). Similarly, a carbonless decomposition of H_2 and CO can be attained from a non-volatile feed in less than 50 ms through reactive flash volatilization with Rh-Ce catalyst. The rapid oxidation of decomposition products prevents the condensation reactions and hence the carbon formation. As a result, higher feed conversion with H_2 and CO components is achieved with a lower C/O ratio (Salge et al. 2006). Another prospective technology for potential tar reforming is hybrid plasma-catalysis due to its high tar conversion rate and syngas yield. Furthermore, dry reforming of tar to H_2 and autothermal reforming (introduction of O_2 to promote tar cracking, thereby limiting C deposition) are alternative emerging technologies to replace the conventional steam reforming at the expense of catalytic deactivation and oxygen purification cost, respectively (Sinaei Nobandegani et al. 2016).

9.12.2 Future Perspectives

With reference to the prior studies, Ni-based catalysts are identified for their outstanding tar reforming capability. The value-addition of Ni catalysts by incorporating noble metals or dolomites is worth researching for further development; Ni-dolomite configurations seek more research attention due to their instant availability and affordability (Wu and Williams 2011a). As a commercially viable process, the gasification of lignocellulose is another area of future scope, where more robust and effective Ni catalysts may take a crucial position (Chan and Tanksale 2014a).

Currently, studies are focusing on the improvement of sintering, sulfur poisoning, and coking resistance of catalysts. But the complexity of developing a catalyst by integrating all of these is still challenging. So, synthesizing a multi-functional catalyst with anti-coking, anti-sintering, and anti-poisoning properties is a highly relevant field that requires more attention. Furthermore, poisoning resistance towards halogen and other organic nitrogen species along with catalytic regeneration and recycling is yet another field for further research (Gao et al. 2020).

Even though attempts continue to optimize the laboratory-scale reactors and catalysts, scaling-up of the same is more complex. The optimization of space velocity, unstable flow rate, etc. on scaled-up reactors is another area of futuristic interest (Nabgan et al. 2017). Moreover, scaling-up of sorption enhanced steam reforming (SESR) with the integrated sorbent, from laboratory to commercial-scale, also entails much research interest (Gao et al. 2020).

Another vital area requiring much attention in the industrial application of biomass gasification is the stability in tar reforming. Sustained tar reforming with simultaneous catalyst regeneration through chemical looping involves relevant consideration (Artetxe et al. 2017). Apart from this, further research should be done in reactor design optimization by incorporating sophisticated techniques employed in bubbling, decoupled triple bed, and countercurrent fluidized bed reactors (Gao et al. 2020). Additionally, elevated temperature steam reforming performance demands further studies on improved reactor material and design. Also, alternative novel improving technologies like dry reforming and autothermal reforming (ATR) are to be explored to their full extent (Sinaei Nobandegani et al. 2016).

Another emerging area with promising research opportunities is the mechanism of tar cracking. The actual tar cracking mechanism should be considered with various types of model compounds in varying amounts accounting for their complex structure containing five-ring aromatic hydrocarbons, oxygenates, and polycyclic aromatic hydrocarbons, rather than a single first-order tar model compound (Ren et al. 2019). Along with the catalytic reforming mechanism, the mechanism involving preparation and pre-treatment of catalyst and combined interaction mechanism of metals supports, and promoters are other relevant areas that demand further research (Gao et al. 2020). Furthermore, research focusing on syngas production as a potential secondary feedstock for synthetic fuel production necessitates a one-step chemical fuel synthesis from biomass tar steam reforming with optimized parameters and a suitable catalyst, opening the possibilities of a new precinct in biomass gasification (Liu et al. 2019).

9.13 Summary

This chapter deals with various aspects of biomass gasification and the requirement for catalytic producer gas enhancement. Biomass gasification is a complex transmutation of biomass to gaseous fuels and chemical feedstock. The performance of the process is mainly governed by reactor design and key operating parameters such as gasifying agent, type of feedstock, temperature, pressure, and residence time. The fruitful application of producer gas can be ensured only if the undesirable tar content in it is reduced beyond specified limits. Reforming tar using catalysts is identified as the most economical and commercially viable route for achieving the same. The chapter also covers catalytic activation and deactivation mechanisms, and a performance comparison of different catalysts in tar reforming and enhancement of gas yield. It is inferred that the selection of a suitable catalyst not only enhances gas yield through tar reforming but also acts as a CO_2 sorbent to sequestrate incombustible CO_2, further enhancing producer gas quality. In this view, Ni-dolomite combinations are identified as an economical and potential catalyst that nourishes producer gas through simultaneous attainment of tar reformation and CO_2 sorption. Further improvement of catalytic performance through new catalyst configurations and novel technologies are also discussed.

Conflict of Interest All the authors declare that they have no competing interests.

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Chapter 10
Recent Advances in Fast Pyrolysis and Oil Upgradation

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Abstract In this chapter, a brief introduction to various pyrolysis processes and a detailed analysis of fast pyrolysis has been explored. A wide variety of feedstocks suitable for the fast pyrolysis process and physicochemical properties of bio-oil has been incorporated. Various types of pyrolyzers that are available in the papers are also mentioned here. Furthermore, enrichment of bio-oil using various upgradation techniques and its physicochemical properties are also discussed. This includes the processes such as steam reforming, catalytic cracking, and supercritical extraction. The application of bio-oil as a fuel requires enhancement in its properties which is achieved using blending with other fuels. Thus, this chapter also strives to explain the recent advances made in bio-oil properties enhancement. Also, a brief analysis of the techno-economic feasibility of bio-oil production and its environmental sustainability is specified. This chapter attempts to give an overview of the whole concept of bio-oil production to its application.

Keywords Pyrolysis · Bio-oil · Fast pyrolysis reactor (pyrolyzer) · Upgradation and enhancement of bio-oil · Techno-economics · Environmental sustainability

Abbreviations

BCO	Bio-crude oil
CE	Capillary electrophoresis
CFBR	Circulating fluidized bed reactor
CR	Cassava rhizome
CS	Cassava stalk
CSBR	Conical spouted bed reactor

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
https://doi.org/10.1007/978-981-19-4312-6_10

dAPCI-TOF MS	Dopant-assisted atmospheric pressure chemical ionization time-of-flight mass spectroscopy
FTIR	Fourier transform infrared
FT-NMR	Fourier transform–nuclear magnetic resonance
GC	Gas chromatograph
GPC	Gel permeation chromatography
HAD	Hydrodearomatization
HDM	Hydrodemetallation/hydrodemetallization
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
HPLC	High-performance liquid chromatography
HTC	Hydrothermal carbonization
HTG	Hydrothermal gasification
HTL	Hydrothermal liquefaction
ICFBR	Internally circulating fluidized bed reactor
iPEPICO	Imaging photoelectron photo ion coincidence spectroscopy
LC	Liquid chromatography
LCA	Life cycle assessment
LQIT-dAPCI-MS	Linear quadrupole ion trap dopant-assisted atmospheric pressure chemical ionization mass spectroscopy
MBMS	Microreactor for pyrolysis connected with molecular beam mass spectrometer
MDGC	Multidimensional gas chromatography
NEV	Net energy value
RTP	Rapid thermal pyrolysis
SFCs	Supercritical fluids
SOC	Soil organic carbon
SPI-TOFMS	Single-photon ionization time-of-flight mass spectroscopy
SVUV-PIMS	Synchrotron-based vacuum ultraviolet photoionization mass spectroscopy
TAP	Temporal analysis of products

10.1 Introduction

As human society progresses towards a new height of technological advancement, the need for per capita energy requirements is also growing tremendously. To meet this necessity of energy, exploration of renewable sources is being highlighted and proposed to fulfill the demands. The dependency of society on non-renewable sources of energy such as fossil fuels will not be accepted in the near future due to scarcity and an increase in population. Also, fossil fuel utilization leads to greenhouse gas emissions that lead to climate change (No 2014). Renewable sources of energy are explored to overwhelm petroleum and its related product (Kumar and Badgujar, 2019, Kumar et al., 2022). Lignocellulosic biomass is a promising renewable source that can be considered feedstock for biofuel (Patel and Kumar 2016; Bhardwaj et al. 2021; Kumar and Verma 2021a, b). Biomass is converted to solid, liquid, and gaseous biofuel through chemical, thermal, thermochemical, and biochemical processes. The thermochemical process has some leverage over the biochemical process in terms of reaction time and conversion. In the case of thermochemical, both liquefaction and pyrolysis can produce bio-oil. Still, pyrolysis has an advantage in terms of capital cost, making this process more suitable for converting biomass to bio-oil (Nanduri et al. 2021; Agrawal and Verma 2022; Goswami et al. 2020a, 2021). Biomass can be converted to bio-oil through a fast pyrolysis process. Bio-oil cannot be used directly with petrol or diesel due to its non-miscibility with hydrocarbon, polar, and unstable nature (Patel and Kumar 2016; Goswami et al. 2020b). Other bio-oils, oil from vegetables, and animal wastes cannot be used in raw form in conventional engines. Raw bio-oil obtained through pyrolysis can be used in boilers and furnaces as a replacement fuel instead of fuel oil (Nanduri et al. 2021). But on further upgradation of bio-oil, it can be used as a transportation fuel in diesel engines, fuel for combined heat and power generation, and fuel for gas turbines (No 2014). Depending upon the upgradation technique of pyrolysis oil, it will also result in valuable chemicals (Jacobson et al. 2013).

10.2 Bio-oil

Bio-oil is found in liquid form with dark brown color, which comprises oxygen-rich compound (Mohan et al. 2006; Goswami et al. 2022). Bio-oil produced from pyrolysis of biomass is also referred with various terms in the literature, such as wood pyrolysis oil, wood oil, wood distillates, liquid wood, wood liquid, liquid smoke, bio-crude, bio-crude oil (BCO), bio-fuel oil, pyrolysis liquid, pyrolysis oil, pyrolytic bio-oil, pyrolytic oil, fast pyrolysis bio-oil, fast pyrolysis liquid, biomass fast pyrolysis fuel, biomass pyrolysis liquid, biomass flash pyrolysis liquids (BFPL), pyroligneous tar, and pyroligneous acid (No 2014; Krutof and Hawboldt 2016; Isahak et al. 2012). In this chapter, a liquid produced from pyrolysis of biomass will be termed bio-oil. If bio-oil is from other sources such as plastic, it will be referred to as pyrolysis oil.

10.2.1 Feedstock for Bio-Oil

Bio-oil or pyrolysis oil can be obtained not only from biomass but also from animal waste, vehicular residue, plastic, and paper waste from paper mills each has been discussed in the latter portion of the chapter. Various feedstock categories are cellulose and lignin, bark, wood, nuts and seeds, agricultural wastes/residues, algae, forestry residues, grasses, and miscellaneous. After harvest, the biomass is pretreated, such as removing moisture content and reducing particle size, before feeding the reactor to increase the bio-oil yield. There are various studies where co-pyrolysis, instead of using a single feedstock, two or more feedstock were used for the fast pyrolysis process to enhance the bio-oil properties (Lu et al. 1994; Mohan et al. 2006; Abnisa and Wan Daud 2014).

10.2.1.1 Lignin, Cellulose, and Forest Residue

Mohan et al. (2006) reviewed the work of Fullana et al. who performed the pyrolysis of cellulose, lignin, and sewage sludge and analyzed the product obtained on multidimensional gas chromatography (MDGC). In the same review, fast pyrolysis of forest residue and grasses was also discussed. Dalla et al. (2016) produce the bio-oil from forest residue, softwood (*Picea abies*), and (*Eucalyptus* sp.). Intermediate, fast, and catalytic fast pyrolysis was performed on these feedstocks. Fast pyrolysis of hardwood and softwood residues shows bio-oil yields of 69% and 70%, respectively.

10.2.1.2 Bark and Wood Trunk

Pinto et al. (2018) performed fast pyrolysis on the bark of Pinus radiata, catechin, and water-insoluble (W-I) tannins from the bark of *Pinus radiata* and compared the fraction of phenol and organosolv-lignin in pyrolysis oil from the given feed materials. Specific compound catechols show the highest percentage in the pyrolysis oil of W-I tannins.

Santos et al. (2018) shows the fast pyrolysis of stump wood and trunk wood from *Eucalyptus urograndis* with 450–480 °C reactor temperature. Combining light and a heavy fraction of pyrolysis oil yield from stump wood and trunk wood is 43.4% (31.6% light fraction and 11.8 heavy fractions) and 47.1 (34.1% light fraction and 13.0 heavy fraction), respectively.

10.2.1.3 Nutshell Waste

Das and Ganesh (2003) showed the yield of pyrolysis oil from cashew nutshell that was in the range of 37% (at 400 °C) to the highest of 42% (500–550 °C) and then dropped to 36% (600 °C) (Das and Ganesh 2003). Another paper related to this study characterized the bio-oil obtained from pyrolysis of cashew nutshell. Shell was first heated up to 175 °C, and oil was collected, represented as CO1. After the removal of CO1, it was further pyrolyzed under a vacuum at 500 °C to get the maximum quantity of bio-oil, denoted by CO2. Both bio-oil CO1 and CO2 show complete miscibility with diesel (Das et al. 2004).

A pressed *Jatropha carcass* was used by Jourabchi et al. (2014) for pyrolysis to study the bio-oil yield in a fixed bed system. The system's temperature was in the range from 573.15 °K to 1073.15 °K with a heating rate of 50 °K/min in the presence of nitrogen. The maximum yield of bio-oil from this is around 50%.

10.2.1.4 Seeds

Seeds are also used for the production of pyrolysis oil. Onay and Kockar (2003) used rapeseed for the production of bio-oil. A maximum bio-oil yield of 46.7% was found in slow pyrolysis at the temperature of 550 °C with a heating rate of 30 °C/min without any sweeping gas in the Heinze retort. This bio-oil yield was increased to 51.7% by introducing sweeping gas, i.e., nitrogen, at a flow rate of 100cm^3/min. In fast pyrolysis, the maximum bio-oil yield was 63.1% at 550 °C at 300 °C/min with a sweeping gas flow rate of 100 cm^3/min. This yield was increased to 68% at similar conditions with 0.6–1.25 mm particle size and the sweeping gas flowrate was between 100 and 200 cm^3/min. On the other hand, flash pyrolysis shows the maximum bio-oil yield of 73% at 600 °C with a sweeping gas flow rate of 100 cm^3/min.

10.2.1.5 Agricultural Residue

Pattiya and Suttibak (2012) experimented on agricultural residue, i.e., cassava rhizome (CR) and cassava stalk (CS). Fast pyrolysis was done on this waste in a fluidized bed reactor in the presence of nitrogen gas. For CR, the optimum temperature is 475 °C, at which bio-oil yield was maximum which was 69.1%, whereas, for CS, the temperature was 469 °C, and yield was 61.4%. In another related study, fast pyrolysis in a free-fall reactor in the presence of nitrogen gas on agricultural residue, i.e., sugarcane and cassava residue, was done by Pattiya et al. (2012) for CR and CS maximum bio-yield was 50.3% and 52.3% at 400 °C and 450 °C, respectively. For sugarcane leaves and sugarcane tops, bio-yield was 53.3% and 44.1% at 400 °C and 350 °C. Yanik et al. (2007) demonstrated fast pyrolysis on oreganum stalks, corncob, and straw at 500 °C in a fluidized bed reactor. Bio-oil yield for oreganum stalks, corncob, and straw was 39%, 41%, and 35%, respectively.

10.2.1.6 Algae

Miao et al. (2004) utilized the microalgae for the fast pyrolysis process. The experiment parameter was as follows: the reaction temperature was 500 °C, the heating rate was 600 °C/s, sweeping gas (nitrogen) flow rate 0.4 m^3/h, and residence time for vapor was 2–3 s. The bio-oil yields from microalgae *M. aeruginosa* and *C. protothecoides* were 23.7% and 17.5%, respectively.

10.2.1.7 Animal Waste

Even some study shows the production of bio-oil from animal waste. Das et al. (2009) showed the production of bio-oil from the fast pyrolysis of chicken manure. Woo et al. (2015) generate bio-oil from swine manure using the fast pyrolysis method. Emrah et al. 2019 produced bio-oil, using goat manure as feedstock for the pyrolysis process.

10.2.1.8 Other Feedstocks

Bio-oil is not only produced using biomass or organic waste, but it can also be generated using industrial waste, plastic, and other sources of feedstock. Papermill residue is also used to generate pyrolysis oil using a fast pyrolysis process, as mentioned by Charusiri (2015). A comparative study on automobile shredder residues (ASR) was carried out after processing it through conventional and fast pyrolysis (Zolezzi et al. 2004). This study shows that fast pyrolysis of ASR produces a high yield of pyrolysis oil, i.e., 58% at 800 °C. Wong (2017) performed the distillation of pyrolysis oil produced from plastic wastes. Fast pyrolysis was conducted at 500–800 °C in a laboratory to obtain the pyrolysis oil. Prurapark et al. (2020)

explored the effect of temperature on pyrolysis oil generated from HDPE (high-density polyethylene) and PET (polyethylene terephthalate). In the case of HDPE, the highest pyrolysis oil yield was seen at 450 °C, i.e., 40.5 L of pyrolysis oil from 100 kg of HDPE. All the above feedstocks are suitable to produce bio-oil or pyrolysis oil. This also shows that feedstock for fast pyrolysis is not limited to just biomass.

10.2.2 Bio-oil from Pyrolysis

The pyrolysis process is done in an oxygen-free environment at a temperature range of 200 °C–900 °C. Pyrolysis process depends upon the thermal pretreatments, peak temperature, heating rate, carbonization particle size, and residence time. Pyrolysis can be of a slow, mild, and fast nature. In all cases, biomass goes under thermal decomposition to give biochar, bio-oil, and syngas [C_1–C_2 hydrocarbon, hydrogen, carbon mono oxide, carbon dioxide] (Baghel et al., 2022; Sakhiya et al., 2020). Pyrolysis products are the transformation of biomass components such as hemicellulose, cellulose, and lignin at various temperature ranges as shown in Fig. 10.1. There are various types of pyrolysis and related processes that mainly produce pyrolysis oil are mentioned in Table 10.1. (Cha et al. 2016).

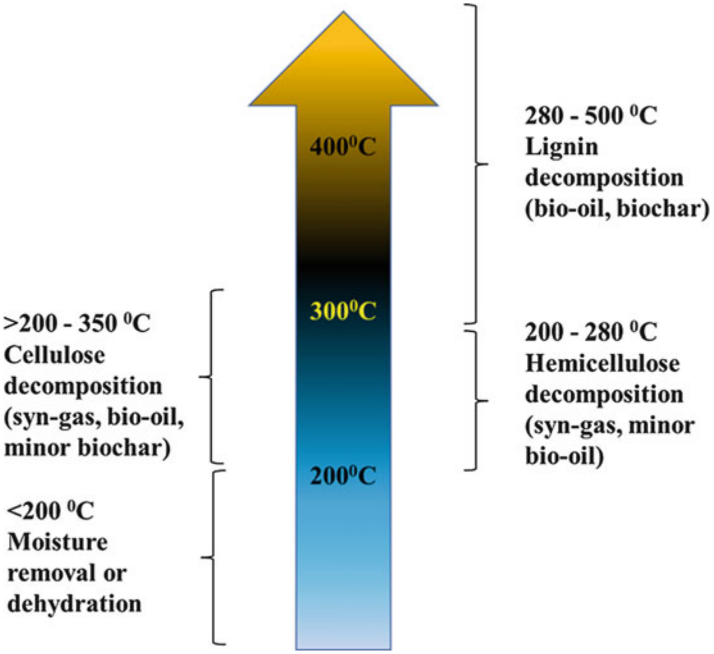


Fig. 10.1 Temperature range for the breakdown of biomass components (Zaman et al. 2017)

10.2.2.1 Slow Pyrolysis

Slow pyrolysis, this process aims to produce high carbon content solid product. The residence time can vary from minute to hour; peak temperature can be in the range of 200 °C–600 °C, and the heating rate is generally less than 50 °C/min, and whole process occurs in an inert environment. Generally, the inert environment is created using nitrogen gas (Antal 2003; Cha et al. 2016).

10.2.2.2 Steam Pyrolysis and Vacuum Pyrolysis

Commonly, nitrogen gas is passed through a pyrolysis reactor to establish an inert environment, also known as sweeping gas. If this nitrogen is replaced with steam, the process is modified from slow pyrolysis to steam pyrolysis. In comparison, steam pyrolysis gives more bio-oil yield than slow pyrolysis (Özbay et al. 2008).

When slow pyrolysis is performed under the vacuum, then this process is modified to vacuum pyrolysis, which can also be used to produce bio-oil. In steam and vacuum pyrolysis, fundamental parameters such as heating rate, residence time, and peak temperature are similar to slow pyrolysis (Carrier et al. 2011; Özbay et al. 2008).

Table 10.1 Generalized values of process parameters for bio-oil production (Khan et al. 2021; Zhang et al. 2020; Farai et al. 2018; Joardder et al. 2014; Yu et al. 2014; Mohan et al. 2006; Tang and Huang 2005; Franke 1994; Anthony 1990)

Process	Process variation/Environment	Pressure	Temperature	Heating rate	Residence time	Product Priority
Slow pyrolysis (conventional)	With nitrogen	Atmospheric	200–600 °C	<50 °C/min	Minutes to hours	Biochar
Steam pyrolysis	With steam	Atmospheric	200–600 °C	<50 °C/min	Minutes to hours	Bio-oil
Hydro-pyrolysis	With hydrogen	Above atmospheric	200–800 °C	<100 °C/min	Minutes to hours	Bio-oil
Methano-pyrolysis	With methane	Above atmospheric	200–800 °C	<100 °C/min	Minutes to hours	Bio-oil
Vacuum pyrolysis	With vacuum	Below atmospheric	200–600 °C	<50 °C/min	Minutes to hours	Bio-oil
Hydrothermal carbonization	With water	Above atmospheric	<250 °C	Slow	Minutes to hours	Hydro Char
Hydrothermal liquefaction	With water or methanol	Above atmospheric	250–400 °C	Slow	Minutes to hours	Bio-oil
Hydrothermal gasification	With water	Above atmospheric	>400 °C	Slow	Minutes to hours	Syngas
Torrefaction (Mild pyrolysis)	Oxygen-free environment	Atmospheric	200–300 °C	Slow	Minutes to hours	Bio-coal
Fast pyrolysis	Oxygen-free or in a nitrogen environment	Atmospheric	650 °C	Very high	0.5–5 s	Bio-oil
Flash pyrolysis	Oxygen-free or in nitrogen environment	Atmospheric	1000 °C	Very high	<1 s	Bio-oil
Flash-hydro-pyrolysis	With hydrogen	Above atmospheric	<500 °C	High	<10 s	Volatile Matter
Vacuum flash pyrolysis	With vacuum	Below Atmospheric	400 °C	Medium	2–30 s	Bio-oil

Microwave-assisted pyrolysis	With nitrogen	Atmospheric	Around 300 °C	Medium	Seconds—minutes	Bio-oil
Fast microwave-assisted pyrolysis	With nitrogen and premixed catalyst	Atmospheric	300–1000 °C	High	Seconds—minutes	Bio-oil
Flash microwave-assisted pyrolysis	With nitrogen and non-premixed catalyst	Atmospheric	300–1000 °C	Very high	Seconds—minutes	Bio-oil
Solar-assisted pyrolysis	Oxygen-free environment	Atmospheric	Around 500 °C	Medium	Minutes	Bio-oil
Plasma pyrolysis	With nitrogen	Atmospheric and above atmospheric	Around 1000 °C	Very high	Seconds—minutes	Syn-gas
Gasification	Oxygen-free environment	Atmospheric and above atmospheric	Around 1000 °C	Very high	Seconds—minutes	Syn-gas

10.2.2.3 Hydro-Pyrolysis and Methano-Pyrolysis

In hydro-pyrolysis and methano-pyrolysis, pressure is also high compared to conventional or slow pyrolysis, which ranges from 5 bar to 50 bar, and other parameters such as heating rate, residence time, and peak temperature are similar to slow pyrolysis (Franke 1994). When sweeping gas is replaced with hydrogen and methane, it is known as hydro-pyrolysis and methano-pyrolysis, respectively. Franke (1994) experimented on coal with these processes, i.e., methano-pyrolysis, hydro-pyrolysis, and conventional pyrolysis with and without impregnation of lithium oxide which acts as a catalyst. In methano-pyrolysis, methane was mixed with nitrous oxide in a 4:1 (methane to nitrous oxide) ratio and then fed to the reactor. Maximum liquid conversion was achieved in methano-pyrolysis which is higher than the yield produced in hydro-pyrolysis.

10.2.2.4 Hydrothermal Carbonization, Liquefaction, and Gasification

The hydrothermal carbonization process is not a single process, but it is a part of the hydrothermal process. This type of thermochemical process is achieved in a close reactor where biomass and water are mixed, and its pressure can go from atmospheric to 350 bar, and temperature generally is in the range of 200–400 °C. Here, the feedstock is mixed with water in a specific ratio and then fed to the hydrothermal reactor. The hydrothermal process is a combination of processes at various temperature ranges, below 250 °C called hydrothermal carbonization (HTC), in between 250 °C and 400 °C is hydrothermal liquefaction (HTL), and above 400 °C is hydrothermal gasification (HTG). These stages HTC, HTL, and HTG have a max yield of biochar, bio-oil, and gases, respectively. The bio-oil yield from HTL ranges from 7.9% to 67% under different conditions with various feedstocks. Some researchers have shown that liquefaction is also performed using methanol instead of water (Tong et al. 2021; Xu and Li 2021; Cha et al. 2016; Xiao et al. 2012; Kruse 2009).

10.2.2.5 Torrefaction

Torrefaction is mild pyrolysis that involves oxygen-free or very minute concentrations at a temperature range of 250–375 °C. This process yields low carbon valued products its percentage varies from 51% to 55%. The product of torrefaction may be used for fuel purposes, and its product can be used as biocoal (Uemura et al. 2011; Meyer et al. 2011; Ghiasi et al. 2014; Cha et al. 2016).

10.2.2.6 Fast Pyrolysis

In fast pyrolysis also termed ultra-pyrolysis or rapid pyrolysis, the particle size is between 1 and 2 mm, moisture content should be less than 10% by weight, and vapor residence time is in seconds. The heating rate can go as high as 1000 °C/s. Fast pyrolysis aims to produce a high percentage of bio-oil; the yield of bio-oil is in the range of 60–75%, which is very high in comparison to other pyrolysis processes (Mohan et al. 2014, Meyer et al. 2011, Gollakota et al. 2016, Mohan et al. 2006, Shen et al. 2020; Mok et al. 1985).

10.2.2.7 Flash Pyrolysis

Flash pyrolysis, sometimes referred to as ultra-fast (ultra-rapid) pyrolysis, consider a process with very high heating rates which can go up to 10,000 °C/s with an intermediate temperature range between 500 and 600 °C and very short residence times less than a second. Around 75% of bio-oil yield can be achieved from this process. An enormous heating rate diminishes the char and tar formation. Due to rapid quenching, liquid products condense before the breakdown of higher molecular weight compounds that may transform into gaseous products (Results 1993; Goyal et al. 2006; Jahirul et al. 2012; Energy Institute 2020).

10.2.2.8 Vacuum Flash Pyrolysis and Flash-Hydro-Pyrolysis

Furthermore, if flash pyrolysis is performed under a vacuum, it is known as vacuum flash pyrolysis. The reason behind this is to get a high yield of bio-oil from this process and, it diminishes the secondary decomposition and inhibits further gas formation. When flash pyrolysis is performed along with hydrogen gas at high pressure (maximum limit of 20 MPa), it is known as flash-hydro-pyrolysis (Pecha et al. 2017; Goyal et al. 2006; Tang and Huang 2005).

10.2.2.9 Microwave-Assisted Pyrolysis

Microwave-assisted pyrolysis is generally performed to maximize the yield of bio-oil. This is different from conventional pyrolysis, as heating is performed using a high-frequency wave, penetrating the feedstock and increasing temperature from inside to outside. This process has advantages over conventional pyrolysis is in terms of response rate, heating rate, heating efficiency, and thermal inertia (Yu et al. 2014; Zhang et al. 2020). It is also modified to microwave-assisted fast pyrolysis or premixed method and ultra-fast (flash) microwave-assisted pyrolysis or non-premixed method. The selection of the method depends on the high heating rate and the way microwave absorbing material or catalyst is used in the process

(Tsubaki 2020). Fast microwave-assisted (premixed) pyrolysis is where feedstock is premixed with a catalyst which rises the temperature quickly due to the fast-absorbing capacity of the microwave by catalyst or microwave absorbent (CaO, NiO, Fe_2O_3, MnO_2, $CuCl_2$, NaCl, $MgCl_2$ γ-Al_2O_3, and TiO_2, etc.). Another method is flash microwave-assisted pyrolysis (non-premixed), here catalyst (such as activated carbon (AC), graphite, and SiC) is poured into the reactor to achieve the desired temperature. Then the material or feedstock is fed to the reactor for instant heating (Zhang et al. 2020).

10.2.2.10 Solar-Assisted Fast or Flash Pyrolysis

In solar-assisted fast or flash pyrolysis, the feedstock is fed to the reactor present at the focal point of the parabolic solar panel acts as a solar concentrator. Heat is applied externally to reach the expected temperature for pyrolysis. This process is more eco-friendly and energy efficient (Joardder et al. 2014). A 50% bio-oil yield is obtained with date seed at 500 °C with a residence time of 2 h. Goyal et al. (2006) mentioned in their paper that Lede and Bouten (1999) reported solar flash pyrolysis of samples of cellulose.

10.2.2.11 Plasma Pyrolysis

Plasma pyrolysis of biomass is performed at high temperatures (around 1000 °C) to produce syngas and biochar. Generally, carbon monoxide and hydrogen percentages are high, and methane percentage is low in syngas from plasma pyrolysis. The power required for this process depends on the nature and amount of feedstock. As plasma torch is the only heat source in this process, controlling it is helpful during the varying nature of feedstock (Tang and Huang 2005; Farai et al. 2018).

10.2.2.12 Gasification

Another way to get a high yield of gas is from gasification. The partial oxidation process of converting biomass into char and syngas and temperature can go as high as 1000 °C. This process focuses mainly on gaseous products (hydrogen, carbon mono oxide, carbon dioxide, nitrogen, etc.). Although carbon content in final residue can reach up to 95%, this process emphasizes gaseous products more (Taba et al. 2012; Tay et al. 2013).

10.2.3 Physicochemical Properties

Bio-oil properties mainly depend on the nature of the feedstock. Physicochemical properties change as feedstock is altered. The nature of bio-oil is determined through various physical and chemical properties. Physical parameter determination is necessary because that will help during the usage, storage, and handling of bio-oil. Different physical parameters are mentioned in Table 10.2 (Fagemas 1995).

Chemical properties include the quantification of various chemical compounds present in bio-oil. Different components of bio-oil can be identified using analytical methods of gas chromatography (GC), liquid chromatography (LC), high-performance liquid chromatography (HPLC), Fourier transform infrared (FTIR), proton(H^1), and carbon (^{13}C) Fourier transform-nuclear magnetic resonance (FT-NMR) spectroscopies, Gel permeation chromatography (GPC), and capillary electrophoresis (CE). Advanced technology includes a combination of two or more technologies, also known as hyphenated methods, for example, GC/MS (gas chromatography with mass spectroscopy), LC/MS (liquid chromatography with mass spectroscopy), GC/FT-IR, and GC/FT-NMR (Fagemas 1995).

Recent advances in an experimental setup that helps in understanding the fast pyrolysis mechanism on the molecular level that can be either catalyzed or non-catalyzed pyrolysis, which includes small level pyrolyzer combined with advanced analytical instruments that are mentioned below (Nanduri et al. 2021):

Table 10.2 Physical properties of pyrolysis oil (Mohan et al. 2006;Elliott et al. 2012;Oasmaa et al. 2012)

Parameters	Value	Test Method
Water (% by weight)	20–30	ASTM E203
Solids (% by weight)	0.01–1.00	Ethanol insoluble, methanol-dichloromethane insoluble
Ash (% by weight)	0.01–0.2	ASTM D482
Nitrogen (% by weight)	0–0.4	ASTM D5291
Sulfur (% by weight)	0–0.05	ASTM D4294
Viscosity at 40 °C (cSt)	15–35	ASTM D445
Density at 20 °C (g/mL)	1.1–1.3	ASTM D4052
Pour point (°C)	from −9 to −36	ASTM D93
Flash point (°C)	45 minimum	ASTM D93 procedure B
Gross heat of combustion (MJ/kg)	15 minimum	ASTM D240
pH	>2.5	ASTM E70–07
Distillability	Not distillable	
Stability	Viscosity can increase and can phase separate	80 °C for 24 h 40 °C for 1 week
Elemental analysis (CHN) (%by wt.)		ASTM D5291
Conradson carbon residue (% by wt.)		ASTM D189

- Micro pyrolyzer combined with GC-MS.
- Micro pyrolyzer interfaced with dopant-assisted atmospheric pressure chemical ionization time-of-flight mass spectroscopy (dAPCI-TOF MS) system.
- Pyro probe coupled with linear quadrupole ion trap dopant-assisted atmospheric pressure chemical ionization mass spectroscopy (LQIT-dAPCI-MS).
- Pyrolysis furnace combined with bio-crude oil (BCO) multidimensional gas chromatography (MDGC), cassava rhizome (CR), cassava stalk (CS), hydrothermal liquefaction (HTL), and above 400 °C is hydrothermal gasification (HTG). Hydrothermal carbonization (HTC), gas chromatography (GC), liquid chromatography (LC), high-performance liquid chromatography (HPLC), Fourier transform infrared (FTIR), proton (H^1), and carbon (^{13}C) Fourier transform-nuclear magnetic resonance (FT-NMR) spectroscopies, gel permeation chromatography (GPC), capillary electrophoresis (CE), dopant-assisted atmospheric pressure chemical ionization time-of-flight mass spectroscopy (dAPCI-TOF MS) linear quadrupole ion trap dopant-assisted atmospheric pressure chemical ionization mass spectroscopy (LQIT-dAPCI-MS).
- Synchrotron-based vacuum ultraviolet photoionization mass spectroscopy (SVUV-PIMS).
- Pyrolysis combined with single-photon ionization time-of-flight mass spectroscopy (SPI-TOFMS) system.
- Microreactor for pyrolysis connected with molecular beam mass spectrometer (MBMS).
- TAP (Temporal analysis of products) reactor connected with imaging photoelectron photo ion coincidence spectroscopy (iPEPICO).

Hundreds of organic compounds such as alkanes, aromatic hydrocarbons, phenol derivatives, ketones, esters, amines, alcohols, ethers, and sugars with a molar ratio higher than 1.5 for H/C. Most of the organic compounds present in bio-oil come from the different biomass fractions, as shown in Fig. 10.2. A complete fraction of bio-oil present in the literature is mentioned in Table 10.3. Inorganic species are present in trace amounts. Inorganic component of bio-oil includes calcium, silicon, potassium, iron, aluminum, sodium, sulfur, phosphorous magnesium, nickel, chromium, zinc, lithium, titanium, manganese, lanthanum, barium, vanadium, chlorine, etc. (Goyal et al. 2006; Isahak et al. 2012).

10.3 Fast Pyrolysis Reactor/Pyrolyzer

In previously found research, various reactors have been employed to enhance bio-oil production. These types of reactors are not just limited to biomass waste, but they are also compatible with plastic waste, tires, and other related waste (Isahak et al. 2012; Basu 2010; Cai et al. 2021; Jahirul et al. 2012; Lewandowski et al. 2019).

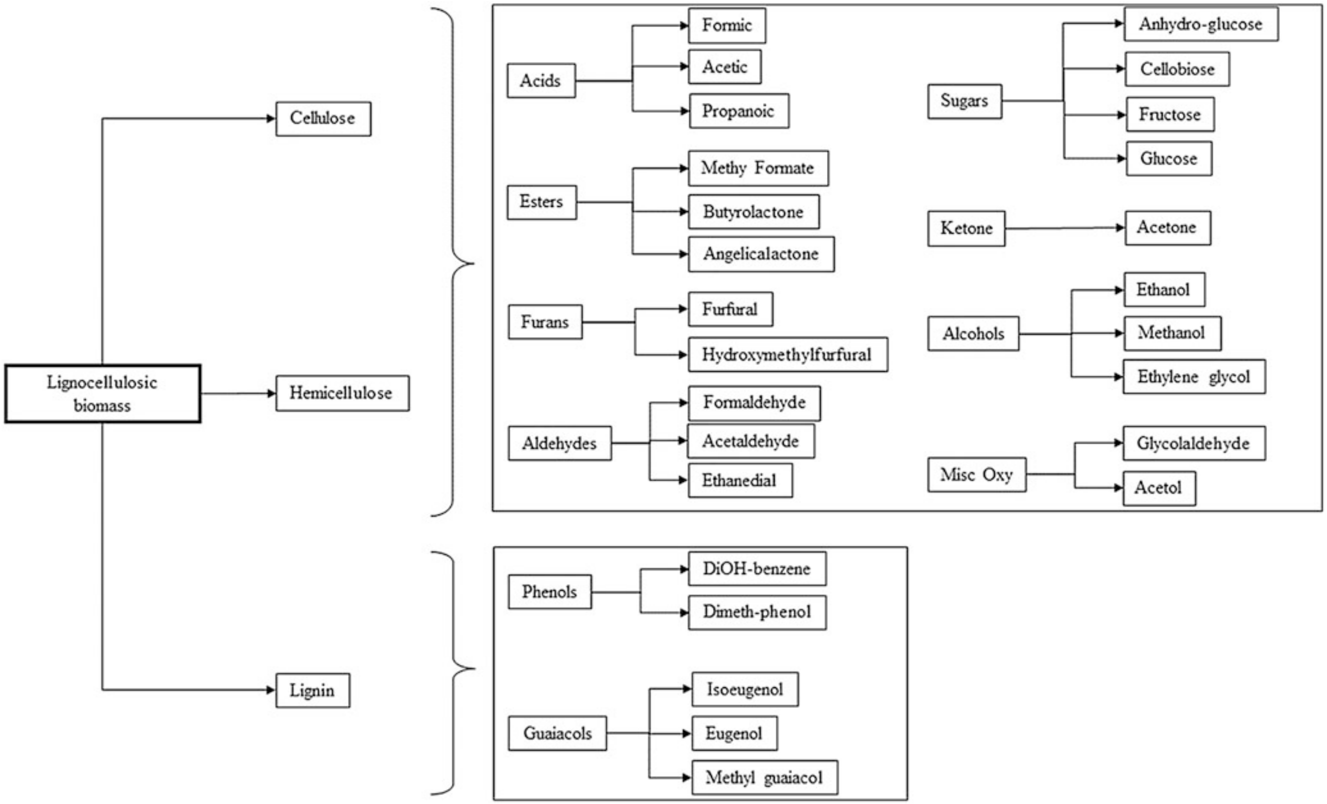


Fig. 10.2 Various components of bio-oil from the different fractions of biomass (Liu et al. 2020)

Table 10.3 The organic groups that are present in bio-oil (Goyal et al. 2006)

Functional group	Related compounds
Acids	Formic, acetic, hexanoic, benzoic, propanoic, etc.
Alcohols	Methanol, ethanol, iso-butanol, 2-propene-1-ol, etc.
Aldehydes	Formaldehyde, acetaldehyde, pentanal, 2-butenal, ethanedial, etc.
Alkenes	2-methyl propene, dimethyl cyclopentene, alpha-pinene, etc.
Aromatics	Benzene, toluene, naphthalene, xylenes, phenanthrene, fluoranthene, chrysene, etc.
Esters	Methyl formate, butyrolactone, methyl propionate, methyl n-butyrate, velerolactone, etc.
Furans	Furan, 2-methyl furan, furfural alcohol, 2-furanone, furfural, etc.
Guaiacols	2-methoxy phenol, 4-methyl guaiacol, eugenol, ethyl guaiacol, etc.
Ketones	Acetone, 2-butanone, 2-cyclopentanone, 2-pentanone, 2-hexanone, 2,3 pentanedione, cyclo-hexanone, etc.
Nitrogen compounds	Ammonia, methylpyridine, methylamine, pyridine, etc.
Other oxygenates	Hydroxy acetaldehyde, dimethyl acetal, hydroxy acetone, acetal, methyl cyclopentenone, etc.
Phenols	Phenol, methyl-substituted phenols
Sugars	Levoglucosan, glucose, D-arabinose, fructose, D-xylose, etc.
Syringols	Hydroxy acetaldehyde, dimethyl acetal, hydroxy acetone, acetal, methyl cyclopentenolone, etc.

10.3.1 Fixed Bed Reactor

A fixed bed reactor for pyrolysis works similarly as in the case of the gasifier. It is a feasible system for small-scale combined heat and power applications. This type of reactor is equipped with a gas cooling system and cleansing system. Cleansing systems consist of the cyclone, wet scrubber, and dry filters as shown in Fig. 10.3. The raw material is fed from the top of the reactor and comes in contact with the gas stream moving upward, which is counter to the movement of raw material. Generally, steel, concrete, or firebricks can be used for the construction of this type of reactor. Fuel introducing unit, ash removal unit, and the gas outlet are also incorporated into this reactor. It operates at the lower side of gas velocity, and ash carries over. A recent study also shows the usage of catalysts for further conversion of tar (Chopra and Jain 2007; Jahirul et al. 2012; Zaman et al. 2017).

Laboratory scale fixed bed reactors deals with a minimal amount of sample, which is in grams. This type of reactor operates in batch mode. They can be either horizontal or vertical reactor types. In some cases, these reactors are combined with a catalyst for the enhancement of bio-oil production. An approximate representation of a fixed bed reactor for fast pyrolysis is shown in the given Fig. 10.4. The system consists of the following parts: the feeder, the reactor, the catalysis portion, and the condensation part. The catalyst is in the lower portion of the reactor in a basket. Construction material for pyrolysis reactor is generally stainless steel. Product, i.e.,

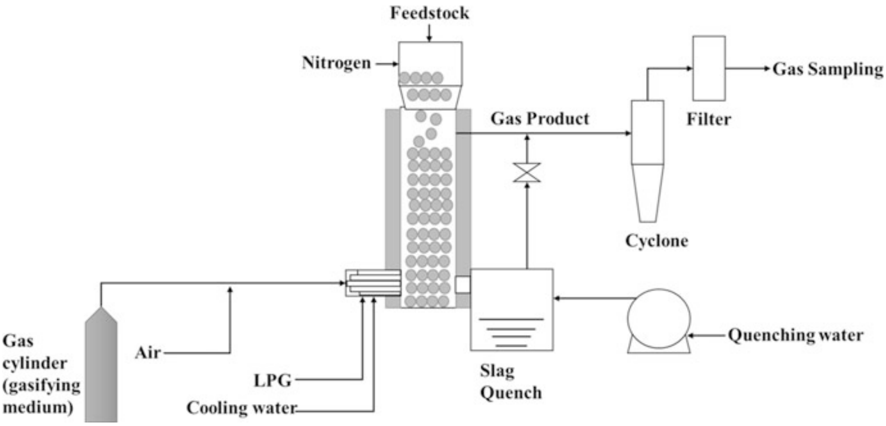


Fig. 10.3 A pilot-scale fixed-bed system (Chopra and Jain 2007)

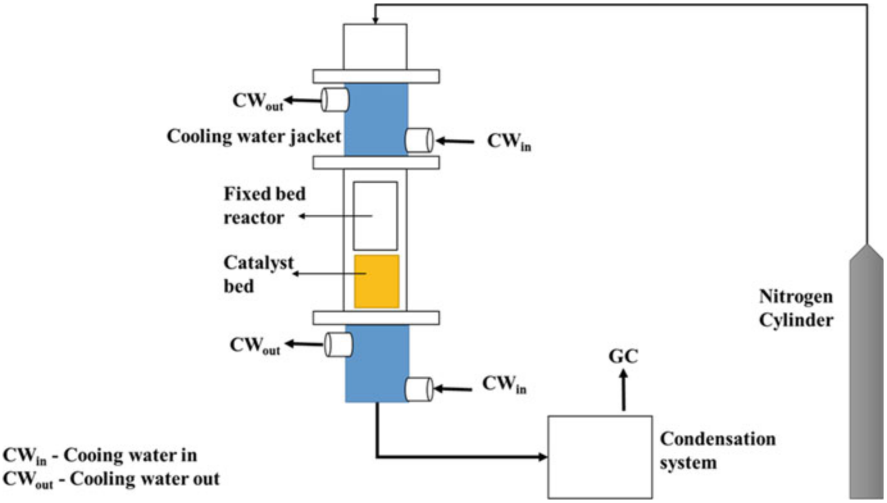


Fig. 10.4 Laboratory scale fixed bed reactor system with catalyst bed for fast pyrolysis (Cai et al. 2021)

gasses (contain bio-oil and flue gas), flow out of the reactor, whereas char remains within the reactor (Cai et al. 2021). Fixed bed combined with other technologies such as induction, microwave, catalyst, and solar, which can be modified to induction-heating fixed bed reactor, microwave fixed bed reactor, two-stage catalytic fixed bed reactor, and solar fixed bed reactor, respectively (Lewandowski et al. 2019; Tsai et al. 2006).

10.3.2 Fluidized Bed Reactor

In fluidized bed reactors, pressurized gas passes through the solid bed of feedstock, creating a solid-gas mixture that increases the contact area between solid and gas. This system provides a reasonable heat transfer rate, better reaction control, vapor residence time, high relative velocity between gas and solid phase. The various categories of fluidized bed types are bubbling fluidized bed reactor, circulating fluidized bed reactor, conical spouted reactor, internally circulating fluidized bed reactor, and rapid fluidized bed reactors (Jahirul et al. 2012; Lewandowski et al. 2019).

10.3.2.1 Bubbling Fluidized Bed Reactor (BFBR)

An illustration of BFBR is shown in Fig. 10.5. Fine particle of biomass is fed on hot fluidized sand. Fluidization is achieved either by inert gas or recycled flue gas. Fluidization velocity ranges from 0.5 to 3.0 m/s to keep the particle bed under suspension. Overhead space in the reactor, also known as the freeboard, can be greater than the diameter of the particle bed in size. The range of bio-oil yield is between 70% and 75%. Biochar is separated rapidly and does not accumulate in the

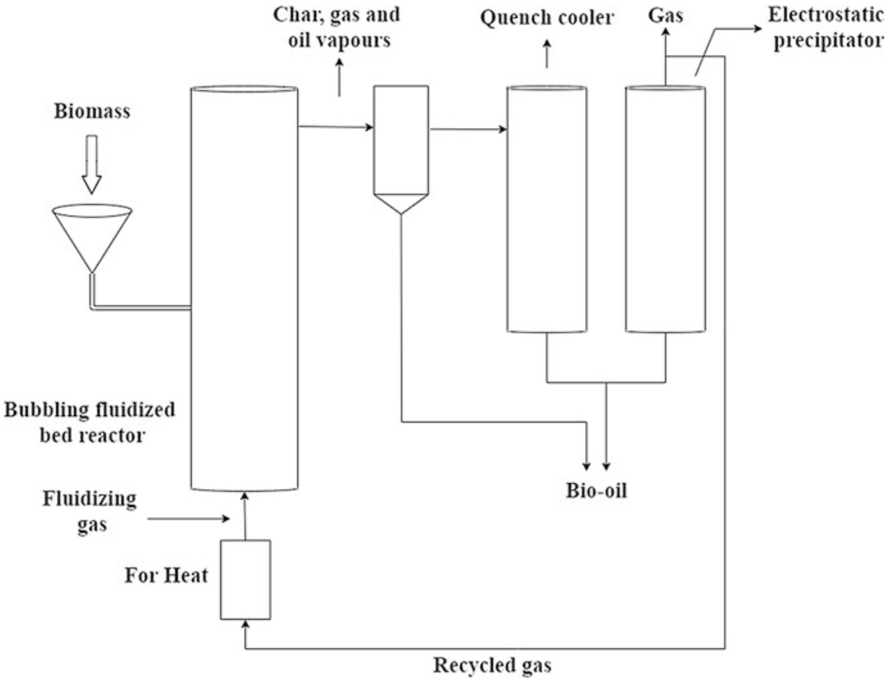


Fig. 10.5 Bubbling fluidized bed reactor (Mohan et al. 2006)

bed. This type of reactor shows product quality and consistent performance (Jahirul et al. 2012; Mohan et al. 2006; Basu 2010). Wang et al. (2018a, b) studied the combined effect of alkali metal oxides and HZSM-5 in fast pyrolysis of bamboo sawdust in a BFBR, combined with a fixed bed reactor of catalyst for enhancing the quality of bio-oil.

10.3.2.2 Circulating Fluidized Bed Reactor (CFBR)

A schematic representation of CFBR has been shown in Fig. 10.6. The working principle is similar to the bubbling fluidized bed reactor. It provides short vapor residence time the uniform temperature distribution with reasonable control. The regime of hydrodynamic for this reactor is referred to as a fast bed. Gas velocity in this reactor is higher than BFBR. The particle bed of this reactor is enlarged, and it has a loop seal which provides an external loop for solids, hence recyclization of the particle occurs, which in turn increases the particle residence time in comparison to BFBR (Basu 2010; Zaman et al. 2017; Lewandowski et al. 2019).

10.3.2.3 Conical Spouted Bed Reactor (CSBR)

Alvarez et al. (2014, 2016), performed fast pyrolysis of sewage sludge and rice husk in a conical spouted bed reactor. A pilot-scale plant for this type of reactor has been picturized in the given Fig. 10.7. CSBR can be used for the pyrolysis of lignocellulosic biomass, tires, plastics, and other waste. The feedstock of irregular textures, sticky solids, and fine particles can be handled easily. It provides low vapor residence time in the spout zone and a little higher in the annulus zone. Bio-oil yield is above 60% for rice husk (Alvarez et al. 2014, 2016). It can be modified to CSBR with an integrated superheater, CSBR with a separate superheater, CSBR

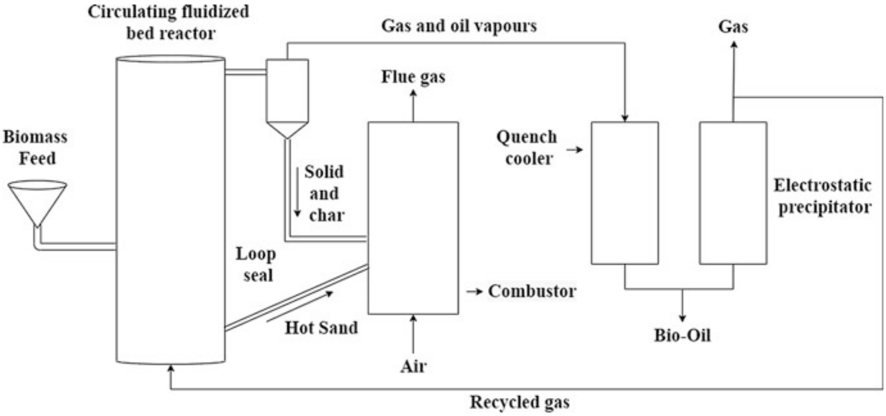


Fig. 10.6 Circulating fluidized bed reactor (Mohan et al. 2006)

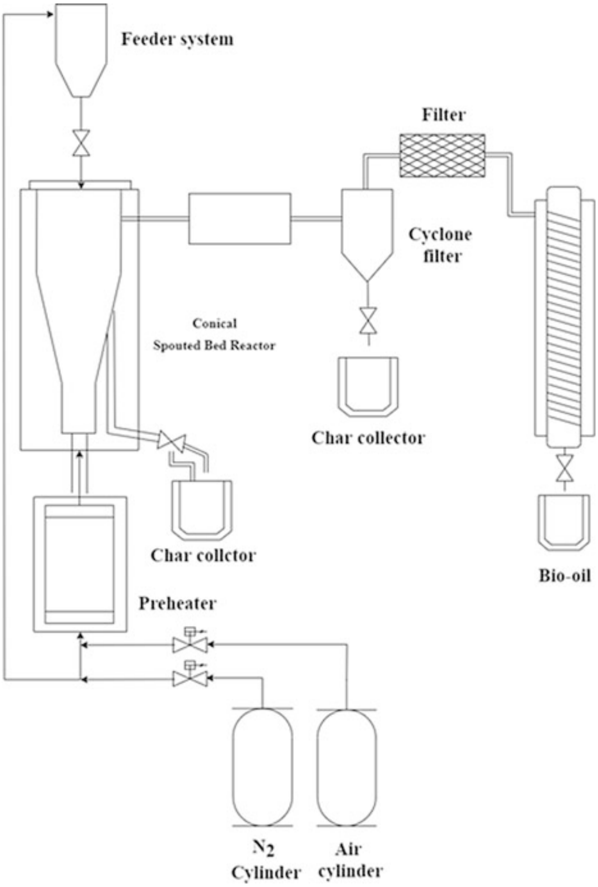


Fig. 10.7 Conical spouted bed reactor (Lewandowski et al. 2019)

with draught tube, CSBR with catalyst, CSBR under vacuum, dual conical spouted reactor (Lewandowski et al. 2019; Fernandez-akarregi et al. 2014).

10.3.2.4 Internally Circulating Fluidized Bed Reactor (ICFBR)

It is classified into the category of ultra-fast or flash pyrolysis due to meager vapor residence time. Here riser and sand heater are combined in a single unit. The raw material is introduced with the riser gas and meets the hot sand particle carried from the annulus to the mixing zone at the bottom of the riser, as shown in Fig. 10.8. The temperature here ranges between 780 and 860 °C with a residence time of 400–600 ms, and the yield for volatile is greater than 90%. It can also produce oil from plastics and tires (Briens et al. 2008; Lewandowski et al. 2019).

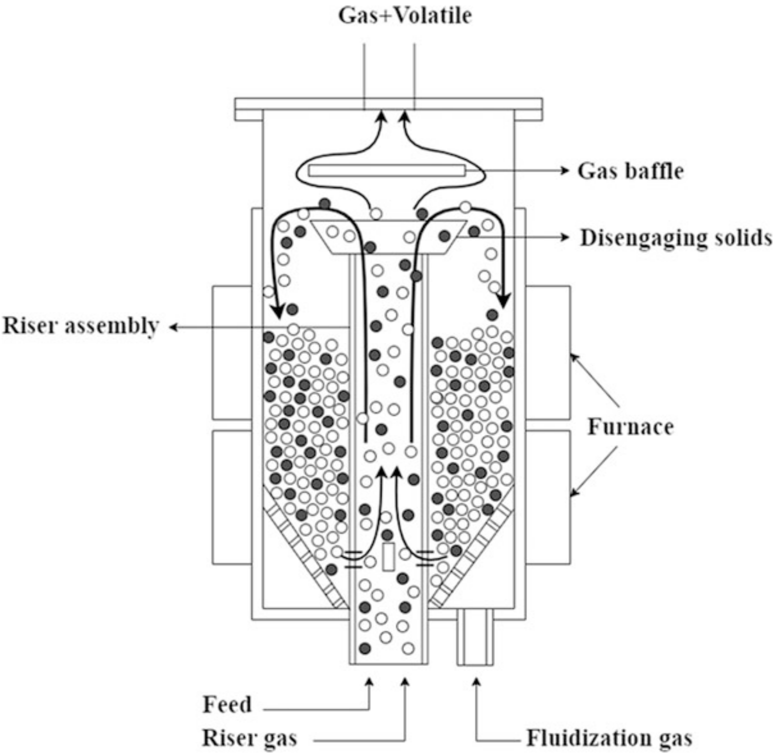


Fig. 10.8 Internally circulating fluidized bed reactor (Lewandowski et al. 2019)

10.3.2.5 Rapid Fluidized Bed Reactors

This type of reactor is used for rapid thermal pyrolysis (RTP). Here feedstock is introduced to high-velocity uprising hot sand (sometimes referred to as Fast Fluidizations or Jet Spouted Beds) at 500 °C, and then it is cooled down within seconds. The heating rate is 1000 K/s and vapor residence time ranges from a few hundredths of milliseconds to 5 s. Here bio-oil yield for wood is in the range of 83% (Lewandowski et al. 2019).

10.3.3 Ultra-Rapid Pyrolyzer

This type of reactor provides a high heating rate, very short residence time and generates a high bio-oil yield. Given Fig. 10.9. shows a pictorial representation of an ultra-rapid pyrolyzer. It provides a concise mixing time (10–20 ms), short residence time (70–200 ms), and quench time (20 ms). Despite the 650 °C temperature of the reactor, liquid yield can reach up to 90%. Preheated inert gas at 100 °C is made to

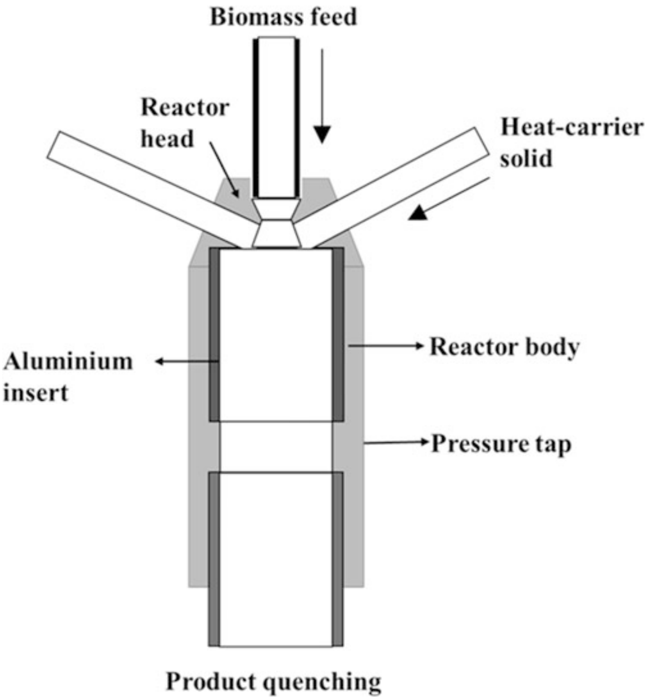


Fig. 10.9 Ultra-rapid pyrolyzer (Basu 2010)

colloid with biomass stream in the reactor. Externally heated thermal carrier, i.e., sand, is bombarded on biomass which enters through multiple jets. This type of collision creates a very high heating rate, and biomass is pyrolyzed within a millisecond. The vapor leaving the reactor is quenched quickly to restrict the cracking or secondary reaction to prevent gas conversion (Basu 2010).

10.3.4 Free-Fall Reactor

The free-fall reactor is also referred to with many other terms: drop tube reactor, entrained flow reactor, a flow reactor, tubular reactor, and a downflow reactor. Biomass or other feedstock is fed from the top of the reactor, which is co-current with the gas stream and falls under gravity. During the fall, sample gets pyrolyzed along the way. It is a relatively simple design for a reactor and easy to scale up; that is why many researchers adopt it. High temperature in the reactor is achieved either using electrical heating or combustible gas such as air and propane mixture. A schematic diagram for a fast pyrolysis system with a free-fall reactor is shown in Fig. 10.10 (Lu et al. 1994; Jones et al. 2009; Papari and Hawboldt 2013; Billaud et al. 2016). Pattiya et al. (2012) worked on a free-fall reactor for fast pyrolysis on

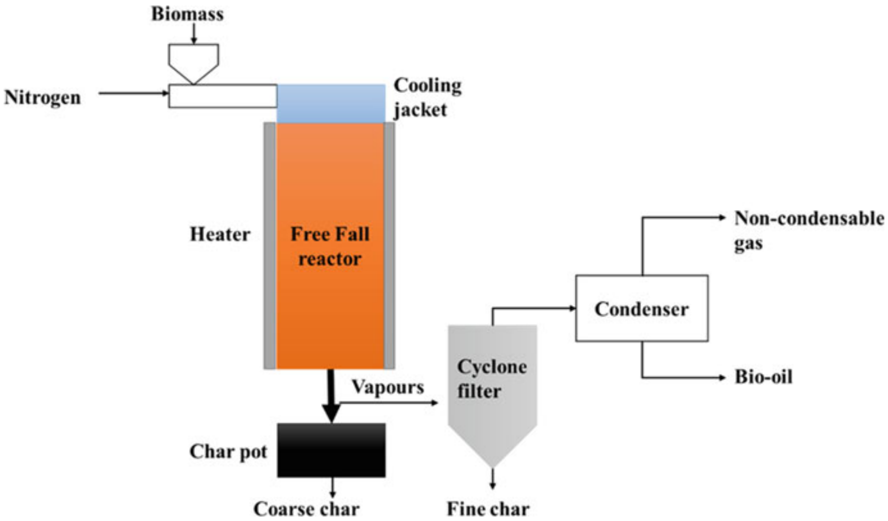


Fig. 10.10 Free-fall reactor (Papari and Hawboldt 2013)

sugarcane and cassava residues. The bio-oil yield of 70% can be produced through fast pyrolysis of cassava stalk in a free-fall reactor at 450 °C.

In a study by Mok et al. (1985) demonstrated increased heating efficiency of biomass by using Thermovortactor on the top of the reactor. Two conical vessels termed vortical contactors, or Vortactors, are used with the entrained flow reactor. One Vortactor at the top of the reactor transfers the heat from preheated nitrogen gas or suspended particles known as Thermofor stream to biomass feed. Other Vortactor supplied with liquid nitrogen, known as cryovortactor, is present at the end of the reactor for fast quenching of vapor products. (Mok et al. 1985).

10.3.5 Rotating Cone Pyrolyzer

This reactor has been in development since the early 1990s in The Netherlands at the University of Twente. Heat carrier, i.e., sand and the biomass feed, is introduced from the top and falls on the base of a rotating cone that revolves at 360–390 revolutions per minute and provides excellent mixing. Biomass pyrolyzed in a small annular volume at a very high heating rate of 5000 K/s. The particle moves spirally along the hot wall up to the lip of the cone due to centrifugal force. A solid particle containing char and sand is spilled over the lip of the cone and generated vapors containing bio-oil move towards the condenser through the other tube. Spilled hot sand and char move towards the bottom of the reactor, where char is combusted in a fluidized bed, as shown in Fig. 10.11. This helps in heating the cone and sand. It provides a short residence time for vapor (0.3 s), and an excellent bio-oil yield ranges from 60% to 70% on dry feed as this reactor does not require any inert

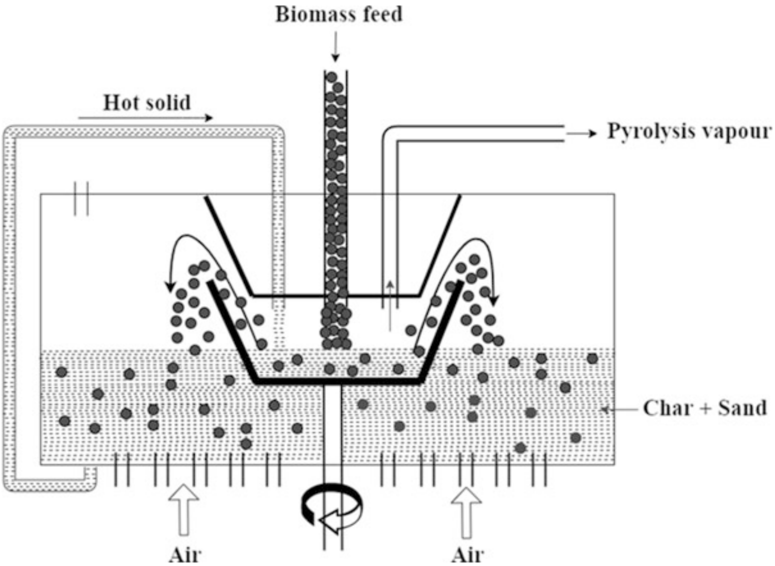


Fig. 10.11 Rotating cone pyrolyzer (Basu 2010)

gas, resulting in small downstream equipment. In Malaysia, a plant with a rotating cone pyrolyzer is commissioned to operate at a capacity of 2 × 10^6 tons per day using empty fruit bunch of palm oil. (Isahak et al. 2012; Jones et al. 2009; Basu 2010).

10.3.6 *Ablative Pyrolyzer*

This type of pyrolyzer comes in the category of advanced type of fast or flash pyrolysis. Here heat transfer takes place through direct contact with a hot rotating disk or a hot surface of the reactor. Biomass is pressed or impacted against this hot surface through mechanical pressure. This type of pyrolyzer can handle large particles compared to another pyrolyzer. Depending upon the requirements, size can vary up to 20 mm. Mainly two types of reactor come under this: Vortex type reactor and rotating disk reactor (Lewandowski et al. 2019; Jahirul et al. 2012).

10.3.6.1 Vortex Reactor

In a vortex reactor biomass particle is fed along with a stream of inert gas or steam as shown in Fig. 10.12. It is injected tangentially into the cyclone reactor (cylindrical reactor) at high pressure with a velocity of 400 m/s. The biomass particle faces the high temperature of the reactor wall which is in the range of 625 °C. High centrifugal

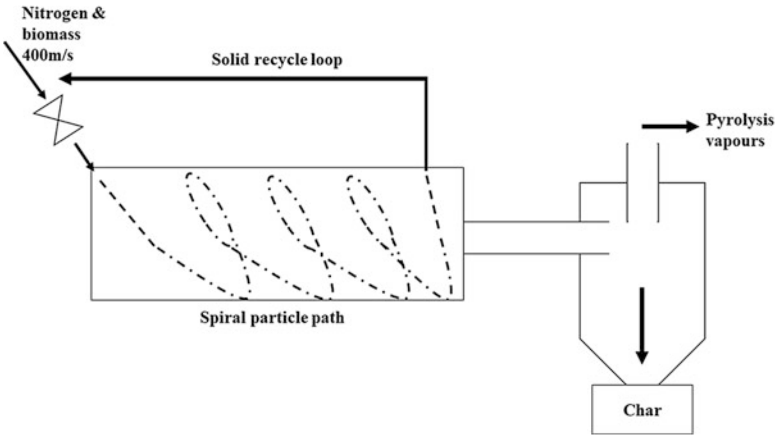
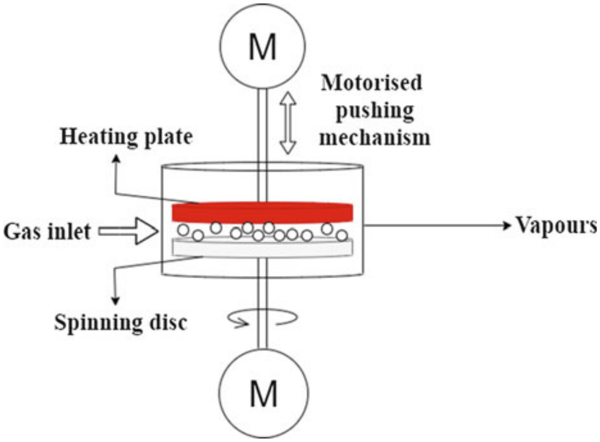


Fig. 10.12 Vortex reactor (Lu et al. 1994)

Fig. 10.13 Rotating disk reactor (Cai et al. 2021)



force is experienced by the particle and induces a high ablation rate. The liquid film is formed at the wall of the reactor and evaporates rapidly. Generated vapor is carried away by sweeping gas very quickly within 50–100 milliseconds. Particles that are not converted but are recycled through the recycle loop. Complete conversion can be seen in 15 cycles and the bio-oil yield reaches up to 80% (Lewandowski et al. 2019; Lu et al. 1994; Jahirul et al. 2012).

10.3.6.2 Rotating Disk Reactor

In this type of reactor, biomass is fed forcefully on top of a hot rotating disk. Biomass is pyrolyzed when it comes in contact with the rotating disk, which melts the biomass and produces vapor, as shown in Fig. 10.13. An inert gas may or may not be used as sweeping gas. Biomass does not require extensive grinding and can save energy. The yield of bio-oil from this reactor of large size biomass is similar to that of a fluidized bed with a particle size of less than 1 mm (Cai et al. 2021; Jahirul et al. 2012; Jones et al. 2009).

10.3.7 Auger Reactor or Moving Bed Reactor

Auger reactor is also called a moving bed reactor, which uses a screw-based reactor that helps move and pyrolyze the biomass particles in a cylindrical tube heated in an oxygen-free environment, as shown in Fig. 10.14. This reactor reaches a temperature range of 400–800 °C, responsible for the devolatilization of biomass particles. This reactor can handle a large amount of biomass, also provides reasonable control of residence times, and generates a high quality of bio-oil. The screw in the reactor can be modified into Twin Screw (a twin-screw mixer reactor) and a concentric screw (dual concentric rotary cylinder reactor) (Jahirul et al. 2012; Henrich et al. 2016; Fu et al. 2018; Cai et al. 2021).

10.3.8 PyRos Reactor

PyRos reactor is equipped with a rotational filter within a cyclonic reactor to produce particle-free bio-oil, as shown in Fig. 10.15. The working temperature range is 450–550 °C, and residence time varies between 0.5 and 1 s to stop further cracking. Biomass particles mixed with preheated sand particles (an inert material) in the ratio of 1:15. A mixture of sand that acts as a heat carrier, biomass, and inert gas is fed into the reactor. Pyrolysis is achieved using direct contact with the heat carrier. Solid particles and gas are separated with the help of centrifugal force. Solid particles are

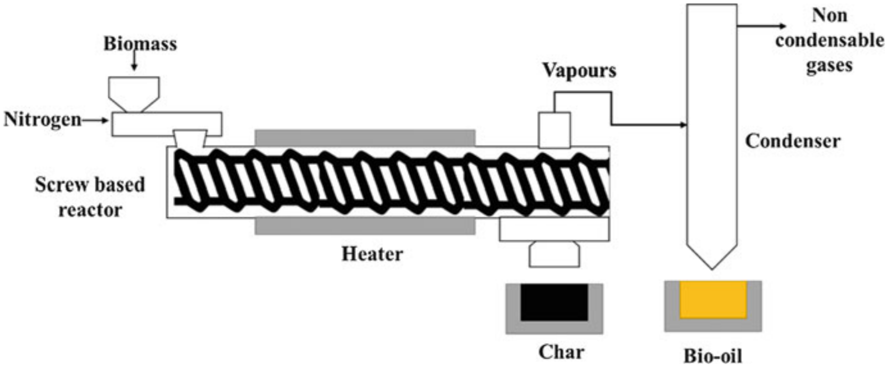


Fig. 10.14 Auger reactor or moving bed reactor (Cai et al. 2021)

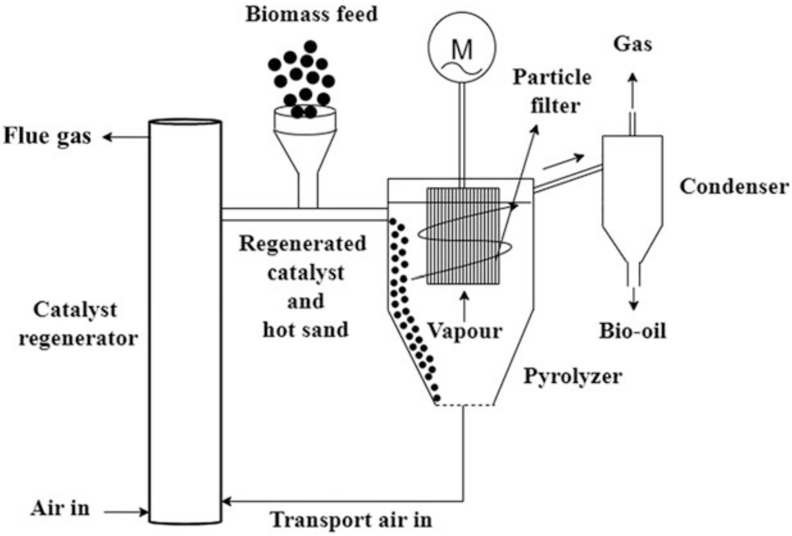


Fig. 10.15 PyRos reactor (Brem and Bramer, 2007)

thrown towards the wall, which slides down. During this time, efficient heat transfer takes place which results in devolatilization. The solid residue is sent back to the regenerator to complete the cycle. The removed gas is passed through a rotational filter, particle-free vapor from the reactor is transformed into bio-oil using a condenser. This reactor produces bio-oil yield of 70–75%. Also, it is low-cost and compact in comparison to other reactors. Along with inert material or heat carrier, a catalyst such as sodium-based alumina can also be used in this reactor (Brem and Bramer, 2007; Jahirul et al. 2012; Imran et al. 2018).

10.3.9 Multiple Hearth or Vacuum Pyrolysis Reactors

Vacuum pyrolysis is combined with a multiple hearth reactor commonly known as a vacuum pyrolysis reactor. Rector is divided into various sections, as shown in Fig. 10.16. The top section of the hearth has a temperature of 200 °C whereas the bottom section of the hearth is around 400 °C. Here, biomass is fed from the top of the multiple hearth reactor. Biomass moves downward due to gravity and a mechanically driven scraper. During downward movement, it passes through various sections of different temperatures. At the bottom of the reactor, only char remains, which can be removed easily. The vapor is removed instantaneously from the reactor using a vacuum pump that works at a 1 kPa pressure. In this process, the heat transfer rate is lower, but vapor residence time is shorter. Due to the low heating rate, bio-oil yield ranges from 30 to 45%, which is very low compared to other reactors. Various

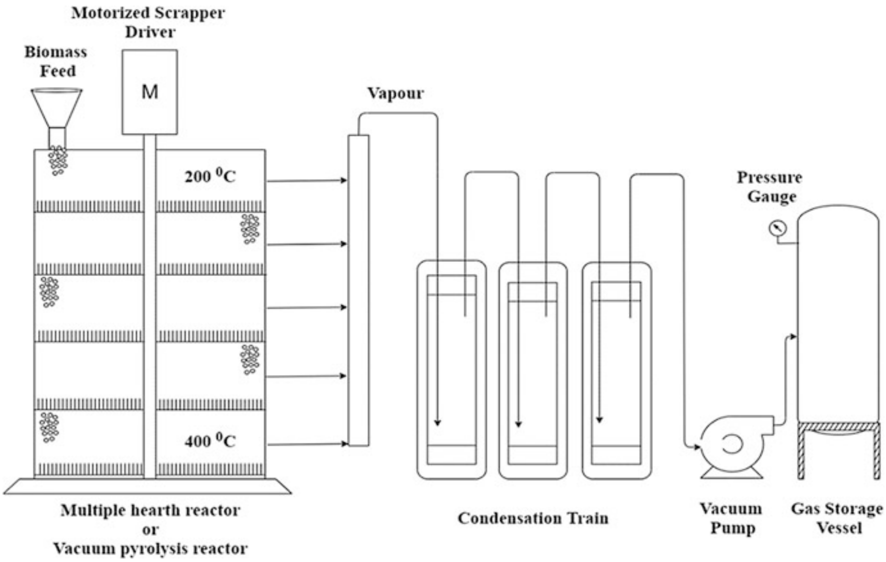


Fig. 10.16 Multiple hearth or vacuum pyrolysis reactor (Lu et al. 1994; Basu 2010)

study shows that scaling up of this reactor will involve considerable expense due to high capital cost and maintenance cost as it will require an increased capacity vacuum pump and large mechanical transporter (Lu et al. 1994; Basu 2010; Isahak et al. 2012).

10.3.10 Microwave Reactor

Microwave-assisted fast pyrolysis reactor consists of a quartz reactor placed inside a microwave oven, as shown in Fig. 10.17. As discussed earlier, it can be either premixed or non-premixed microwave-assisted fast pyrolysis. In both cases, absorbed microwave energy is used to pyrolyze the sample. This type of reactor has efficient heat transfer, heating process with exponential control, and enhanced chemical reactivity. Sometimes hotspot appears in the microwave, which is responsible for the production of syngas. A wide range of biomass and industrial waste can be used as feedstock in this reactor, generating a high yield of bio-oil and syngas. Various modification is seen in microwave-assisted pyrolysis, such as the recent study by Wang et al. (2018a, b) demonstrated continuous fast microwave pyrolysis, and Zhang et al. (2018) worked on two-step microwave-assisted catalytic fast pyrolysis (Jahirul et al. 2012; Wang et al. 2018a, b; Zhang et al. 2018; Lewandowski et al. 2019).

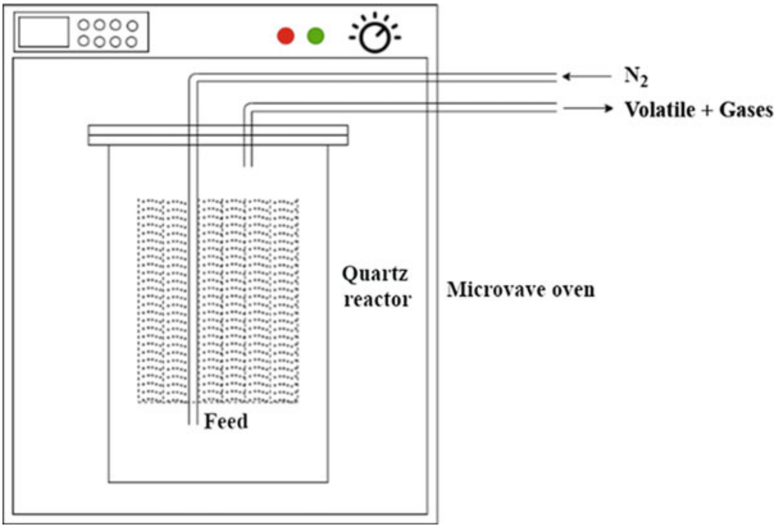


Fig. 10.17 Microwave reactor (Lewandowski et al. 2019)

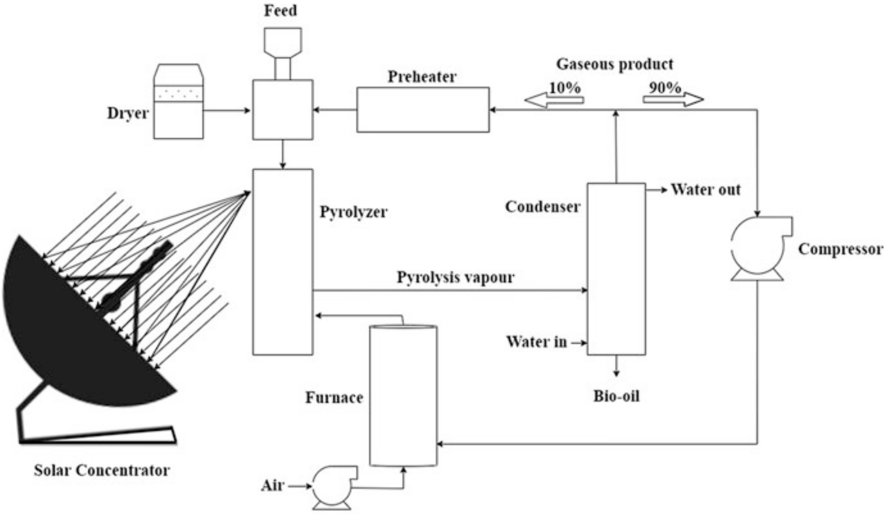


Fig. 10.18 Solar pyrolyzer (Joardder et al. 2014)

10.3.11 Solar Reactor

The construction material that is used for the reactor is quartz. The reactor is opaque, located at the focal point of the concentrator, as shown in Fig. 10.18. The reactor temperature can reach higher than 700 °C. Solar reactors offer a quick start-up and shut-down period in comparison to slow pyrolysis reactors. Joardder et al. (2014) showed the various arrangements of the reactor and solar concentrator. The reactor can be equipped with rotating capability and sliding capability along with a solar concentrator for continuous heating (Jahirul et al. 2012; Joardder et al. 2014).

10.3.12 Plasma Reactor

A plasma reactor is made from quartz in the form of a cylindrical tube surrounded by copper electrodes. Biomass is fed in the middle of the tube using a screw feeder present at the top of the tube as presented in Fig. 10.19. The reactor is filled with inert gas (nitrogen, argon) to create an oxygen-free environment. Electrical energy is provided through electrodes to generate plasma from the inert gas. This plasma is used to pyrolyze or gasify the biomass present in the tube. From the reactor, pyrolysis vapors are removed using a variable speed vacuum pump. On the one hand, the high operating cost of the reactor and high electricity consumption are limitations of this process and on the other hand, it generates high energy density within the reactor. This form of energy creates a high temperature that eliminates the tar formation by cracking (Tang and Huang 2005; Van Oost et al. 2006; Jahirul et al. 2012).

10.3.13 Pulse Shock Tube

Fast pyrolysis can also be performed on a shock tube using pulses of high energy. This process focuses on producing tar-free gas, mainly CO_2, CO, CH_4, C_2H_2, and

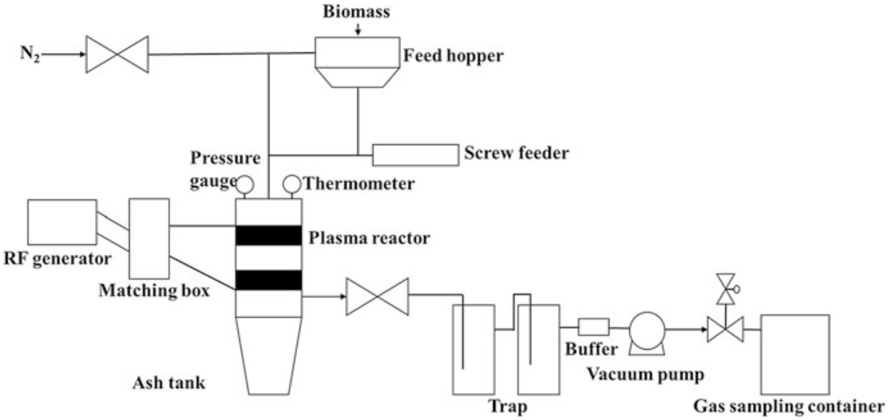


Fig. 10.19 Line diagram of a radio frequency (RF) plasma pyrolysis rector system (Tang and Huang 2005)

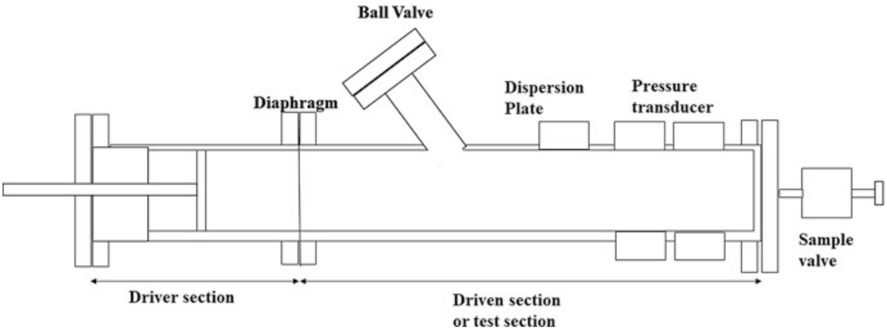


Fig. 10.20 A schematic of a shock tube (Mebklin 1994)

C_2H_4. The temperature in the shock tube is greater than 700 °C. The heating rate can reach as high as 10^4 °C/s, and the reaction time is less than 0.5 s. The shock tube consists of two main sections: the driver and test (driven unit) sections separated from the flanged diaphragm, as shown in Fig. 10.20. Helium was used in the driver section as high-pressure gas, and argon was used in the driven section as a low-pressure gas. Diaphragm gets ruptured due to high pressure from the driver section, which creates a shock wave that heats the sample in the test section and is heated again by reflected shockwave to reach the desired temperature for fast pyrolysis (Mebklin 1994).

10.4 Enhancing Bio-Oil Properties

Raw bio-oil or unprocessed pyrolysis oil is not fit for direct application. During bio-oil storage for an extended period, it may lead to oxidation that deteriorates bio-oil quality. Due to the high viscosity of bio-oil balancing pressure drops during its transports, it can be overcome at the expense of high maintenance of the instruments or equipment. Low pH indicates the acidic nature of bio-oil that can lead to corrosion of storing equipment. The increased presence of various component that differs in chemical nature is the reason for phase separation or layering, which is responsible for creating hindrance during filtration. The presence of alkali metal in the bio-oil leads to depositions in the boilers and in combustion chambers that affect the equipment's efficiency. High moisture content in bio-oil reduces calorific value and stability, proceeds to phase separation, and complicates in nature of viscosity. To eliminate these problems bio-oil needs to be upgraded. It requires some chemical change for stabilization, viscosity reduction, deoxygenation, and reduction of molecular weight that can be achieved using various upgradation techniques (Gollakota et al. 2016; Jacobson et al. 2013).

10.4.1 Bio-Oil Pretreatment Methods

In some cases, pretreatment of bio-oil is required for further upgradation. Pretreatment includes the removal of moisture, and fine particles (char) that improve viscosity, calorific value, density, and reduce catalyst poisoning. Fine particles can be removed using a centrifuge. Moisture can be removed from bio-oil through various means such as distillation, dehydration, reactive rectification, and physico-chemical separation. (Wang et al. 2009; Jacobson et al. 2013).

Dehydration of bio-oil can be performed using the chemical sodium sulfate (Na_2SO_4). Na_2SO_4 was mixed with bio-oil in a ratio of 1:3. This technique removes water partly and also increases the concentration of sulfur in bio-oil. In reactive distillation, lower molecular weight carboxylic acid (volatile organic acid) is converted to ester and is separated using reactive distillation. Also, a layer of water and the non-volatile compound is formed. This process shows the water reduction from 33% to 11%. Fractionation of bio-oil can be done with the help of excess water when a large quantity of water is added in bio-oil two-layer form. The top layer consists of high polarity compounds and some carbohydrate derivatives (Jacobson et al. 2013).

Fine particles can be removed directly from vapor termed as hot vapor filtration (HVF) and if the fine particle is removed from bio-oil then it is termed liquid phase filtration. HVF can be in situ or ex situ; in situ filtration is performed within the reactor, and ex situ filtration is performed outside the reactor. Liquid filtration is achieved using a membrane (ceramic) after pyrolysis condensation (Kumar and Strezov 2021).

10.4.2 Upgradation Technique

There are various methods as mentioned below for upgrading bio-oil or transforming it into a resourceful fuel. (Patel and Kumar 2016; Zhang et al. 2013; Kumar and Strezov 2021; No 2014):-

- Catalytic pyrolysis
- Hydroprocessing
  - Hydrotreating
  - Hydrocracking
- Steam reforming
- Supercritical fluids
- Esterification
- Emulsification and blending
- Molecular distillation
- Electrochemical or electrocatalytic upgrading of bio-oil

10.4.2.1 Catalytic Pyrolysis

The fast pyrolysis process with catalyst, also called the catalytic process, provides upgraded bio-oil. Mainly, oxygenated molecules are transformed into less oxygenated molecules or hydrocarbons. There are three variants of this process that can be found in the literature which are mentioned below (Kumar et al. 2019):

- The in situ catalytic upgrading process involves mixing feedstock and catalyst before feeding it to the reactor, as shown in Fig. 10.21(a). This type of upgradation is generally incorporated with fixed bed reactor, fluidized bed

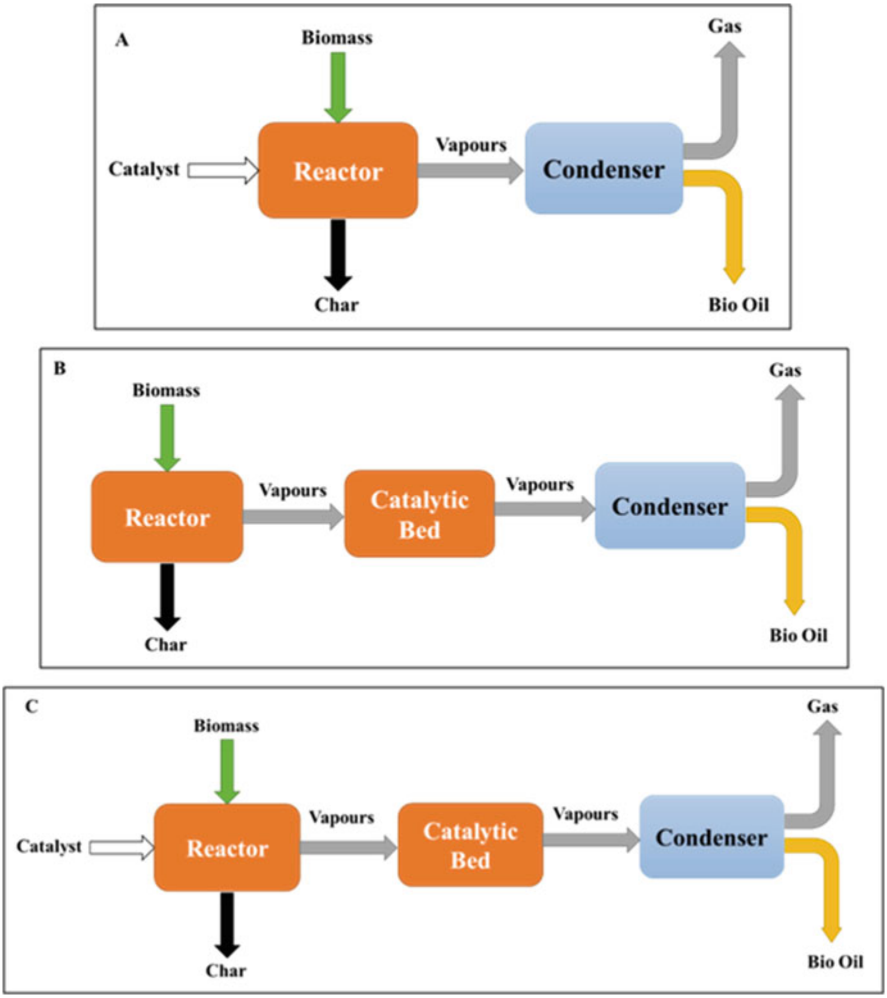


Fig. 10.21 Above picture represents various configurations of catalytic processes: in situ (**a**) ex situ (**b**) and combined in situ and ex situ (**c**) process. (Imran et al. 2018; Kumar et al. 2019)

reactor, microwave reactor, etc. The required catalyst is high to maximize the contact between generated vapors and the catalyst surface. This can be either in continuous or batch reactors. (Fan et al. 2018; Imran et al. 2018; Wang et al. 2014).

- Ex situ catalytic upgrading process: The pyrolysis and catalytic (reactor with catalytic bed) reactors are separate. Here vapor generated from the pyrolysis reactor is passed through the downstream catalytic reactor for upgradation, as shown in Fig. 10.21(b). Individual reactors provide reasonable control over temperature. Due to separate reactors, vapor does not mix with char during the upgradation process. Catalyst consumption is lower in comparison to the in situ method (Fan et al. 2018; Imran et al. 2018).
- Combination of in situ and ex situ process: As the name suggests, it is the combination of in situ and ex situ processes as shown in Fig. 10.21(c). The combined upgradation technique can achieve remarkable transformation of the oxygenated compound. Kumar et al. (2019) performed a study on a combined process and completed 98% conversion of oxygenated compounds higher than the individual in situ and ex situ processes (Kumar et al. 2019).

Conventional catalytic cracking in the petroleum industry referred to the transformation of heavy distillate to light and medium distillate. The same process can be used to reform the large and highly oxygenated molecule of bio-oil. This process is set up under high pressure, temperature above 350 °C in the presence of a catalyst (e.g., HZSM-5) along with hydrogen gas. Catalytic cracking has been performed in two patterns. One is only catalytic cracking, and the second is the combination of catalytic pyrolysis and catalytic cracking (Jacobson et al. 2013; Zhang et al. 2013; Baloch et al. 2018).

10.4.2.2 Hydroprocessing

Conventional catalytic cracking in the petroleum industry referred to the transformation of heavy distillate to light and medium distillate. The same process can be used to reform the large and highly oxygenated molecule of bio-oil. This process is set up under high pressure, temperature above 350 °C in the presence of a catalyst (e.g., HZSM-5) along with hydrogen gas. Catalytic cracking has been performed in two patterns. One is only catalytic cracking, and the second is the combination of catalytic pyrolysis and catalytic cracking (Jacobson et al. 2013; Zhang et al. 2013).

Hydroprocessing, also referred to as catalytic hydrogenation, is the combined process of hydrotreating and hydrocracking, as shown in Fig. 10.22 (Patel and Kumar 2016).

- Hydrotreating unit: The preliminary stage for removing heteroatoms from the feed before introducing them to the hydrocracking unit. Here, the reaction occurs in the presence of hydrogen and catalyst, whereas temperature varies between 300 and 400 °C and pressure is in the range of 50–200 bars. It involves the following reactions (Patel and Kumar 2016; Jacobson et al. 2013).

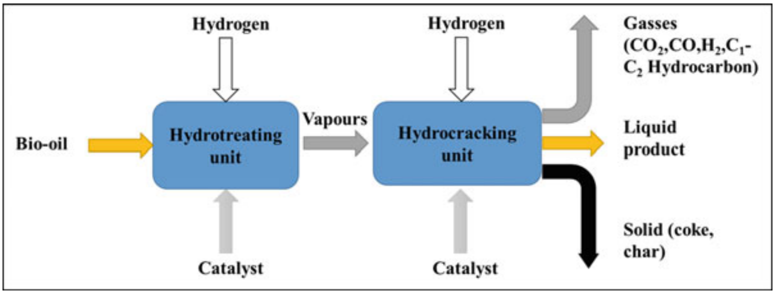


Fig. 10.22 Hydroprocessing flow diagram (Patel and Kumar 2016)

  - Hydrodesulfurization (HDS): It involves the removal of sulfur from the compound and transforming it into hydrogen sulfide as mentioned in the given reaction:

$$R - SH + H_2 \rightarrow R - H + H_2S \tag{10.1}$$

  - Hydrodenitrogenation (HDN): It involves the removal of nitrogen from the compound and transforming it into ammonia as mentioned in the reaction:

$$\text{Pyridine} + H_2 \rightarrow \text{Pentane} + NH_3 \tag{10.2}$$

  - Hydrodeoxygenation (HDO): The hydrotreating process can be of high severity, meaning complete hydrodeoxygenation, and low severity, which means partial hydrodeoxygenation depending upon temperature. This process removes oxygen from the compound and converts it to water, as mentioned in the reaction:

$$R - OH + H_2 \rightarrow R - H + H_2O \tag{10.3}$$

  - Hydrodearomatization (HDA): It involves transforming polynuclear aromatics into three rings, then two rings, then one ring, and then the end products (The Crankshaft Publishing, n.d.).
  - Hydrodemetallation/Hydrodemetallization (HDM): Removal of metals and transforming them to relative metal sulfide (The Crankshaft Publishing, n.d.; Jacobson et al. 2013).

- Hydrocracking unit: This unit further improves the quality of bio-oil. Reaction in this unit occurs at elevated temperature and pressure in the presence of hydrogen and catalyst. The following reactions take place in this unit:
  - Hydrodealkylation: It involves the removal of an alkyl group from the compounds as shown in the reaction:

$$R-C_6H_5+H_2 \rightarrow C_6H_6+R-H \tag{10.4}$$

- Hydrocracking: Cleavage of high molecular weight compound results in the formation of two lower hydrocarbons as mentioned in the reaction:

$$R1-CH_2-CH_2-R2+H_2 \rightarrow R1-CH_3+R2-CH_3 \tag{10.5}$$

- Isomerization of alkanes: It involves rearrangement of molecules such as:

$$\text{Pentane} \rightarrow \text{Isopentane} \tag{10.6}$$

- Hydrodecyclization: Reduction of the number of cyclic compounds.

- Another reaction takes place in both units.
  - Decarboxylation: Removal of a carboxylic acid group from the compound.

$$R-COOH \rightarrow R-H+CO_2 \tag{10.7}$$

- Decarbonylation: Removal of aldehyde group from the compound.

$$R-CHO \rightarrow R-H+CO \tag{10.8}$$

- Water−gas shift reaction:

$$CO_2+H_2 \rightarrow CO+H_2O \tag{10.9}$$

- Methanation: Carbon monoxide and carbon dioxide convert to methane in the presence of hydrogen.
  - Coke formation:

$$\text{Polyaromatics} \rightarrow \text{Coke} \tag{10.10}$$

10.4.2.3 Steam Reforming

Steam reforming or catalytic steam reforming process helps to produce hydrogen from bio-oil simultaneously upgrading the bio-oil in the presence of steam in a temperature range of 350–1000 °C. This process is affected by steam to carbon ratio, temperature, and material space velocity. A high amount of steam leads to a water-gas shift reaction. At low temperatures, generated hydrogen reacts with carbon monoxide to form methane. The problem associated with this is the formation of coke that deactivates the catalyst. A fluidized bed reactor or fixed bed reactor is generally used in this process. Other reactors are spouted bed reactor, tubular quartz microreactor, and combined two-stage pyrolysis-reforming reactor. Sometimes the process can be modified to use two reactors of the exact nature or different nature, for example, two-stage fixed bed reactor, fixed bed reactor combined with fluidized bed reactor, spouted bed reactor combined with fluidized bed reactor (Kumar and Strezov 2021; Zhang et al. 2013; Wu et al. 2008).

10.4.2.4 Supercritical Fluids Extraction

Supercritical fluids (SFCs) provide a medium to upgrade the bio-oil with low viscosity and high calorific value. Various solvents such as ethanol, methanol, water, and CO_2 are used to improve the quality of bio-oil. Further enhancement in bio-oil can be achieved by adding catalysts such as aluminum silicate and HZSM-5. Upgrading of bio-oil can be performed with an autoclave reactor. SCFs, catalysts, and bio-oil are mixed and fed into the reactor. The reactor is purged with a gas (e.g., hydrogen) to remove oxygen. Then the reaction is performed at high temperature (563 K) and high pressure (2 MPa) with a certain value of residence time (5 h). The disadvantage of this process is that it is only applied on a laboratory scale, due to economic feasibility it cannot be applied on a large scale (Li et al. 2011; Zhang et al. 2013).

10.4.2.5 Esterification

The presence of carboxylic acid creates an opportunity to transform it into ester with the help of catalytic esterification. The process improves bio-oil quality by lowering its viscosity, acid number, and water content. Its stability and corrosion properties are also promoted. This process is similar to the supercritical fluids process. The only difference is the priority of targeting species, i.e., carboxylic acids, and the temperature, which is lower in comparison to SFCs (60 °C) (Hong-you et al. 2010; Zhang et al. 2013).

10.4.2.6 Emulsification and Blending

Emulsification and blending are the physical upgrading techniques for bio-oil. In emulsification, two immiscible liquids are mixed, where one liquid forms tiny droplets and suspends on the second liquid. If droplet size is between 1 and 10 μm, it is simply emulsion, and when droplet size is in the range of 1–100 nm, it is known as a microemulsion. Bio-oil is emulsified with diesel and biodiesel in a particular ratio along with surfactant (Span 80), and co-surfactants (methanol) that decrease the viscosity increases the calorific value, and cetane number. Mixing can also be performed using ultrasound. Emulsified diesel and biodiesel can be introduced as fuel for the combustion engine. Bio-oil blended with diglyme and alcohols (such as methanol ethanol and isopropyl alcohol), decreases the value of viscosity, flashpoint, pour point, and density but increases its heating value (No 2014; Zhang et al. 2013; Kumar and Strezov 2021).

10.4.2.7 Molecular Distillation

It is also termed short path distillation because the distance between evaporation and condensation surface that is less than the mean free path of the molecule. This process is performed under a high vacuum to reduce the boiling point of the liquid. Due to a very short path molecule that is evaporated, condensed before even their collision with another molecule. Wang et al. (2009) use the molecular distillation apparatus KDL-5 developed by UIC Corporation, Germany. Bio-oil was divided into three categories, i.e., light middle and heavy fraction. The bio-oil recovery rate was higher than 97% (Wang et al. 2009).

10.4.2.8 Electrochemical or Electrocatalytic Upgrading of Bio-oil

This process is also termed electrolytic hydrogenation converts carbonyl and oxygenated compounds into valuable hydrocarbon. It uses an electrolytic cell that comprises cathode and anode compartments divided by a membrane. It can be either a cationic or anionic exchange membrane. Water is reduced to proton and oxygen at the anode, and bio-oil is hydrogenated through the addition of proton and evolution of hydrogen at the cathode as shown in Fig. 10.23. This evolved hydrogen can be

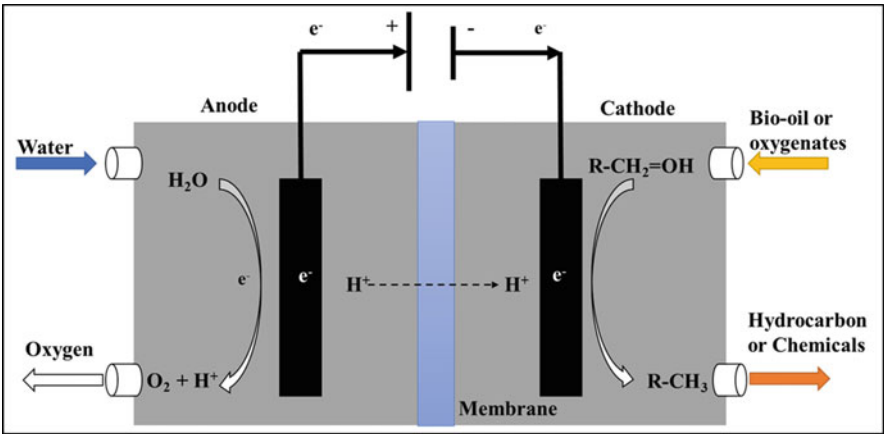


Fig. 10.23 Bio-oil upgradation through the electrochemical cell (Kumar and Strezov 2021)

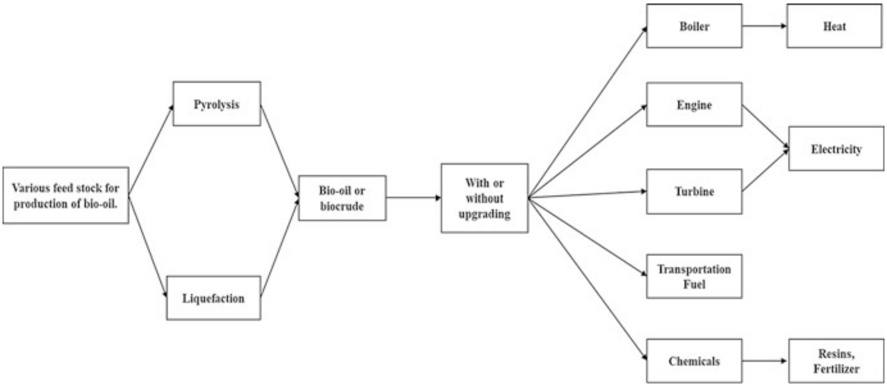


Fig. 10.24 Production to application of bio-oil (No 2014; Jahirul et al. 2012)

reduced by increasing the potential that increases conversion efficiency (Kumar and Strezov 2021).

10.4.3 *Applications of Bio-oil*

Upgraded bio-oil has the following application (Fig. 10.24) (Gollakota et al. 2016):

- It can be used as fuel for combustion.
- It can be used as fuel for power generation.
- It can be used as a transportation fuel (directly or blended with diesel).
- It can be used for the production of chemicals, resins, and anhydrous sugars (levoglucosan).
- It can be used as a binder for briquetting and palletization.
- It can be used as a wood preservative.

10.5 Techno-Economics and Environmental Sustainability of Bio-oil

Techno-economics analysis of production and upgradation of pyrolysis oil for various applications has already been stated in multiple research projects. Generally, the techno-economic analysis includes capital cost, operating cost, and cost of production per unit. Wright et al. (2010) studied the techno-economics for producing transportation fuel from biomass through fast pyrolysis. The plant was operated at 2000 tpd (ton per day) corn stover capacity. The upgradation technique involves in this process is hydroprocessing. Two scenarios involved one where hydrogen for upgradation is manufactured within the system using bio-oil, and the other is where

Table 10.4 Comparison of two processes (Wright et al. 2010)

Type of process	Includes hydrogen production unit	Includes purchased hydrogen
Capital cost	$287 million	$200 million
Operating cost	$109 million	$123 million
Fuel yield	134 × 10^6 L/year	220 × 10^6 L/year
Cost of fuel (equivalent to gasoline)	$3.09/gallon or $0.82/L	$2.11/gallon or $0.56/L
Production of bio-oil	104 × 10^6 gallon/year or 394 × 10^6 L/year	104 × 10^6 gallon/year or 394 × 10^6 L/year

hydrogen was purchased for upgradation. Various techno-economic parameters are discussed in Table 10.4 (Wright et al. 2010).

Another techno-economic simulation was performed on in situ and ex situ upgradation technique of pyrolysis oil with a plant capacity of 2000 MTPD (metric ton per day) by Li et al. (2015). Bio-oil yield generated was 438, 439 kg per BDMT (bone dry metric ton), and biofuel yields were 152.6 and 143.5 liters per dry metric ton (Li et al. 2015).

Zhu et al. (2014) simulated the techno-economic analysis of biofuel produced by upgrading the bio-oil derived from hydrothermal liquefaction. Here bio-oil was upgraded through hydroprocessing which involves hydrocracking and hydrotreating. Here plant capacity is 2000 MTPD of feedstock. The total capital cost of the plant turned out to be $512 million, whereas the operating expense was $100.64 million. The minimum fuel selling price comes out to be $4.44 per gallon gasoline equivalent. It was also mentioned that the cost of biofuel is not competitive enough to beat the pricing of conventional gasoline (Zhu et al. 2014).

Lam et al. (2019) studied a microwave non-premixed pyrolysis system to produce bio-oil using activated carbon and under a vacuum. As the process is non-premixed, activated carbon is used as the radiation absorber before feedstock (waste plastic and waste cooking oil) is fed to the reactor. Two studies were performed on a lab scale; one is in the presence of nitrogen, and the other is without it. Results have shown that without using nitrogen in the process, the liquid yield was high. Process without nitrogen was scaled up from 0.1 kg/h to 100 kg/h. Total capital cost and the annual operating cost were $3146 and $30,233. The cost of a liquid fuel unit per liter was found to be $0.25 (Lam et al. 2019).

Hsu (2012) has structured a study on LCA (life cycle assessment) on diesel and gasoline produced through fast pyrolysis of forest residue and hydroprocessing as an upgradation technique. GHG emission in the case of gasoline derived from bio-oil was 117 g/km, which is much lesser than conventional gasoline 300 g/km (in 2005), and net energy value (NEV) was 1.09 MJ/km. In the case of diesel derived from bio-oil, GHG was 98 g/km, and NEV was 0.92 MJ/km. If the hydrogen and electricity generation plant were built within the system, the GHG emission could be further lowered to 62 g/km for diesel and 74 g/km for gasoline (Hsu 2012).

Fan et al. (2011) estimated the GHG emission on conventional Rankine power plants using fast pyrolysis bio-oil and fossil fuel. In this scenario, CO_2 that was absorbed by feedstock was also considered. Study shows that GHG emission for pyrolysis oil was 77–99% lower than that of fossil fuel. A more efficient system can be developed by generating electricity within the system and using it in pyrolysis (Fan et al. 2011).

Shemfe et al. (2016) investigated the greenhouse gas (GHG) emission generated by one-ton biofuel production from the upgradation (hydroprocessing and zeolite cracking technique) of bio-oil obtained from the fast pyrolysis of *Miscanthus*. This was further categorized based on soil organic carbon (SOC) sequestration rates (feedstock CO_2 absorption): excluding (SOC), low (SOC), and high (SOC) for the best and worst scenarios. Hydroprocessing technique for worst-case generated 738, 627, and − 268 kg CO_2 equivalent per ton of biofuel for exclusion, low and high SOC, respectively. For the best case 390, 212, and −1221 kg CO_2 equivalent per ton of biofuel was generated for exclusion, low and high SOC, respectively. Similarly, it was calculated for zeolite cracking for the worst scenario it was 1328, 1104, and −697 kg CO_2 equivalent per ton of biofuel was generated for exclusion, low and high SOC, respectively, and for the best-case scenario, it was 627, 268, and −2614 kg CO_2 equivalent per ton of biofuel was generated for exclusion, low and high SOC, respectively (Shemfe et al. 2016).

10.6 Conclusion

This study mentions that there are no boundaries from where we can take the feedstock to produce bio-oil or pyrolysis oil. Still, most research focus on biomass, animal manure, or non-organic wastes such as plastics. Recent advances provide enough data to justify that fast pyrolysis and hydrothermal liquefaction are the best source for bio-oil production. In terms of economic feasibility, hydrothermal liquefaction may not be a good idea to scale up without some improvements. To understand the complex fast pyrolysis process, various advance experimental setups are present that help in the understanding of the process on a molecular level. On large-scale setup and lab-scale setup, various fast pyrolysis reactors or pyrolyzers are mentioned in various studies that can be used to produce bio-oil. However, some of the reactors do not come to the category of fast pyrolysis, but their bio-oil yield is high, such as (multiple hearth reactor) and some of the reactors are under the category of fast pyrolysis reactor (plasma reactor and pulse shock tube), but their product priority is other than bio-oil, i.e., gases. A thorough study on the reactor should be attained before applying any reactor to the field, either for research or industrial application. Upgrading technology also showed promising results. Upgrading the bio-oil for various applications, not just for fuel, but various chemicals that can also be obtained from the bio-oil. It was also mentioned in some of the studies that upgraded biofuel has been used as a fuel for transportation and electricity generation. Most of the studies over techno-economics of the process discussed are simulated, but they provide an idea for total capital and annual operating costs. In terms of environmental sustainability, it was shown in many studies that GHG emissions are lower in comparison to fossil fuels. This is mainly because a large amount of CO_2 is absorbed during plant's growth period. The above study provides enough information showing the possibility of fossil fuel independency from various stationary and mobile application sectors, which can be moved towards the bio-oil sector.

Competing Interests All the authors declare that they have no competing interests.

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Chapter 11
An Overview on Organosolv Production of Bio-refinery Process Streams for the Production of Biobased Chemicals

Veluru Sridevi, Dadi V. Suriapparao, Hemanth Kumar Tanneru, and K. S. N. V. Prasad

Abstract The potential of renewable energy and chemical sources is more important than ever before due to the combination of diminishing crude oil supplies and population increase. The bio-refinery concept is evolving from a fascinating notion to a viable replacement for a variety of fossil-fuel-based goods. Pre-treatment processes designed for a comprehensive bio-refinery shall show selective dissociation of each constituent of a biomass feedstock, ease of access to and detachment of the constituents after separation, high yield revival of every component, process components readily available for conversion into chemicals with negligible purification, as well as economic feasibility. These criteria are typically met by organosolv pre-treatments. To be broadly accepted by markets and the public, the generation of renewable chemicals, as well as biofuels, should be price and performance competitive employing crude oil-derived counterparts. The focus of this study is on developing a biomass conversion technique that maximizes the transformation of lignocellulosic biomass into commercially viable high-value products, allowing for effective translation to an economically feasible commercial process.

Keywords Bio-refinery · Biomass feedstock · Economy · Organosolv technology · High-value products

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P. Verma (ed.), *Thermochemical and Catalytic Conversion Technologies for Future Biorefineries*, Clean Energy Production Technologies,
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Abbreviations

AFEX	Ammonia fiber explosion
IEA	International Energy Agency
LCB	Lignocellulosic biomass
LHW	Liquid hot water

11.1 Bio-refineries

The scientific community's major goals for the development of green-type businesses are bio-refineries as well as biobased "green" chemistry. Another goal of the bio-refinery is to maximize or optimize the economic, environmental, and social advantages by utilizing all synergies for an efficient and viable operation. The projected future expansion of biofuel industry, as well as the development of novel biofuel production technologies, need the construction of the new integrated bio-refineries.

The present work on biodiesel, ethanol, and sophisticated biofuel production to displace a fraction of the vast quantity of shipping gasoline and diesel consumed yearly in the USA addresses the energy objective. Fuel, however, is a low-value product despite its enormous volume. As a result, achieving the bio-refinery's economic aim will be difficult due to the low return on investment on the biofuel-only operation (Goswami et al. 2021; Kumar and Verma 2021a**,** b). Integrating chemical products into bio-refinery's portfolio, however, poses two major problems. The manufacturing of biobased chemicals is hampered by a lack of conversion technologies. (i) Renewable carbon to chemical conversion is the least developed and most difficult of all bio-refinery activities when compared to nonrenewable hydrocarbon conversion methods. The existence of the requisite conversion technology is not required for promising hypothetical situations involving fuels and chemicals. (ii) An oversupply of targets poses a difficulty to biobased chemical synthesis. Engineering process analysis is great for setting pricing objectives and selecting technologies that provide the best possibilities for the research investment as the molecular configuration of the intended product is understood. Yet, because of the basic difference between chemical research and fuel, these analytical approaches are less helpful when applied to multi-product chemical scenarios (Fig. 11.1).

Bio-refinery is a novel word that refers to two primary topics: bioproducts and bioenergy, both of which are critical to a more biobased society. The use of lignocellulosic materials in bio-refineries as a substitute for fossil-fuel refineries necessitates effective fractionation and product recovery technologies (Bhardwaj et al. 2021a, b; Kumar et al. 2020). The focus of the bio-refinery idea for biomass use has changed from the construction of more or less energy-driven bio-refineries to considerably more flexible facilities that can generate chemicals and energy carriers.

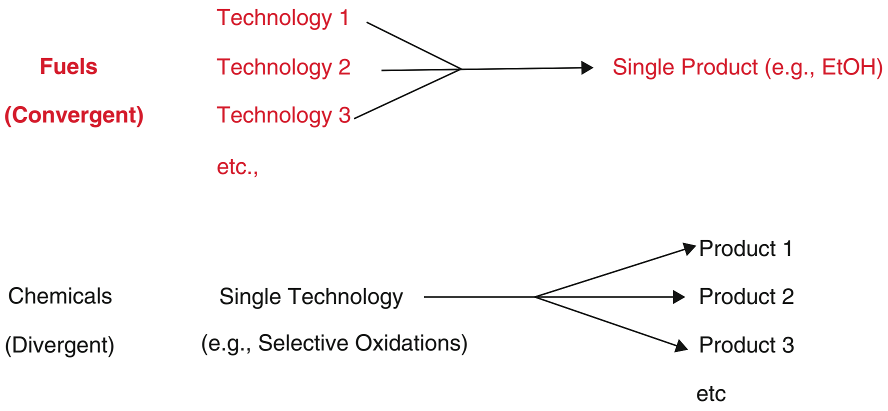

Fig. 11.1 Biobased fuels and chemicals research methods

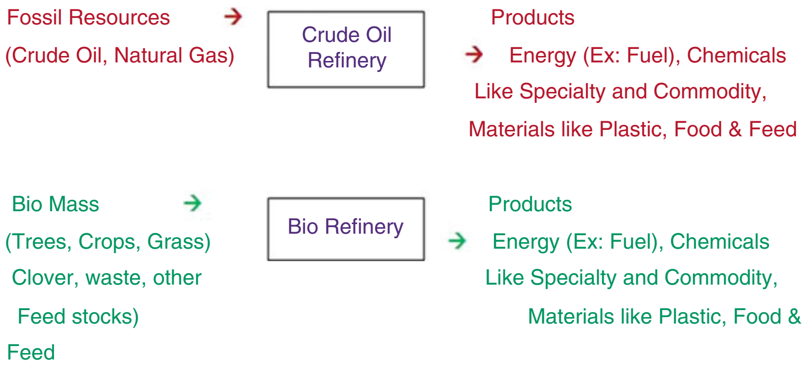

Fig. 11.2 Biomass as a renewable feedstock for bio-refineries

According to the huge number of articles published, biomass pre-treatment is critical for the full-scale implementation of the bio-refinery idea.

Bio-refinery is defined as "the viable conversion of biomass into a variety of biobased goods and bioenergy" by the International Energy Agency's (IEA) Bioenergy Task (Fig. 11.2) (International Energy Agency 2012). It implies that a bio-refinery can be an idea or a facility or a process or a plant, or a cluster of facilities that necessitates the integration of several disciplines of expertise, including chemical engineering, biomolecular engineering, chemistry, biology, and biochemistry (Clark et al. 2006). If a fully integrated strategy is established, biorefining can give a viable route to value products while also improving biomass processing costs and environmental footprint.

The growing biobased economy is a very attractive industry with a lot of potential for the future and a lot of business prospects (Luoma et al. 2011; Mehariya et al.

Table 11.1 A list of problems that must be overcome for bio-refineries to be implemented successfully

Issues	Key points
Increase the size of the project to an industrial level	It necessitates a considerable financial commitment. Strong financial motivation is required. Investors believe the return on investment is too low
Uncertainty about the future	Laws and rules are ambiguous
Construction and design	Plant construction delays equipment evaluations.
Availability of biomass	Ensure that appropriate resources are available at all times of the year Possibility of running on several materials
Supply and logistics	Reliable storage and transportation are required
Data for the development of processes	Data transfer from a small to a large scale
The degree to which a process has reached maturity	Handling and feeding under high pressures

2021). There are several definitions for bio-refinery, but in general, the term refers to the use of renewable raw resources (such as biomass) to generate energy and a variety of common commodities in an economically and environmentally sound manner (Dermibas 2009; Aresta et al. 2013; Himmel 2008; Agrawal and Verma 2022; Goswami et al. 2020). Fossil fuels are the world's primary energy source; nevertheless, the most pressing issue of one of the contemporary societies is reducing our reliance on fossil-fuel sources while also promoting rural development. The bio-refinery idea tries to use the same technologies which have been utilized to refine crude oil into biomass conversion (Dermibas 2009). Bio-refineries are viewed as a highly promising path to achieving our goals of long-term development and environmental preservation. Bio-refineries should comprise a variety of facilities, unlike oil refineries, which are huge industrial complexes (Rodrigues 2011). In the near future, renewable energy sources will be necessary for the long-term growth of our civilization (Dewulf and Van Langenhoven 2006). Plant biomass is the world's most abundant source of renewable resources and a major source of renewable energy.

Table 11.1 summarizes the obstacles that have been identified for the effective deployment of future bio-refineries. According to Sanford et al. (2016), the first step toward a major financial commitment is to scale up a solid small-scale operation into a large-scale bio-refinery. As a result, there has to be a very strong monetary advantage to justify the expenditure. Furthermore, investors understand the poor return on invested money as well as an uncertain future scenario, since regulations governing biofuels and bio-chemicals are still short-term stable, implying that the financial groundwork for major investments is not yet complete. They also find that many biotechnology firms that had a successful early-stage procedure have faced serious issues as a result of scale-up hurdles and the consequences of delays in building, testing, and operation. Capital expenditures have been reduced in certain situations by adapting existing facilities. A few of the significant factors are (i) biomass availability, which comprises a year-round flow of lignocellulosic biomass at a reasonable price, as well as access to a biomass of a comparable sort to operate a bio-refinery within a limited working range. (ii) All logistics and a fully functional supply chain, such as transports of low-density materials and storage facilities, must be provided in order for continuous operation to be viable. The most significant expenditures connected with the bio-refinery idea are feedstock management and shipment. Feedstock accounts for 40–60% of full-scale biofuel production expenses (Humbird et al. 2011; Joelsson et al. 2016). Tao et al. (2011) analyzed 6 biomass pre-treatment methods from a process and techno-economic standpoint.

11.1.1 Processing for the Bio-Based Economy: Bio-refineries

The biggest hurdle to the expansion of the biobased chemicals industry, according to scientists, is the cost of manufacturing, which is still greater than their traditional equivalents. Furthermore, some biobased chemicals are still regarded as high risk in terms of upfront infrastructure investments. Policy interventions designed to stimulate these markets could include investment incentives, making the production of their fossil-fuel counterparts more expensive—for example, through carbon taxes—or attempting to make the use of biobased chemicals mandatory in certain industries, thereby increasing demand.

The goal of the bio-refinery idea is to make the most of plant components. Energy generation is not the main application of biomass in this idea, but rather an optional one. To maximize the value of available functions and biomass usage, feedstock selection, transportation, and biorefining processes are utilized. Intricate input-output chains aid in realizing the best social and economic outcomes. This is accomplished by first producing (small volume) high added value items, which are then followed by less-valued products (Fig. 11.3).

Green bio-refineries, which feed grass through a series of processing steps, provides a new option for grass feedstock processing. The mechanical separation of grass into a liquid phase containing soluble chemicals and a solid phase mostly

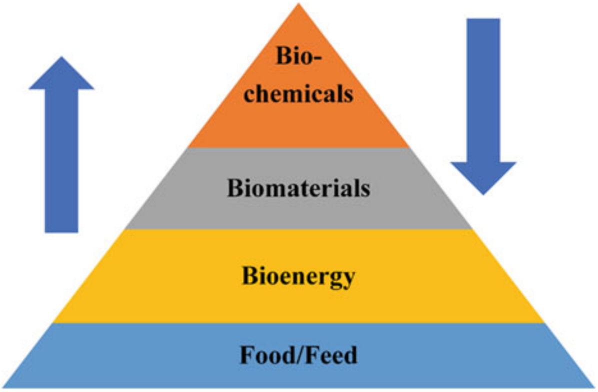

Fig. 11.3 Biobased "products" market pricing vs. market volume (De Jong et al. 2009). *The up arrow indicates Market Price and the down arrow indicates Market Volume*

Table 11.2 Characteristics of the most common bio-refinery types

Bio-refinery	Feedstock and conversion	impact	Remarks
Whole crop	Cereal crops, dry or wet milling	Although there is a link between monomer and polymer manufacturing, large-scale production competes with food production. Straw that may be used in lignocellulosic bio-refineries. Straw that may be used in lignocellulosic bio-refineries	Mainly from maize, wheat, moderately capital intensive
Oleochemical feedstock bio-refinery	Oil crops (rape seed, soybean, oil palm)	Links to production of chemicals, functional monomers, lubricants, and surfactants. Direct completion with food	Close to full commercialization. Capital intensity is moderate
Lignocellulosic bio-refinery	Lignocellulosic crops, residues of food and feed crops	Reduced completion with food, feed production, high water use efficiency, high potential for GHG emission reduction	Not yet on commercial scale. Capital intensive
Green bio-refinery	Grass	Links to the production of proteins, sugars, and fibers. No direct completion with food	R & D phase

composed of fibers is critical. The economic return of the fibers determines the bio-refinery's overall economic efficiency (De Jong et al. 2009). Table 11.2 summarizes the key features of the most common bio-refinery processes.

To make bio-refineries more cost-effective, chemicals made from biomass, a viable feedstock, are highly sought as a replacement for petrochemicals. Improved interest in becoming less energy reliant than in the past has been fueled by a dependency on fossil-based energy sources, diminishing crude oil accessibility, a desire to preserve the environment from devastating carbon emissions, and an ever-increasing global population. These concerns have prompted researchers to explore methods to replace crude oil derivatives with renewable resources. Biomass processing in integrated bio-refineries is the best way to compete with fossil-fuel refineries. To generate biofuels and biobased chemicals, the integrated bio-refineries used a variety of biomass feedstocks and conversion methods. A bio-refinery ought to require the most effective conversion methods for the production of high-value chemicals and biofuels from an industrial standpoint (Ragauskas et al. 2006a, b; Huber et al. 2006; Stephanopoulos 2007). Agricultural residues and wood chips, for example, are affordable renewable feedstocks for commercial large-scale bio-refineries because they are widely accessible and can store carbon.

11.2 Biomass Feedstocks

Hard and softwoods have long been the world's primary raw materials for pulp manufacturing, and they consistently produce high-quality results. However, due to a variety of causes, including the newly generated demand for bio-refinery applications, the cost of these raw materials has skyrocketed in the previous decade. As a result, alternative raw materials which can compensate for the absence of low-cost wood have been actively explored. As a result, each person should be able to select the best biomass source for bio-refinery applications. Plants with high productivity, like grasses, have the ability to provide low-cost biomass to fulfill present demand (Vilela et al. 1997; Vilela et al. 2001; Paulino et al. 2007; Mazzarella 2007). Presently, biomass sources are classified as either woody or non-woody. In North America, Europe, and other temperate regions, forest and agricultural wastes have been the primary targets. In tropical regions, such as Brazil, there is a lot of potential for using fast-growing, high-productivity woody and non-woody biomass to implement the bio-refinery idea.

Biomass as a variety of bio-refinery feedstocks, biomass from trees, agro-forest leftovers, grasses, plants, aquatic plants, and crops, as indicated in Fig. 11.4, is a flexible and essential renewable feedstock for the chemical industry. Plants convert CO_2 and water into primary and secondary metabolite bio-chemicals through the photosynthesis process. Both of these compounds are significant in the industry. Carbohydrates and lignin, known as lignocellulose, are the primary metabolites

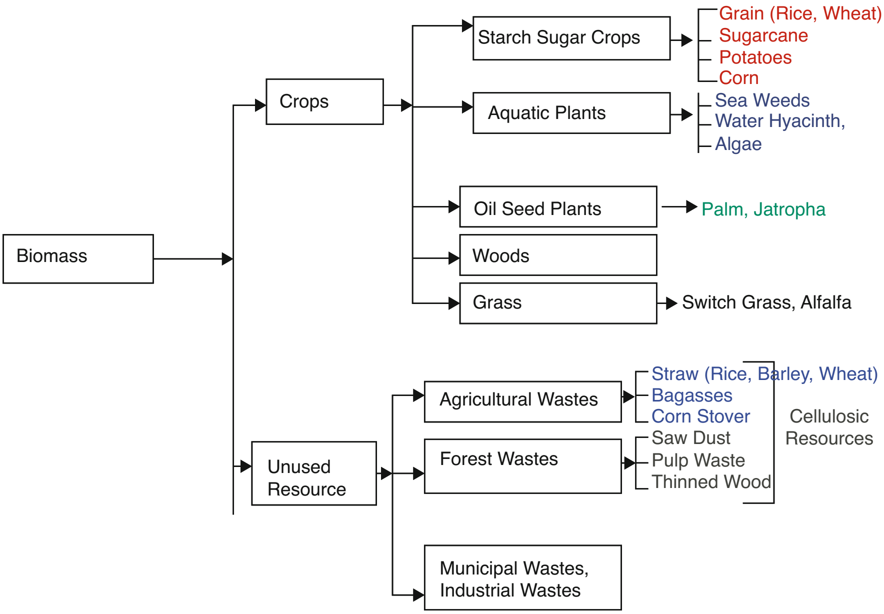

Fig. 11.4 Biomass as a viable bio-refinery feedstock

found in large amounts of biomass. Biofuels may be produced from lignocellulosic biomass. High-value bio-chemicals such as gums, alkaloids, resins, plant acids, rubber, tannin, waxes, triglyceride, terpenes, steroids, terpenoids, and other secondary metabolites are found in little amounts in plants (Ragauskas et al. 2006a, b). Using an integrated processing approach, secondary metabolites may be used to make high-value compounds such as food flavors, feeds, medicines, cosmeceuticals, and nutraceuticals, among other things.

11.3 The Full-Scale Operation of the Bio-refinery Concept

A bio-refinery is a renewable version of a crude oil refinery, with the primary distinction being the raw material used. Biomass may be turned into a variety of chemicals and energy carriers in a bio-refinery, and it can also help to build a circular economy; this notion is based on the idea that lignocellulosic materials used to make biobased goods can be recovered (to a degree) and recycled (Capolupo and Faraco 2016). Biorefining is defined as “the viable conversion of biomass into a range of marketable biobased goods and bioenergy” by International Energy Agency (2012). When it comes to a large-scale production plant, however, the many types of raw materials provide a significant difficulty. Figure 11.5 depicts a schematic diagram of a possible bio-refinery for the synthesis of energy carriers and chemicals.

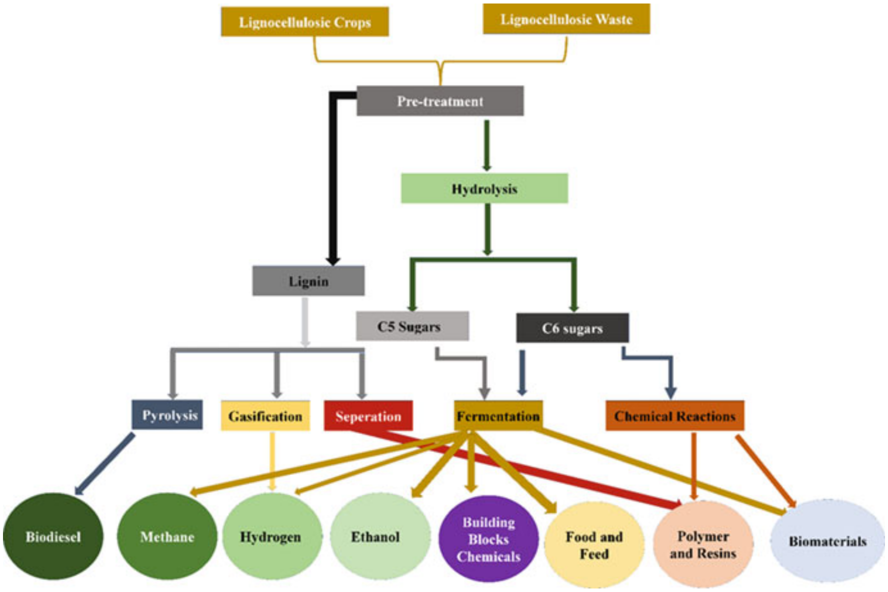

Fig. 11.5 A schematic overview of potential energy carriers and chemicals is produced in a bio-refinery

Some significant considerations have been made in order for the bio-refinery idea to become a viable path toward a society that is less reliant on fossil fuels. Bio-refineries are an important part of the future integration of fuels, food, chemicals, and energy production.

11.4 Biobased Chemicals

Biobased products are often believed to be greener substitutes to crude oil-based materials, which are non-biodegradable, have the potential to harm animal and marine life, and, for the most part, have an intrinsically hazardous life cycle from manufacture to disposal (Werpy and Petersen 2004; Chemical and Engineering News 2006). Biobased products are commonly marketed as being made from "renewable" resources, even though biomass production requires nonrenewable inputs, such as fossil fuels, and locks up other limited resources like land and water. The notion that biobased products are more environmentally friendly than their crude oil-based equivalents is being extensively investigated (Frankfurt 2011; US Department of Agriculture 2008).

The quantity and variety of compounds that may be generated using a biomass source and/or bioprocessing method are astounding. The US Department of Energy selected 12 compounds or chemical classes in 2004 as possible building blocks from which numerous value-added chemicals might be made. Because of this variety, it is hard to develop a policy framework that is the same for extremely low production volume compounds like enzymes and a biobased version of ethylene, the world's greatest production volume organic molecule.

11.4.1 Cost and Performance of Biobased Chemicals

It is hard to sell biobased compounds only on the basis of their environmental credentials. In a world where the triple-bottom-line is king, economics and societal concerns must also favor bio-over petrochemicals. This, however, implies that this relatively new business will have to compete directly with the petrochemicals industry, which has had decades to refine its methods. As a result, if biobased chemicals provide a long-term triple-bottom-line benefit, society should anticipate having to reward the sector until it can compete on price and performance.

By disrupting these chemical connections, biomass can be used as a prospective energy resource for humans. Biomass is considered a viable energy source, thus making use of this perspective energy resource is a significant focus of study. The simplest and most popular approach is to convert this energy into heat through a simple combustion process. The present focus is on turning biomass into a form with a greater energy value as a crude oil fuel alternative. Biomass has been studied in a variety of ways, and first-generation biofuels have even experienced success in industrial settings. Biodiesel, ethanol, and tiny quantities of biogas are among the first-generation biofuels produced. The present biofuel industry, on the other hand, is dominated by fuels generated from food sources, which has caused heated discussion about their influence on biodiversity, land usage, and competition with food crops. Furthermore, others argue that first-generation biofuels do not achieve the greatest reduction in greenhouse gas emissions. This chapter will concentrate solely on the context of fuels generated from the processing of lignocellulosic biomass (LCB), often known as second-generation biofuels, for the reasons stated above. Forest remnants that are developed, especially to create bioenergy, agricultural leftovers like maize stover, rice, wheat straw, etc. are also sources of LCB. Second-generation biofuels are presently not cost-competitive and are not being produced commercially. Many of the issues presented by first-generation biofuels appear to be addressed by the creation of second-generation biofuels. Biomass is made up of several kinds of lignin in addition to varied quantities of hemicellulose, lignin, and cellulose. As a result, any effort to use biomass in a processing atmosphere must be strong enough to accept the diversity of biomass forms.

The availability of various forms of lignocellulosic materials varies greatly between countries and continents. Forests are numerous in certain areas, whereas agricultural plants are more frequent in others. The composition of lignocellulosic components varies depending on the species. The fundamental components, however, are essentially the same, but the amounts of specific carbs, aromatics, and other compounds vary: around 50–60% are carbohydrates, 20–30% lignin, and the remainder is extractives, fatty acids, ash, etc. (Ståhl et al. 2018). The fundamental components, however, are essentially the same, but the amounts of specific carbs, aromatics, and other compounds vary: around 50–60% are carbohydrates, 20–30% lignin, and the remainder is extractives, fatty acids, ash, etc. (Sjöström 1993). Hemicelluloses have higher hydrophilicity than cellulose, making them simpler to hydrolyze. Lignin is the most important non-carbohydrate component of lignocellulosic materials, with a complex structure of aromatic compounds. It is linked to both cellulose and hemicelluloses, and it is a big reason why lignocellulosic materials are so strong.

11.5 Biomass Pre-treatment's Objectives

The primary focus of the biomass pre-treatment phase has altered in recent years; before, the primary focus was on using lignocellulosic materials for bioethanol synthesis. The other major components, lignin, and hemicelluloses drew less attention. Today, it's critical to figure out how to increase the total yield of the important chemicals found in lignocellulosic materials. Pre-treatment techniques that allow for effective carbohydrate and lignin recovery are desirable; however, this is dependent on the circumstances and the ultimate product. The energy requirements of the manufacturing process must be satisfied in any case, either by externally or internally integration of high-energy streams, such as in a pulp mill where surplus lignin is the primary source of process energy. It is anticipated that between 20% and 30% of the lignin in an efficient mill is accessible for purposes apart from internal energy requirements (Mistra, 2003).

11.5.1 Lignocellulosic Biomass Physical and Chemical Characteristics

Agricultural wastes are sometimes known as biomass or lignocellulosic materials. While referring to high-grade plants, such as soft or hardwood, the phrase "lignocellulosic biomass" is used. Hemicellulose, lignin, and cellulose are the major components of lignocelluloses, with minor quantities of pectin, protein, extractives, ash, and water. Within the lignocellulose complex, cellulose is essential for the crystalline fiber structure, hemicellulose is located between the cellulose chains, and lignin is essential for the matrix's structural role (Srivastava and Lisle 2004).

Cellulose is the most important structural component of plant cell walls, providing chemical and mechanical stability. The process of photosynthesis absorbs solar energy and stores it as cellulose. Whereas hemicellulose is a co-polymer of various C_5 and C_6 sugars; lignin, on the other hand, is an aromatic compound polymer that provides a protective coating for plant walls (Fig. 11.6).

11.6 LCB Pre-treatment Technologies

The major objective of LCB pre-treatment is to break the refractory structure to allow enzyme access in subsequent downstream processing, as shown in Fig. 11.7. There are a variety of ways to achieve this, and each technique has various outcomes. Enzymatic hydrolysis, for example, may necessitate the removal of hemicellulose due to the lack of hemicellulases, but consolidated bioprocessing makes use of organisms that naturally release hemicellulases and can efficiently manage hemicellulose (Bhardwaj and Verma, 2021). Each of these processes might make use of biomass that has been pretreated differently. As a result, identifying a single pre-treatment strategy that will serve as the industry's "gold standard" is nearly

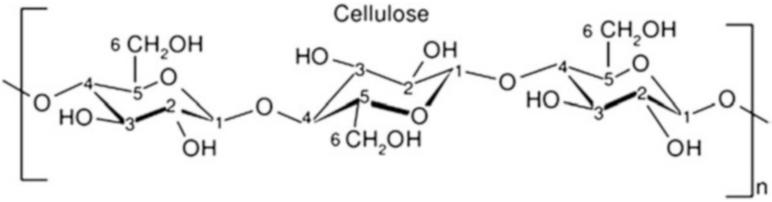

Fig. 11.6 Structure of cellulose molecule

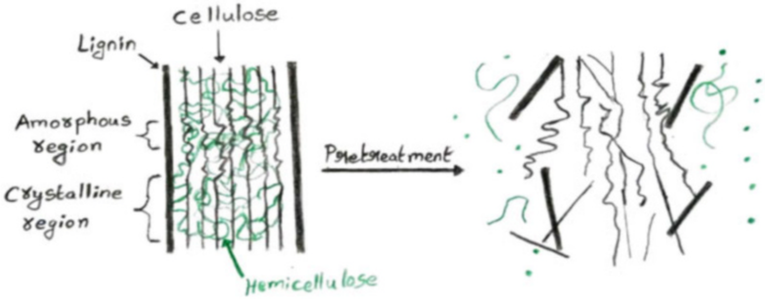

Fig. 11.7 Pre-treatment of LCB

impossible. However, the advantages and disadvantages of each will be recognized, and this knowledge may be utilized to develop a system-wide biomass use strategy.

Pre-treatment is required to break the microstructure of lignocellulosic biomass, which is made up of hemicellulose, lignin, and cellulose, to make carbohydrates more available. The goal of pre-treatment is to eliminate lignin and hemicellulose, lessen cellulose crystallinity, and enhance biomass porosity. A good pre-treatment must prevent the degradation of carbohydrates, as well as the emergence of inhibitors to the resulting hydrolysis and fermentation processes, while also improving the creation of sugars or the capacity of pretreated material to form sugars by water treatment, all while remaining cost-effective. The optimal pre-treatment relies on the expected usage of the primary biomass components, among other things. Physical, chemical, and biological pre-treatments, as well as combinations of these, are classified as physical, chemical, and biological pre-treatments, with physicochemical pre-treatments receiving special attention.

11.6.1 Mechanical Comminution

The goal of mechanical pre-treatment of biomass is to improve its digestibility. Cutting, grinding, etc. are some of the mechanical methods which can be used to minimize particle size, enhance the accessible specific surface area, through various fractions. In terms of energy consumption, this approach has certain drawbacks. The energy needs for mechanical comminution are determined by the desired end particle size and biomass properties.

11.6.2 Steam or Water Vapor Explosion

The most frequent physicochemical technique of biomass preparation is steam or water vapor explosion. Biomass is to be treated by high-pressure steam and then rapidly decompressed in this technique. Following that, an explosive reaction occurs, culminating in the breakdown of hemicellulose and the rupture of the lignin matrix. The crystallinity of cellulose may decrease, and the surface area of the substrate may rise, increasing cellulose digestibility (Li et al. 2007).

11.6.3 Liquid Hot Water Pre-treatment (LHW)

Liquid hot water (LHW) procedures are biomass pre-treatments that employ pressure to maintain extreme temperatures (160–240 °C) in water. LHW used water as a reaction medium at relatively high reaction temperatures. The liquid state is maintained by increasing the pressure. Changing the process temperature and pressure alters the dielectric strength and ionic product of LHW and effectively removes hemicelluloses from the lignocellulosic matrix at 220 °C. Increasing Ro (severity factor measures the combined effect of temperature and time in each pre-treatment) increases the yield of undesired by-products. Hence, compromise must be found between biomass solubilization and concentration of undesired degradation product.

11.6.4 Ammonia Fiber Explosion (AFEX)

AFEX is a physicochemical pre-treatment in which lignocellulosic biomass is treated for a length of time with high pressure and temperature for liquid ammonia, and then the pressure is rapidly decreased. The AFEX technique is quite similar to the processing of steam explosions. The chemical action of ammonia under pressure causes the biomass to expand, resulting in an increase in accessible surface area and a decrease in cellulose crystallinity at the same time (Mosier et al. 2005a, b).

11.6.5 CO_2 Explosion Pre-treatment

The pre-treatment procedure for carbon dioxide explosions is comparable to steam and AFEX. It was created in an attempt to enhance lignocellulosic biomass pre-treatment by using a green, low-temperature, and low-cost technique.

11.6.6 Wet Oxidation Pre-treatment (WOP)

By oxidizing soluble suspended materials with oxygen at elevated temp (150–350 °C), wet oxidation pre-treatment was utilized in the industry for wastewater treatment and soil remediation (Zerva et al. 2003). It was later proposed as an alternative to steam explosion for the processing of lignocellulosic biomass.

11.6.7 Acid Hydrolysis

Strong acids, such as sulfuric acid, have also been used to treat lignocellulosic materials since they are potent cellulose hydrolysis agents that do not require the use of enzymes to achieve acid hydrolysis and generate fermentable sugars. They are poisonous, dangerous, and corrosive, which makes the pre-treatment procedure highly costly.

11.6.8 Peroxyformic Acid

Peroxyformic acid pre-treatment is a chemical pre-treatment technique for oxidative delignification. By combining formic acid with hydrogen peroxide in situ, peroxyformic acid is produced. This combination is then supplemented with lignocellulosic biomass and left to sit for many hours. Formic acid dissolves hemicellulose chains and functions as a solvent for lignin. Peroxyformic acid causes oxidative delignification by increasing lignin solubility. The temperature of the reaction is raised and the majority of the delignification happens. Any residual lignin is degraded in the last step.

11.6.9 Alkaline Hydrolysis

Pre-treatment of lignocellulosic materials is possible with certain bases. Alkaline pre-treatment treatments are appropriate. Sodium hydroxide or lime (calcium hydroxide) is commonly utilized. The biomass is soaked in an alkaline solution and combined for a period of time at a low temperature in the alkaline pre-treatment. Other pre-treatment processes use higher temperatures and pressures, but alkali pre-treatment uses lower temperatures and pressures. It can be done under normal settings, but it takes a long time to process.

11.6.10 Ozonolysis

The lignin composition of lignocellulosic biomass, as well as trash, is reduced by ozone pre-treatment. During carbohydrate breakdown, lignin absorbs the majority of ozone. The degradation is primarily restricted to lignin, however, hemicellulose is impacted in a little way, while cellulose is unaffected.

11.6.11 Organosolv Pre-treatment

The use of organic and aqueous organic solvent mixtures having inorganic acid catalysts is used to pretreat lignocellulosic biomass using organic solvents. Catalysts can also be organic acids like oxalic acids. Methanol, acetone, and ethylene glycol are common solvents. Pre-treatment is generally done at a high temperature (up to 200 °C) and under high pressure (Chen et al. 2015; Kabir et al. 2015). With alcohol, the catalytic process is identical to that of the autohydrolysis pre-treatment. Lignin and lignin–carbohydrate linkages are hydrolyzed by the solvent. Lignin is eliminated in large amounts, and hemicellulose is almost entirely dissolved, while cellulose remains solid. Organic acid pre-treatment accelerates delignification and hydrolysis of cellulose, as well as lignin breakdown, by dissociating hydrogen ions. At high temperatures, the inclusion of a catalyst is not required in this situation. A large portion of soluble carbohydrates is broken down further into by-products like furfural, which hinder fermentation bacteria.

11.6.12 Biological Pre-treatment

Biological pre-treatment is a secure and ecologically acceptable pre-treatment that involves the use of enzymes produced by fungi and bacteria that can transform lignocellulosic biomass into more easily hydrolyzed chemicals. To break down lignin, hemicelluloses, polyphenols, etc., microorganisms are employed. Brown rots target cellulose primarily, whereas white and soft rots target both cellulose and lignin. Lignin degradation enzymes are involved in the process of lignin breakdown (Eggert et al. 1997). Table 11.3 lists the benefits and drawbacks of several lignocellulose biomass processes.

11.7 Organosolv Technology Outperforms Other Pre-treatment Methods

Early elimination of the raw material into smaller components is critical to both processes, allowing intermediates to be more adaptable and easier to utilize than the raw material itself. natural gas and crude oil are transformed into fuels through physical separations through cracking as well as chemical transformation. Pre-treatment is a term used to designate similar activities that allow biomass

Table 11.3 Different pre-treatment techniques for lignocellulose biomass: advantages and drawbacks

Pre-treatment technique	Advantage	Drawback
Milling	The level of polymerization and crystallinity of cellulose are decreasing Particle size reduction to improve specific surface area and pore size	More power and energy consumption
Steam explosion	Hemicellulose solubilization, lignin transformation are the results The two-step technique produces more glucose and hemicellulose	Generation of toxic compounds Partial hemicellulose degradation
Liquid hot water	Biomass size reduction is not needed No chemicals or corrosion-resistant materials are generally required	High energy and water requirements Formation of toxic compounds
Ammonia filter expansion (AFEX)	Increase accessible surface area Low inhibitors formation. Does not require a small particle size of biomass	Not that much is effective for the biomass having high lignin content High cost of large amounts of ammonia Very high-pressure requirement
CO_2 Blast	Improve accessible surface area Low cost No inhibitory compounds Not flammable Easily recoverable after extraction	Pressure requirements are high
Wet oxidation	More degree of solubilization of hemicellulose and lignin	High cost of oxygen and alkaline catalyst
Concentrated acid	High glucose yield Ambient temperatures	High cost of acid Corrosion-resistant equipment is required
Diluted acid	Recovery of sugars at the end of the process is high	The concentration of reducing sugars is relatively low degradation products
Alkali	The reduced degree of polymerization and crystallinity of cellulose Disruption of lignin structure	High cost Not used for large-scale plants
Ozonolysis	Successfully removes lignin content	Cost of ozone is more
Organosolv	Cause lignin and hemicellulose hydrolysis	High cost
Biological	Reduction in the degree of polymerization of cellulose Partial hydrolysis of hemicelluloses	Reduced process rate Treatment rate is less

downstream processing in a bio-refinery. Pre-treatment methods have been created and evaluated in a wide range of ways (Mosier et al. 2005a, b). Future bio-refineries will adopt the petrochemical industry's paradigm, combining the production of low-value fuel with the manufacture of high-value chemicals generated from each of lignocellulose's major components.

As a result, pre-treatment procedures will need to place a much higher focus on the yield and purity of the various bio-refinery process streams utilized in chemical synthesis. While more selective techniques may incur greater costs, the capability to combine valuable chemical products into an integrated operation will generate a revenue stream capable of covering the expense of improved selectivity upfront (Bozell 2008). Pre-treatment processes optimized for an integrated bio-refinery will demonstrate selective dissociation of each constituent of a biomass feedstock, easiest access to and segregation of the constituents after separation, high yield recuperation of each component, process components ready for transformation to chemicals with minimal purification. Pre-treatments with organosolv often satisfy these criteria. Pre-treatment of the cellulosic with solvents has been the topic of many reviews covering technique and mechanism and was first mentioned in a patent in 1932 outlining the use of ethyl alcohol for wood segregation (Zhao et al. 2009a, b; McDonough 1993; Kleinert and Tayenthal 1932; Johansson et al. 1987; Jimenez et al. 1999). Several feedstocks have been utilized with formic acid, acetic acid, and peroxyformic acid (Poppius-Levlin et al. 1991). Organosolv methods are typically omnivorous in terms of the raw material they work with and have been used to pretreat hardwoods, softwoods, and grasses (Pan et al. 2006; Munoz et al. 2007; Jimenez et al. 2008). Organosolv technology has a variety of benefits over more traditional pulping methods, according to reports. Organic solvents lower the viscosity of the pre-treatment medium, allowing for better penetration into the biomass, more effective lignin removal, and less lignin recondensation and molecular weight rise during fractionation (Oliet et al. 2002; Pye and Lora 1991; Sarkanen 1990). Although cellulose separated from eucalyptus following an ethyl alcohol pre-treatment has been observed to have redeposited lignin, the presence of solvent can delay the redeposition of lignin onto the other biomass components once the separation is complete. pH control or alkali washing of the cellulose has been used to combat redeposition (Oliet et al. 2001; Xu et al. 2007; Paszner and Cho 1989; Zhang et al. 2007). Organosolv cellulose is more easily purifiable. This is essential in the paper industry as a solution to environmental concerns related to pulp bleaching, as well as in the chemical sector, which typically demands high purity starting materials. Furthermore, as compared to cellulose produced utilizing traditional methods such as kraft or soda, the cellulose had better bleachability and viscosity retention. Organosolv cellulose's enhanced characteristics have been used in the manufacture of viscose and carboxymethylcellulose (Cronlund and Powers 1992; Shatalov and Pereira 2007; Sixta et al. 2004; Ruzene et al. 2007).

11.7.1 Different Solvents for Organosolv Pulping

The need for more viable manufacturing techniques for commodities like paper and cardboard has increased as industrialized countries' environmental consciousness has grown. Traditional pulping methods generate enormous volumes of polluting waste known as "black liquor." As a response to this, the experts are increasingly focusing on developing new pulping processes. These processes, which are referred to as "organosolv processes" in general, allow for the manufacture of high-quality pulp and paper with minimal capital investment, high yield. Because alcohol is the most commonly used solvent for organosolv pulping, this chapter examines the limited research that has been done thus far on the use of other solvents.

The first scientific reference to organic solvent delignification originates from 1893. Organosolv methods accepted the dominance of classic chemical pulping techniques in those days. During the 1970s, however, scientists began to find alternatives to the traditional methods' numerous disadvantages, including foul aromas. Initially, efforts were concentrated on improving the pulping process; later, alternative methods that did not utilize sulfur as a reagent was created. However, these efforts ran into additional issues, such as the difficulty in recovering chemicals and the waste's contaminating character. New organic solvent-based methods began to develop in the 1980s. The fact that they could make the best use of the raw materials was their biggest advantage. Despite the fact that the Kraft process was still in use in the 1990s, the global environmental concerns it produced and the large expenditures required concluded that other pulp manufacturing methods must be developed. The Kraft or sulfate process is the most widely used pulping method in the industry. Wood, particularly softwood is by far the basic raw material for this procedure, whose main drawback is that a few of them have high ash content, which also causes serious troubles in black liquor recovery circuits. Although the true agent that works during the delignification reaction is the sulfur that is produced, sodium sulfate is used as a replacement reagent in this procedure. The process may be separated into two parts: (i) pulp manufacturing and (ii) chemical recovery. Some of the black liquid from Kraft pulping can be recirculated and utilized as a pulping solution. In certain situations, black liquor can make up 40–60% of the pulping solution without impacting the pulping yield or the properties of the pulps produced. By doing so, a portion of the reagents may be reused without an expensive evaporation step, the chemicals' penetration into the chips is aided, and the black liquor's heat energy is used.

The best pre-treatment technique should be chosen based on feedstock properties such as relative hemicellulose, lignin, and cellulose proportions, as well as manufacture capability and intended product kinds. Organosolv pre-treatment has recently received more attention due to its effectiveness in eliminating refractory particles from lignocellulosic biomass. The major advantage of organosolv pre-treatment is its capacity to take out pure lignin, known as organosolv lignin, which is then used as a useful co-product rather than an unwanted by-product. As a result, a viable and renewable energy market is formed, with economic and decarbonization advantages.

11.8 Overview of Organosolv Pre-treatment

The technique of extracting lignin from lignocelluloses using organic solvents is known as organosolv pulping. Organosolv pulping has piqued attention since the 1970s, owing to the fact that traditional pulping processes, such as Kraft and sulfite, have severe drawbacks. Pre-treatment with organosolv is comparable to pulping with organosolv; however, the level of delignification for pre-treatment is not needed to be like that of pulping. Likewise, organosolv pre-treatment provides the following benefits: (i) organic solvents are easy to distill and reuse for pre-treatment; (ii) chemical recovery in organosolv pulping procedures may separate lignin as a solid substance and carbohydrates as syrup, both of which have potential as chemical feedstocks (Aziz and Sarkanen 1989). Organosolv pre-treatment appears to be more viable for lignocellulosic biomass bio-refinery, which addresses the use of all biomass components. The organosolv pre-treatment does, however, have certain disadvantages. To shun the accumulation of dissolved lignin, which leads to complex washing arrangements, pretreated particles must always be washed with an organic solvent prior to water washing. Organic solvents are usually costly, therefore as much as feasible should be recovered, but this increases energy consumption. Due to the volatility of organic solvents, organosolv pre-treatment must be done under effective supervision. Because of the inherent fire and explosion risk, no digester leaks may be permitted. As a result, organosolv pre-treatment is now too costly to be utilized for biomass pre-treatment. It may be carried out in a wide range of organic solvent systems using additional catalysts at temperatures ranging from 100 to 250 °C, whereas organic peracid pre-treatment may be carried out at much lower temperatures. Solvents with low boiling points, as well as a range of alcohols with greater boiling points and other groups of organic molecules, have been investigated. It is thought that organic acids produced from the biomass function as catalysts for the breakdown of the lignin–carbohydrate bond in most organosolv procedures if the pre-treatment is carried out at greater temperatures, while acid catalysts are introduced, however, the level of delignification is enhanced, resulting in greater xylose yields. Mineral acids are effective delignification catalysts, whereas organic acids can also be employed. The majority of hemicellulose and lignin is dissolved, whereas cellulose remains solid. To cut costs, the organic solvents which were used must be recycled. Solvents, on the other hand, must be removed from the system since they may impede the development of organisms, enzymatic hydrolysis, and fermentation. Dry lignin, an aqueous hemicellulose stream, and a reasonably pure cellulose fraction are all separated by the organosolv process.

11.9 The Chemistry of Organosolv Delignification

Organosolv pulping is gaining popularity due to its potential for cost-effectively increasing additional pulp production capacity as well as potential environmental benefits. Delignification of wood in non-aqueous media, also known as organosolv pulping. Since the idea was established early in the century, it has been the focus of a lot of research. Much of this activity has occurred in recent years, however, and most has been empirically directed toward the identification of efficient solvent systems and optimum process conditions. Until recently, very little work is done regarding fundamental aspects of these systems, so little detailed information is available on their mechanisms. On the other hand, the mechanisms of the Kraft and sulfite pulping processes and their variants have been studied in detail, and there has been considerable basic work on non-aqueous lignin solvolysis, although most of it has not been primarily directed at understanding the related industrial processes. For example, numerous studies have been done to elucidate lignin structure by analyzing its solvolysis products. As a result, there exists a substantial amount of information that can serve as a basis for inferences concerning organosolv pulping mechanisms. In addition, increased levels of basic research on the subject during the past few years have added to a growing store of theoretical knowledge that should facilitate further development of organosolv pulping technology.

11.9.1 The Nature of Organosolv Pulping

Traditional chemical pulping techniques rely on the capacity to gradually break down and alter the lignin macromolecule until the resultant molecular fragments are small enough to dissolve in the aqueous pulping fluid for them to be effective. It’s possible that organosolv pulping delignifies by physically dissolving lignin without first chemically fragmenting it by substituting most or all of the water with an organic solvent. In reality, no solvent has yet been discovered that can achieve this desired result, and all organosolv methods rely on chemical lignin breakdown before dissolving it.

11.10 Advantages and Disadvantages of Organosolv Pre-treatment

Traditional pulping methods, yield good-quality pulps with a huge cellulose concentration, whereas liquid lignin-hemicellulose fractions comprising 50–55 % dry weight of lignocellulosic biomass are utilized by low-value applications such as direct burning (Vila et al. 2003a, b; Xu 2006). Organosolv pre-treatment is an improved pulping technique used in the manufacture of second-generation bioethanol (Mesa 2011). It is a biomass pre-treatment process that primarily eliminates lignin and hemicellulose while also making cellulose more digestible (Cybulska 2015). It is very efficient when used with lignocellulosic biomass for refractory material removal and cellulose saccharification (Zhang et al. 2016; Pande and Bhaskarwar 2012; Jimenez 2004; Garcıa et al. 2014). Furthermore, it leads to an enlarged surface area and huge pore volume (Zhao et al. 2009a, b). Because the lignocellulosic biomass's stiff structure is broken down, the hydrolysis time is decreased and enzyme usage is lowered (Geng et al. 2012; Kim and Pan 2010). Table 11.4 summarizes the basic benefits and drawbacks of organosolv pre-treatment. The basic mechanism of organosolv pre-treatment is to handle lignocellulosic biomass with an organic solvent with or without a catalyst, in order to separate lignin fractions in a liquid state from cellulose fractions in solid form (Sun and Cheng 2002; Taherzadeh and Karimi 2008). Figure 11.8 depicts the overall flow diagram of the organosolv pre-treatment. Solvent and water are combined to provide a solvent's concentration of 35–70% then added to the lignocellulosic biomass with such dry biomass to solvent/water mix proportion between 1:4 and 1:10. To speed up the process, a catalyst can be introduced. In general, the working temperature range is 120–200 °C, the pulping duration is 30–90 min, and the median pH is 2–3.8 (Koo 2011; Behera 2014; Kumar 2009). During the organosolv process, lignin bonds and lignin-carbohydrate linkages hydrolyze, resulting in a solid phase mostly composed of cellulose and hemicellulose. To prevent lignin precipitation, this prepared material must be rinsed with an organic solvent.

Following this, the pretreated material is washed using water to eliminate the organic solvent. Following this, filtering separates the solid and liquid phases, and the pretreated solid is transported to a saccharification and fermentation reactor to generate bioethanol. Waste liquor is mostly composed of ethanol, water, other by-products. The wasted liquor is pumped into a distillation column to recover the solvent. The solvent-free liquid is diluted using water after distillation to precipitate the lignin, which is subsequently separated by filtering from water-soluble fractions.

Table 11.4 Advantages and disadvantages of organosolv pre-treatment

Advantage	Disadvantage
• As a feedstock, both woody and non-woody biomass might be utilized • The yield of enzymatic hydrolysis is increased when lignin is separated • The amount of water, energy, and reagents required is smaller than that of other pre-treatment techniques • Solvents may be recovered simply • Small-scale applications are less expensive than other pre-treatment techniques • The environmental effect is considerably reduced because it is Sulfur-free • By-products are transformed into valuable goods	• High solvent usage is required. As a result, solvents must be recovered • Energy usage rises as a result of solvent recovery • Due to the volatile nature of the components, process control must be exercised with utmost caution

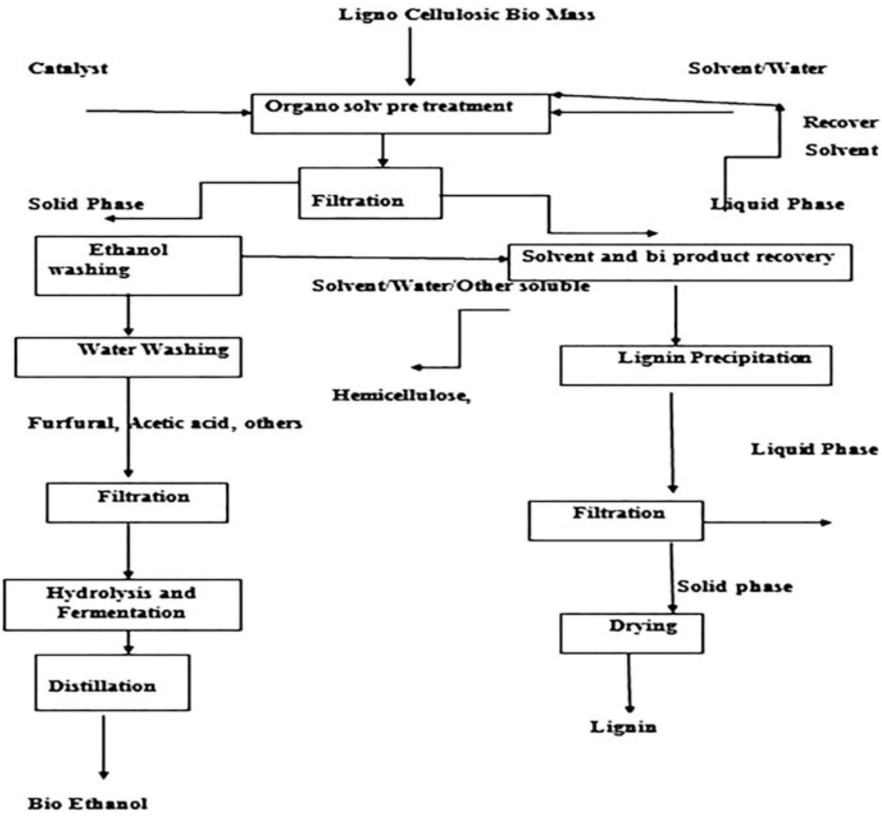

Fig. 11.8 The diagram of the pre-treatment of organosolv

It is rinsed in water to eliminate impurities before being dried to produce high-purity lignin. Because all of the biomass molecules involved are quickly translatable to high-grade fuels and chemicals. It is one of the most ideal pre-treatment procedures for use in LCF bio-refineries (Li 2012; Perttunen et al. 2001). Furthermore, the moderate pre-treatment conditions of temperature, pressure, and pH reduce the quantity of carbohydrate breakdown. In the solid phase of the organosolv pre-treatment, nearly pure cellulose is produced with just a little degradation, while hemicellulose and lignin are formed in the liquid phase. In the solid phase, the main constituents are glucan (60–65%), Klason lignin (25–30%), xylan (5–10%), arabinan (0.1–3%), and acetylated forms (1–3%), and in the liquid phase, monosaccharides, oligosaccharides, and degradation products. The concentration. of these components varies depending on the kind of feedstock used and the operating circumstances (Ruiz 2011). Furfural, HMF, etc. are among the main hemicellulose degradation products in increased bioethanol production efficiency (Wang 2012; Sannigrahi et al. 2010; Hallac et al. 2010; Lloyd and Wyman 2005; Pan et al. 2005). In contrast to typical pre-treatment procedures, organosolv pre-treatment produces a high yield of hemicelluloses. A variety of useful chemical compounds such as bioethanol, furfural, and xylitol may be produced from this.

The advantages of employing organic solvents for the delignification of certain cellulose materials are highlighted. The main features of published organosolv pulping techniques are described, and softwood pulp yields and strengths are compared to equivalent values of Kraft and sulfite pulps. Despite these benefits, the Kraft method has some significant disadvantages. Some of them, such as the issue of malodorous material emissions, are so serious that they have effectively prevented the Kraft process from being implemented in Germany.

One more significant issue is connected to the product; while better in terms of strength quality, Kraft pulp needs a very efficient bleaching process in order to achieve the necessary levels of brightness. As a result of colorful and poisonous effluents, particularly chlorinated lignin particles from bleaching, severe water pollution issues have arisen. At the opposite end of the spectrum, technological constraints permit the max size of the boiler, resulting in most contemporary mills today aiming for a modular size of close to 300,000 tonnes of pulp per year. Although the Kraft process employs dissolved organics as fuel, making it energy self-sufficient, the bulk of the energy generated is required for the concentration of these wasted liquors before combustion. Furthermore, lignin alone accounts for the higher calorific value of the dissolved material. Chemical pulp mills employing traditional technology have grown prohibitively costly. There is an obvious need to create innovative pulping technologies to minimize the amount of capital required to establish new chemical pulp mills while also using less wood, energy, and chemicals. One solution to current difficulties is to remove lignin from lignocellulosic raw material using organic solvents rather than reacting with inorganic chemicals. The significant conceptual benefit of employing an organic solvent for lignin

11.11 Organosolv Pre-treatment for Biofuel Production

The second generation biofuels derived from lignocellulosic biomass are commonly regarded as a means of meeting future transport needs without raising food costs (Field et al. 2008). Because lignin cannot be fermented, the utilization of lignocellulosic materials results in lignified leftovers that can be burned or used as co-products. To make cellulose to be saccharified for fermentation, lignin must be separated from cellulose during a pre-treatment phase (Bommarius et al. 2008; Zhu et al. 2008). Typically, lignocellulosic biomass is pretreated in one or two stages to fractionate the various polymers and enhance glucose yield (Pan et al. 2005; Panagiotopoulos et al. 2013). Softwoods produced responsibly and away from food markets are good raw materials for biofuel generation (Shuai et al. 2010). To allow saccharification, their lignin content, which is generally 30% of the dry matter, must be decreased. A delignification phase utilizing organosolv pre-treatment increased softwood saccharification yields (Arato et al. 2005; Mabee et al. 2006).

Some organisms can ferment the saccharification products of non-cellulosic polysaccharides. However, xylose and, more specifically, its breakdown product furfural are unusable or poisonous to many of the most often utilized bacteria (Pienkos and Zhang 2009). As a result, pentosans and xylose may have a negative value rather than being helpful co-products. The bio-refinery idea is based on the efficient synthesis of a variety of commercially viable co-products, and realizing this concept is a significant twenty-first-century problem (Ragauskas et al. 2006a, b). New pathways to lucrative co-products would thus be pleasing, other than the possibilities are dependent on the raw material (Pan et al. 2005).

11.11.1 Organosolv: A Potential Pre-treatment Technology for Bioethanol Production

When compared to the standard Kraft process, organosolv pulping methods provide relatively few advantages. However, organosolv methods, which seek to delignify and open the cell wall matrix, may prove to be promising (Kautto et al. 2013). According to Murinen et al. (2000), a successful organosolv method for kraft process substitution includes the following properties: (i) completely sulfur-free, (ii) most of the lignin is dissolved with little loss, (iii) operating parameters should be kept to a minimum, (iv) chemical recovery method that is both efficient and easy, (v) there are no environmental issues, (vi) the process's optimum size-tiny in comparison to the kraft process, (vii) adaptable to a wide range of raw materials, (viii) recuperation of useful by-products, (ix) superior pulp quality, (x) excellent bleachability without the use of chlorine, (xi) elevated yield of pulp, (xii) the procedure consumes little energy, and (xiii) the process has a closed chemical cycle.

The quest for pulping procedures that might meet the aforementioned parameters resulted in the invention of numerous organosolv techniques capable of generating pulp with characteristics similar to kraft pulp. The discussed technologies were all pilot or full-scale tries, but none of them resulted in continuous production (Lora and Aziz 1985; Young and Baierl 1985; Dahlmann and Schroeter 1990; Funaoka and Abe 1989; Gottlieb et al. 1992; Hamelinck et al. 2005). Organosolv methods are thus particularly appealing for non-woody raw materials, and at least one of them, the formic acid procedure, has been commercialized (Rousu et al. 2002). The Lignofibre (LGF) process is a unique flexible organosolv technique that meets the majority of the parameters stated above, and it applies to both annual plants and wood raw materials (Liitiä et al. 2011).

11.12 Conclusions

Bio-refineries will be an important part of a resilient and viable economy, ideally with feasible small-scale alternatives to help marginal and rural areas thrive economically. The development of bio-refineries and bioprocesses for the manufacture of biobased chemicals and polymers should be based on a sustainability assessment that takes into account feedstock availability along with techno-economic, and social implications. One of the most significant roadblocks to the development of effective biomass-based bio-refineries that can race with existing crude oil refineries is the proficient breakdown and transformation of lignocellulosic material into chemicals and fuels. The discussed methods are all under research at the laboratory scale. In comparison to other pre-treatment techniques, the organosolv pre-treatment enables high-efficiency ethanol and lignin synthesis from biomass. The rate of delignification of the solid phase, glucose retrieval yield from the solid phase, and lignin retrieval yield from the liquid phase are three parameters that can be used to describe the efficiency of the organosolv pre-treatment. The most significant challenge they confront is the cost of treatment procedures. To address this, first and foremost, cost-cutting is required. Efficient solvent recovery, holding out the organosolv reaction at the air pressure, efficient by-product recovery, identification of marketplace for bioproducts, and rises in the sales price of value-added products should all lead to more widespread industrial use of organosolv-based bio-refineries. This will contribute significantly to the establishment of a viable green economy, decarbonization, and climate change mitigation. The pulp business looks to be a very attractive potential since it already has an effective method for separating the lignin and extractives fractions from the polysaccharides; this cracking is highly appropriate for bio-refinery applications and is required. For the manufacture of glucose and its by-products, organosolv pre-treatments were effectively used to Sitka spruce wood. This strategy is in line with the bio-refinery idea, which calls for the efficient production of a variety of commercially viable co-products. The holistic use of biomasses and the reduction of pre-treatment costs should be the emphasis of prospective organosolv pre-treatment development. This may be accomplished by lowering the quantity of organic liquid needed in pre-treatment, improving the value of by-products, and optimizing the entire process, as well as certain other factors connected to energy and chemical usage reduction. As a result, this study can give some data and suggestions for future organosolv pre-treatment development.

Competing Interests All the authors declare that they have no competing interests.

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