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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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.

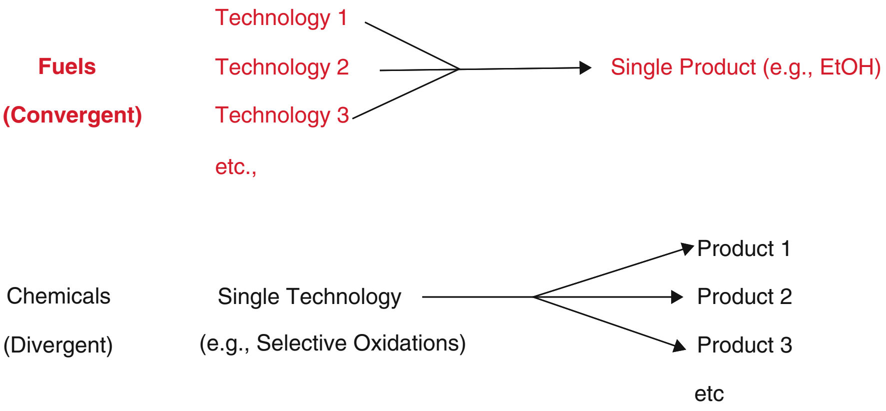

Fig. 11.1 Biobased fuels and chemicals research methods

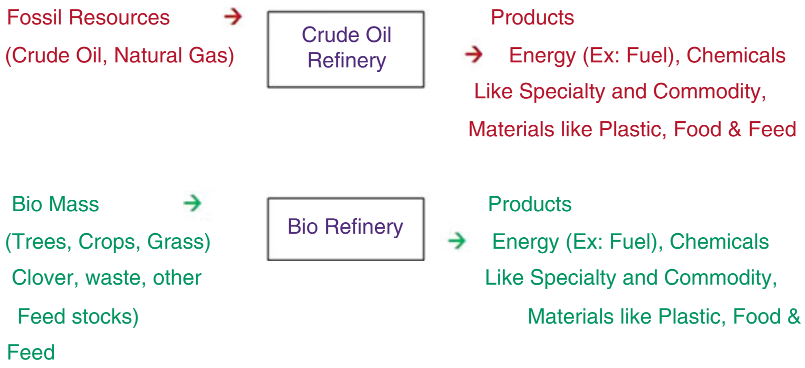

Fig. 11.2 Biomass as a renewable feedstock for bio-refineries

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

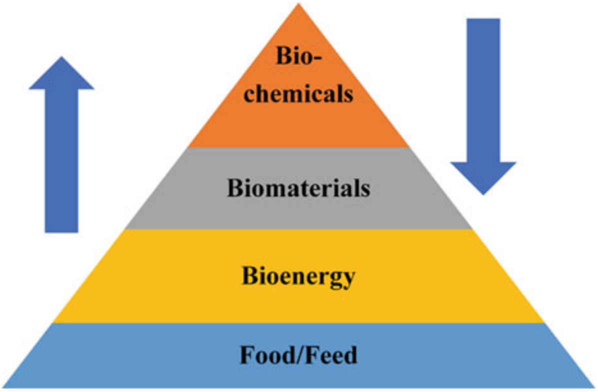

Fig. 11.3 Biobased "products" market pricing vs. market volume (De Jong et al. 2009). *The up arrow indicates Market Price and the down arrow indicates Market Volume*

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

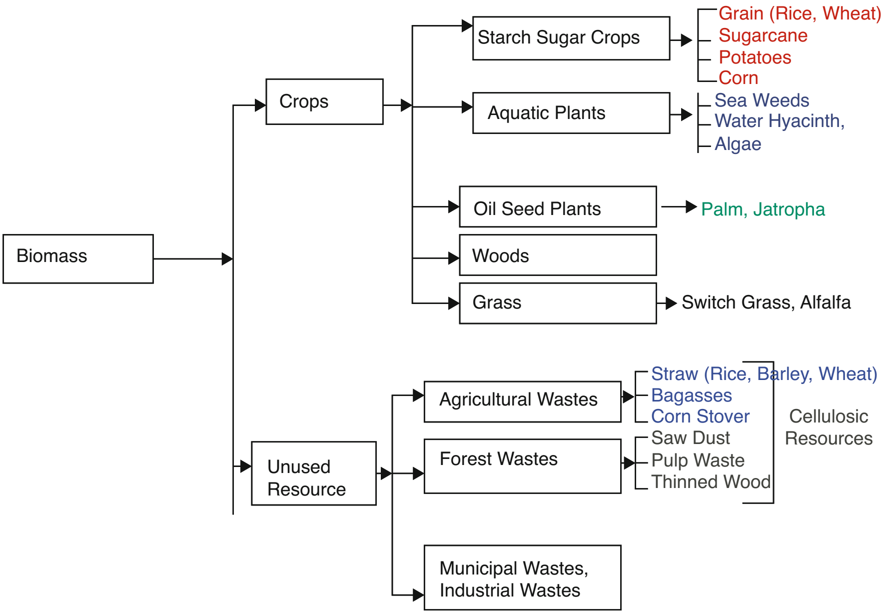

Fig. 11.4 Biomass as a viable bio-refinery feedstock

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.

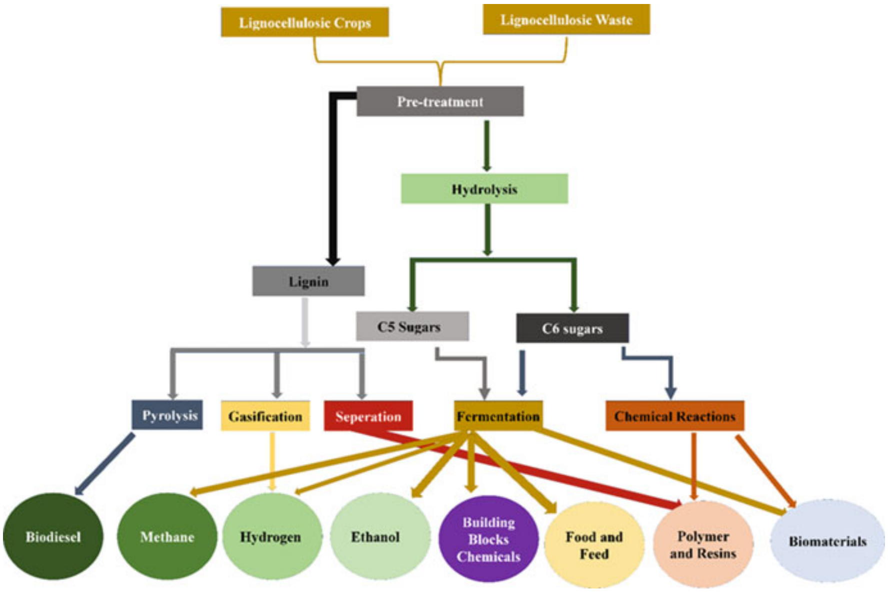

Fig. 11.5 A schematic overview of potential energy carriers and chemicals is produced in a bio-refinery

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

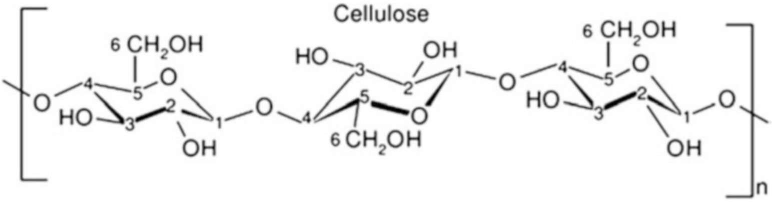

Fig. 11.6 Structure of cellulose molecule

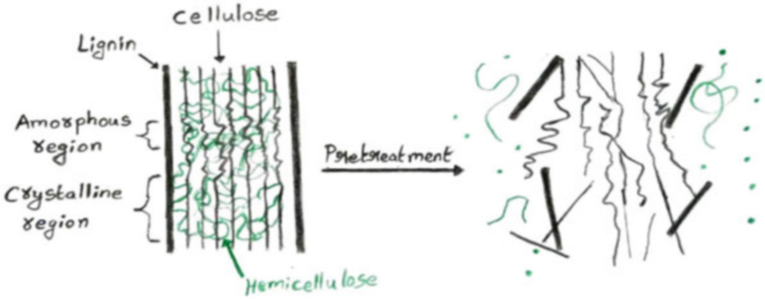

Fig. 11.7 Pre-treatment of LCB

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

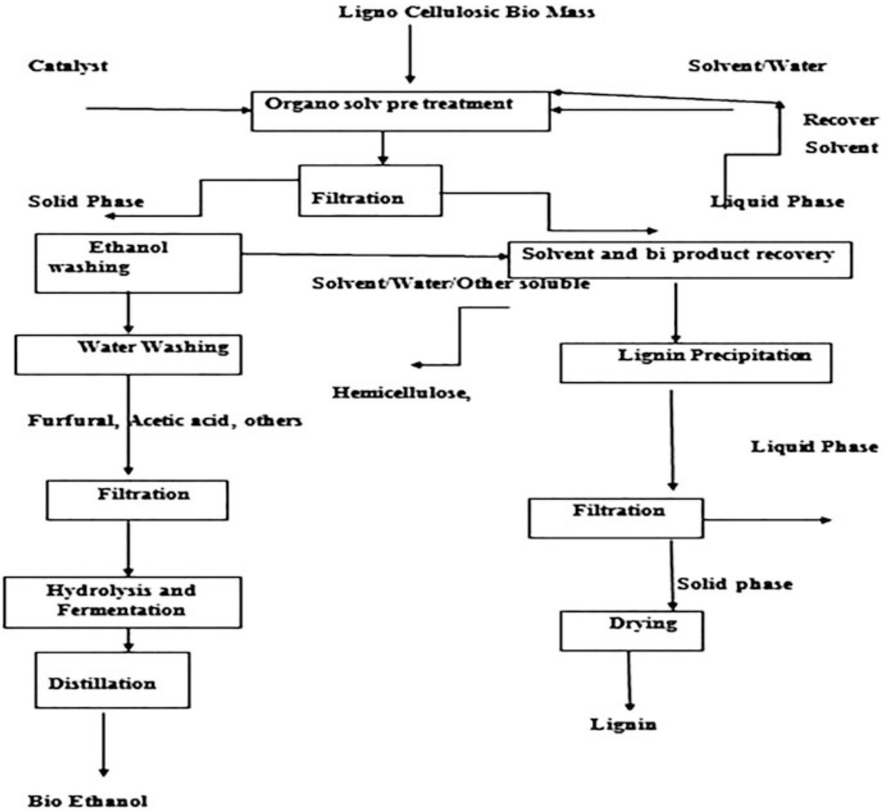

Fig. 11.8 The diagram of the pre-treatment of organosolv

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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