CHAPTER 9

Lignocellulosic biomass as an alternate source for next-generation biofuel

M. Rajamehala[1], A. Kaviprabha[1], A. Muthu Kumara Pandian[1], M. Vijay Pradhap Singh[1], S. Karthikadevi[1], B. Gopalakrishnan[2] and S. Chozhavendhan[3]

[1]Department of Biotechnology, Vivekanandha College of Engineering for Women, Tiruchengode, Tamil Nadu, India
[2]Department of Chemical Engineering, Annamalai University, Chidambaram, Tamil Nadu, India
[3]Department of Biotechnology, VSB Engineering College, Karur, Tamil Nadu, India

9.1 Introduction

Biofuels from natural resources could help in reducing greenhouse gases from atmosphere and also in maintaining carbon balance in the environment (Pérez et al., 2002). Lignocellulosic biomass is used as a primary substance for burning and generating heat and electricity. The utilization of these wastes is the source of generating biofuel in an eco-friendly method. Other advantage of biofuel is to reduce the dependency on woody biomasses from forest, which results in minimizing deforestation. Energy demand has recently increased significantly due to the deterioration of natural resources and the fast industrial reformation (Ravi et al., 2020).

A few examinations have focused on biofuel creation utilizing modern feedstock and green procedures of biomass. Approximately 80% of global energy consumption is derived from nonrenewable fossil fuels (Singh et al., 2021). The age of biofuel is divided into first and second era. Original biofuels differ from the fuel created from consumable feedstock, including starches got from wheat, corn sugarcane, and sugar beet (Sheehan, 2000). There are three sorts of biofuel in original which is significantly utilized in transportation with huge creation around the globe. These powers incorporate biodiesel, ethanol, and biogas. Second-era biofuels are created from noneatable sources particularly from lignocellulosic biomass (Sanderson, 2011). The burning of these biofuels releases less volume of carbon dioxide in the nature which significantly helps in maintaining greenhouse gas level. Plant biomass is the promising feedstock for the creation of the second-era biofuels. The drawbacks of biofuel incorporate local appropriateness, food security, and worldwide temperature alteration (Palmqvist and Hahn-Hägerdal, 2000). As indicated by contemplates, nonrenewable energy sources will exhaust by 2050 (Chozhavendhan et al., 2020a,b).

Biofuels and Bioenergy
DOI: https://doi.org/10.1016/B978-0-323-90040-9.00013-8
© 2022 Elsevier Inc.
All rights reserved.

Biofuels are the powers gotten from natural biomasses. As per International Energy Agencies, biofuels that are delivered meets about 1.5% of worldwide transportation. To diminish greenhouse gases, biofuel creation from biomass is considered to be an appropriate method (Chozhavendhan et al., 2018). There are various sorts of biofuels dependent on creation and properties, for example, bioethanol, biodiesel, biogas, biobutanol, bioethanol, and biohydrogen (Ojeda et al., 2011). Biofuels are ordered into original, second era, third era, and fourth era. Original-era biofuels are created from farming harvests (Dias et al., 2009) (sugarcane, sugar beet, wheat, rice, soybean oil, and so on). Second-era biofuels are created from sustainable assets (distinct squanders, utilized cooking oil, agribusiness squanders, modern waste, and sewage ooze). Third-generation biofuels are generated from feedstock (Rathore et al., 2019). The nations which are confronting heaviest biofuel request include the United States, India, China, Brazil, and EU representing about 90% of worldwide biofuel request until 2035 (world vitality standpoint 2010). It is normal that (Barakat et al., 2015) global ethanol creation will increment by 14% during the period from 2017 to 2027, that is, 120 to 131 bln L. Fifty level of this expansion is normal from Brazil, to fill household request.

Crude materials that are released into the environment everyday act as a resource for the production of biofuels (Somerville et al., 2010). It generally contains carbohydrate polymer (cellulose, hemicelluloses), and sweet-smelling polymer (lignin). The starch polymer contains sugar monomers (6- and 5-carbon sugar) in which they are firmly bound to the lignin (Chozhavendhan et al., 2020a,b). Lignocellulosic material is grouped into biomass, squander biomass, and vitality crop (Pérez et al., 2002). Biomass incorporates every earthly plant, for example, grass, tree, and shrubbery. Squander biomass contains low worth results, for example, corn, sorghum, wheat, sugarcane, saw plant, and paper factory. Energy crop containing high return of lignocellulosic biomass is considered to be a crude material for the creation of second-era biofuel such as switchgrass and elephant grass (Sheehan, 2000).

The lignocelluloses and cellulose fiber strands are shaped by cellulose connecting to one another by hydrogen holding (Hasunuma et al., 2013). Cellulose strands resemble the structure of skeletons encompassed by hemicelluloses and cellulose material. Cellulose fiber structure ensures hydrolysis of polysaccharides' structure by utilizing concoction, physical, and enzymatic techniques (Singh et al., 2015). The hemicelluloses contain polysaccharides, in which it is straight and stretched heterogeneous polymer and composed of five-sugar segments such as D-glucose, L-arabinose, D-mannose, D-galactose, and D-xylose (Boerjan et al., 2003). Homopolymer and hetropolymer are the foundation of chain of hemicelluloses, they are contrasted by sugar parts as well as by their subatomic morphology, in which the little chains are extended from the fundamental chain particles (Sheehan, 2000). In this way, the hemicellulose is simpler to be hydrolyzed than cellulose.

Lignin, the complex polymer which is organic in nature composed of phenolic polymers present widely in forest is an alternate resource for biofuel production

(Vinardell and Mitjans, 2017). Lignin is made of phenyl propanoid alcohols, coniferyl, sinapyl, and coumarly alcohols with hydroxyl, methoxyl, and carbonyl group. They can be broken into both acidic and antacid arrangements depending on their dissolvability (Palmqvist and Hahn-Hägerdal, 2000).

9.2 Raw materials

9.2.1 Wheat

Procedure for utilization of wheat into biofuel like bioethanol is similar to the method followed for other raw materials. The difference is it will undergo malting procees for making wheat as a source for biofuel production. Before soaking in water, the major grain and germ are commonly evacuated by handling dry in a flour mill. Malting is a process in which wheat proteins break starches into C_6 sugars under regulated conditions of temperature and dampness. Despite that, this procedure is moderate, and the business procedure acquaints fake compounds with separate the starch into sugar (Hendriks and Zeeman, 2009). After the malting process, the sugars obtained from wheat undergo washing with water and the remaining material is being used as an animal feed. Maturation of C_6 sugars involves the utilization of yeast at a temperature of around 32 to 35°C and pH of 5.2. Ethanol is delivered at 10%–15% focus and the arrangement is refined to create ethanol at maximum fixations (MacAllister and McCarthy, 2016).

9.2.2 Corn

This process is similar to that of wheat, with slight variations in the underlying corn preparation (Fig. 9.1). Maize (*Zea mays*) must be processed in one of two ways: wet processing or dry processing. The processing yields deposit of coproducts which could be

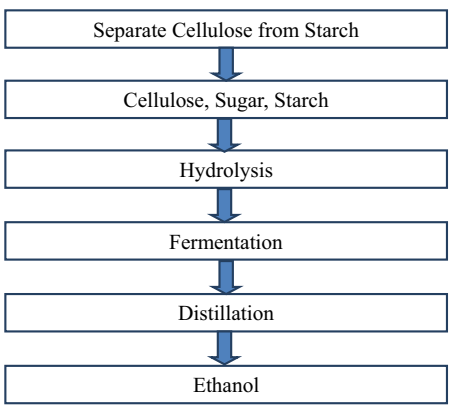


Figure 9.1 Bioethanol production from cellulose, starch, and sugar.

sold as livestock feed. Wet processing produces a few variety of buildups, but dry processing creates only one type of livestock feed (Nauman Aftab et al., 2019). Wet milling involves saturating the grain with sulfur dioxide-laced water for approximately 40 h, followed by crushing and separating the starch and coproducts. Cooking at low and high temperatures gelatinizes the starch component, after that the expansion of α-amylase, which generates dextrin oligosaccharides. Breakdown of starch to glucose will be done by glucoamylase and then it is matured to ethanol during the saccharification process. The primary difference between both dry and wet processing is that in dry processing, the whole corn is processed to have a size of around 1 mm, the different components of the oat grain are not separated before the addition of enzymes and water. The slurry obtained during the process is treated as per wet processing. The juice that is rich in sugar comes out after the process needs to maintain sterility in order to overcome the difficulties during purification (Hamelinck et al., 2005). The procedures are entrenched, yet there is some restricted extension for proficiency enhancements.

9.2.3 Sugarcane

This is one of the easiest procedures for delivering bioethanol through fermentation (Fig. 9.1). Crushing of sugar beets and sugarcane will take place initially and the sugars that are soluble undergo washing with water. After that, yeast is added for the maturation process in which the same temperature and pH will be maintained as in wheat. (Hendriks and Zeeman, 2009). On the basis of wet weight, sugarcane (*Saccharum officinarum*) contains 12%−17% all sugars. The typical extraction proficiency for creating stick juice by smashing is around 95%, with stick fiber (bagasse) as the long-term buildup (Hamelinck et al., 2005). In production lines that lone produce ethanol, the stick juice is warmed up to 110°C to decrease microbial contamination and tapped, once in a while focused by dissipation and fermentation. In consolidated sugar−ethanol plants, sucrose precious stones that are shaped after stick juice fixation are evacuated by centrifugation, leaving syrup (molasses) that contains up to 65% w/w sugars. Both sugarcane juice and molasses ordinarily contain adequate minerals and natural supplements to be promptly appropriate for ethanol creation by maturation with *Saccharomyces cerevisiae* (Karthiga Devi et al., 2020). Sugarcane has a vitality creation for every hectare that is considerably higher than different feedstocks, yet the procedure transformation productivity is just about 0.35−0.40-GJ bioethanol per GJ feedstock and yield of 80 L ethanol/ton. Sugarcane bagasse obtained after the process is utilized to generate power of about 0.08 GJ per feedstock (Farzad et al., 2017). During the fermentation process, the ethanol is converted to succinic acid and glycerol, respectively. Researchers have taken steps to increase the yield of ethanol by reducing the undesirable metabolites and decreasing yeast intensity within fermenters (Dias et al., 2009). It is currently thought of that the procedure could be not progressively improved.

9.2.4 Wood/straw dust

The way toward delivering ethanol from wood or straw feedstocks requires the creation of ethanol from both C5 and C6 sugars—not at all like the main C6 sugars in regular ethanol creation from sugarcane (Fig. 9.1). This procedure is viable but is unpredictable and costly. Advancement in innovative work in the United States entails addressing the cost issues and developing a more efficient procedure (Hendriks and Zeeman, 2009).

9.3 Lignocellulosic material

Lignocelluloses are made up of carbohydrate polymers (cellulose and hemicellulose) as well as an aromatic polymer (lignin) (Bharathiraja et al., 2015). The most plentiful biopolymer abundantly found in the Earth is cellulose which is generated through photosynthesis process and will be around 7.5×10^{10} tons per year. Cellulose is also present in other sources such as plants as well some microbes and few species of algae (Lynd et al., 2002).

Agricultural lignocellulosic deposits are plentiful inexhaustible assets of fiber that can be converted into sugars and ethanol, respectively. Production of ethanol from biomass has several advantages such as reduction in CO_2 emissions, therefore decreasing the environmental impact (Levin et al., 2004, 2006).

Lignocellulosic biomass is an intricate substrate ordinarily contains 80% (dry) starches, which are polymeric materials composed of 5-carbon and 6-carbon sugar units, respectively. It is made up of 45% dry weight of cellulose, 30% dry weight of hemicelluloses, and 25% dry weight of lignin, respectively. (Sun and Cheng, 2002).

When compared to cellulose, the hemicellulose is hydrolyzed effectively. The arrangement of carbon in the hemicellulose gives a well-defined structural arrangement. Lignin, a polymer having sweet smell, is a macromolecule that contains phenol and lack the hydration of three monomeric alcohols (Srivastava et al., 2021).

9.3.1 Composition of lignocellulosic feedstocks

9.3.1.1 Biomass from woody and herbaceous trees

The most promising feedstock for bioethanol production is woody biomass from Timberland as it offers carbon biosequestration. When compared to other biomass, woody biomass is utilized effectively for biofuel production (Zheng et al., 2014). About 30% of the biomass used for bioenergy in the United States is woody biomass. *Pinus ponderosa, Pinus contorta*, and *Pseudotsuga menziesii* rich in cellulose and hemicellulose are the widely used substrates (Liu et al., 2021). Cellulose, hemicellulose, lignin, and gelatin are found in dry heap of boondocks (Prasad et al., 2016). In particular, the customary biomass contains 30%–60% cellulose, 15%–40%

hemicellulose, and 10%–25% of lignin (Limayem and Ricke, 2012; Menon and Rao, 2012; Rosales-Calderon and Arantes, 2019). Plants belong to the family Populous is the abundant substrate for bioethanol production (Limayem and Ricke, 2012). Woody biomass from backwood have high lignin content and due to its nature of thickness (Limayem and Ricke, 2012).

Furthermore, boondocks woody biomass offers an inexorably versatile biomass gathering time appeared differently in relation to agribusiness stores. Rapid growth of high-yielding grass *Miscanthus giganteus* is another opportunity for producing biofuel. About 50%–70% of biomass from this grass is used for the production of biofuel (Limayem and Ricke, 2012). It has been shown that 133 × 109 L of bioethanol could be created by devoting 9.3% of the croplands in the United States to miscanthus advancement, and through which one-fifth of the country's fuel usage could be adjusted (Heaton et al., 2008) It was reported that the advancement of switchgrass and giant miscanthus on recouped mine goals in the eastern United States and that the bioethanol yield was increasingly vital for miscanthus when diverged from switchgrass (Scagline-Mellor et al., 2018).

9.3.1.2 Microalgae

Microalgae have been suggested as a potential animal feed for energy recovery in recent times. Their sugar content has the capability of transmitting fermentative ethanol and butanol, while their lipid content has the ability to generate biodiesel. After lipid extraction and ethanol regeneration, swirling biofuels such as biomethane and biohydrogen can be obtained from microalgae (Cheah et al., 2016b). Microalgae species, such as *Chlamydomonas* sp., *Spirogyra* sp., *Chlorella* sp., *Spirulina* sp., and *Dunaliella* sp., are rich in sugar content to form promising feedstock (Cheah et al., 2016a,b). Besides this, microalgae have maximum biomass benefit, photosynthetic development, and CO_2 biosequestration capacities (Cheah et al., 2015). When compared to terrestrial plants, microalgae have low lignin content which makes them to float in both seawater and wastewater, respectively (Limayem and Ricke, 2012). In order to use such algae as a feedstock for bioethanol production, several improvements were made to increase the sugar content. For instance, 71% content of sugar was achieved in *Chlamydomonas reinhardtii* under photoautotrophic system (Wang et al., 2015). Fifty-four percent of starch was achieved in *Chlorella vulgaris* for the production of bioethanol and biobutanol under mixotrophic and nitrogen starvation conditions (Srivastava et al., 2021).

9.4 Process for converting the lignocellulose to biofuels

Basically, the production of biofuels from sugar-based raw materials was mainly classified into two types: first- and second-generation biofuels (Cheah et al., 2015).

In general, the conversion of sugar-based carbohydrates to biofuels is given by Eq. 9.1:

$$(C_6H_{10}O_5)n + nH_2O \rightarrow nC_6H_{12}O_6 \rightarrow 2nC_2H_5OH + 2nCO_2 \quad (9.1)$$

The raw materials based on lignocellulose for the production of biofuels were categorized into several types such as agrowastes (fruits, soya residues, peanut residues, rice, and wheat); waste from forest region; and waste of herbaceous plant (wood, grass, and straw). There are two types of process, that is, biological and thermochemical, that help to convert the lignocellulosic biomass into biofuels.

9.4.1 Biological process

There are three kinds of process involved in the conversion of lignocelluloses into value-added biofuels: (1) pretreatment, (2) enzymatic hydrolysis, and (3) microbial fermentation (Beig et al., 2021).

9.4.1.1 Pretreatment

9.4.1.1.1 Physical method

a) Mechanical disruption

Lignocellulosic material is pretreated by grinding, crushing, chipping, and milling. By this method, the cellulose chain gets diminished and includes in the interruption of biomass. For the most part, ball processing is the commonly utilized technique, which is the most agreeable strategy utilized by the researchers in the method of mechanical disruption (Lari et al., 2019).

b) Pyrolysis

Pyrolysis is a process of heating the material at high temperature, breaking chemical bonds in its molecules (Chozhavendhan et al., 2020a,b). At the temperature 300°C, the cellulose breaks and produces gaseous product and char residues (Fig. 9.2). Pyrolysis at low and high centralization of synthetic concoctions and warmth is utilized as productive type of pyrolysis. The substrate is warmed with gentle corrosive for hydrolysis, in which 80%–85% of cellulose is changed into decreased sugar (Hassan et al., 2020). Indeed, even at low temperature, the cellulose gets deteriorated by utilizing impetuses. In this zinc chloride and sodium bicarbonate are catalyzed in the strategy pyrolysis.

c) Steam explosion

Steam explosion is a thermochemical pretreatment which permits the breakdown of lignocellulosic segment by the activity of warmth, natural acids shaped during the procedure and shearing powers coming about to the development of the dampness (Singh et al., 2015). Squashed biomass is treated with high-weight steam and afterward the weight is diminished because of which the cellulose material experiences

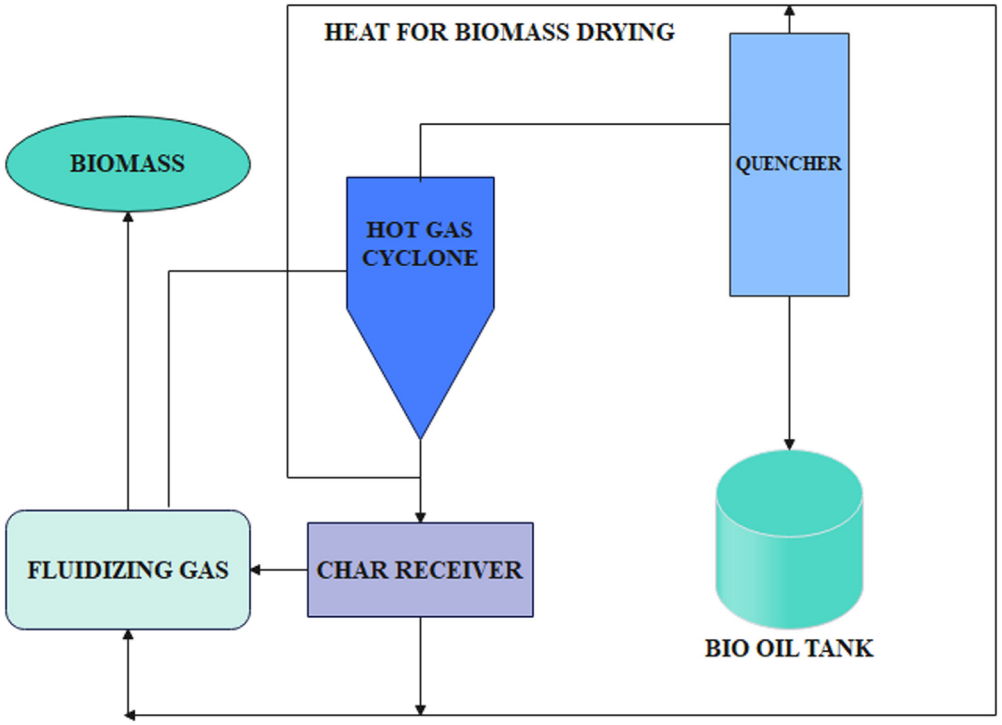


Figure 9.2 Pyrolysis process in conversion of lignocellulose into bioethanol.

blast disintegration (Fig. 9.3). At high temperature, the hemicelluloses and lignin changes are acquired and thus the cellulose hydrolysis is weakened with sulfuric corrosive treatment. However, the low temperature and longer habitation time can be utilized usefully and has high rate substrate treatment (Sarker et al., 2021). A bit of leeway of steam blast is the point at which we contrasted with pyrolysis, in which the expense is low and furthermore it requires low vitality. Hard woods, horticulture squanders, and other high cellulose-rich components can be utilized in this technique. (Soltanian et al., 2020).

9.4.1.1.2 Chemical method

a) Acid pretreatment

For pretreating the lignocellulose, most generally utilized solvents are H_2SO_4 and HCl. High focus acids are not utilized in pretreatment of lignocellulose, on account of its harmfulness and hydrolysis of cellulose and hemicelluloses (Converse et al., 1988). Besides, a few issues arise when high grouping of acids is utilized for the erosion of gear and well-being for human administrators. Weakened acids are not for the most

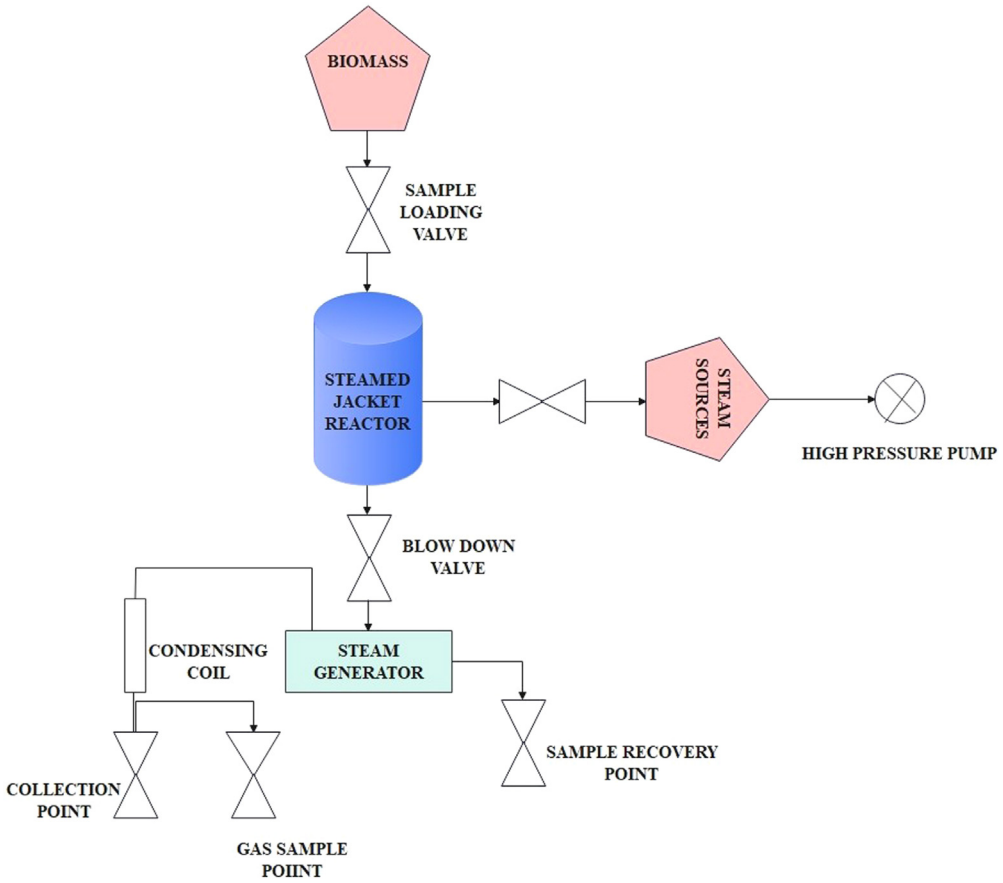


Figure 9.3 Steam explosion process in conversion of lignocellulosic biomass to bioethanol.

part favored due to the furfural compound during the pretreatment process, which controls the development of microorganism (Devi et al., 2019) in the aging procedure (Phillips et al., 1990). A few scientists utilized weakened fluid H_2SO4 with convergence of 0.2, 0.4, and 6.0 wt.% at 60, 80, and 120°C to pretreat the corn stalks preceding maturing the material to bioethanol (Esteghlalian et al., 1997).

b) Alkaline pretreatment

Like acid, a few bases can likewise be utilized for pretreatment strategy for lignocellulosic material. Its focus is on the material of lignin (Murphy and McCarthy, 2005). The permeable structure of the lignocellulosic material increments when the cross-connection of xylan and hemicellulose bonds is being expelled. In basic hydrolysis saponification process is generally utilized. For the most part, NaOH

and dissolvable smelling salts have been utilized in antacid hydrolysis pretreatment technique (Lee, 1997).

c) Ozonolysis

Ozone can be used to degrade the all-lignocellulosic material such as lignin and hemicelluloses. Ozone can be used on the substrate such as wheat, grass, rice, saw dust (Ben-Ghedalia et al., 1983), peanut, and cotton (Vidal and Molinier, 1988). Some of advantages are (1) no toxin residues, (2) removal of lignin more effectively, and (3) no decrease and increase in temperature. But there is also a limitation of ozonolysis as it requires high ozone substrate which is expensive (Sulfahri et al., 2020).

9.4.1.1.3 Biological method

a) Microbial pretreatment

White decay organism produces lignin peroxidases and manganese subordinate peroxidases during auxiliary digestion for the corruption of lignin. Proteins such as polyphenol oxidases, laccases (Lewandowska and Kujawski, 2007), H_20_2-delivering catalysts, and quinine-diminishing compounds can likewise debase the lignin and hemicellulose. The advantage of natural pretreatment is that it is a low vitality process with delicate environmental conditions (Roy et al., 2014). In organic pretreatment, the pace of hydrolysis is extremely low (Weber et al., 2010). Many exploration works in the lignin and the hemicellulose debasement are conveyed for powerful and quick corruption of substrate. Another advantage is that it is a low essentialness process with delicate biological conditions. The pace of hydrolysis in the vast majority of natural pretreatment forms is low.

b) Enzymatic pretreatment

It includes utilization of compound cellulase for the pretreatment of cellulose. The cellulase compound breaks the cellulose into the decreased sugar. Breakdown of cellulose by cellulase can likewise include the utilization of the natural pretreatment technique which utilizes microorganism that produces protein cellulase which thus debases the cellulose. Microorganisms delivering cellulose protein are *Clostridium* sp. (Rolz et al., 1986) *Cellulomonas* spp., *Bacillus* spp., *Thermomonospora fusca*, *Bacteroides cellulosolvens*, and so forth. Contagious strains creating cellulase catalyst are *Scterotiumrolfsii, Penicillium chrysosporium, Trichoderma* spp., *Aspergillus* spp., and *Schizophyllum* spp., in addition to other *Penicillium* strains and *Trichoderma* spp. (Mes-Hartree et al., 1987). It is most broadly utilized in the lignocellulosic maturation process. Consequently, these are the different pretreatment strategies utilized for improving hydrolysis of the substrate (Itoh et al., 2003). The most generally strategies applied rely upon the idea of the substrate, the hydrolysis rate, time of response, cost viability, or the ecological issues identified with the method (Nazarpour et al., 2013).

9.4.1.2 Hydrolysis

Before going to fermentation process, the carbohydrate biomass obtained from pretreatment process was hydrolyzed into simple sugars such as glucose and xylose (Rolz et al., 1986). There are two types of methods, that is enzymatic and chemical, available for the hydrolysis of lignocellulosic biomass (Arokiasamy et al., 2016).

9.4.1.3 Fermentation

Simple sugars from hydrolysis process were converted into beneficial biofuels such as bioethanol, succinic acid, butanol, lactic acid, and biohydrogen via microbial fermentation. There are many types of beneficial microbes that help in the production of biofuels from hydrolyzed simple sugars such as *Bacillus anthracis*, *Clostridium* sp., *Enterobacter* sp., *Enterobacter aerogenes*, *Enterobacter cloacae*, *Clostridium butyricum*, and *Rhodobacter sphaeroides* (Itoh et al., 2003; Mes-Hartree et al., 1987; Esteghlalian et al., 1997).

9.4.2 Thermochemical process

In thermochemical process, the presence of oxidizing agents in the lignocellulosic biomass has been heated at high temperature (Bharathiraja et al., 2018). There are three kinds of products developed from lignocellulosic biomass such as solid (biochar), liquid (pyrolytic oil), and gas (syngas) (Pérez et al., 2002). Finally, it was converted into biofuel such as ethanol through catalytic conversion (Sun and Cheng, 2002) (Fig. 9.4).

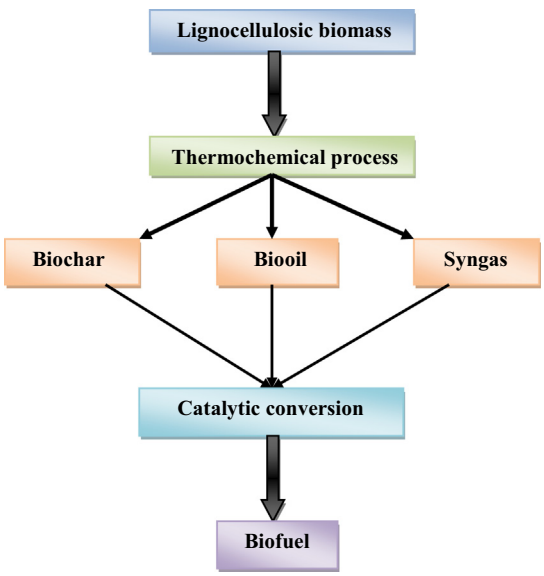


Figure 9.4 Thermochemical process for conversion of lignocellulosic biomass into biofuel.

9.5 Conclusion

Increasing ecological contamination, reduction in oil assets, and significant expense of oil-based goods prompt the creation of biodiesel. Renewable vitality and powers have caught the interest of individuals, when petroleum products are depleted and extreme weather change increases. The creation of lignocellulosic bioethanol helps in keeping up the maintainable vision of a green world. As worried for substrates, lignocellulosic biomass is available in wealth and can be exceptionally maintainable. The individuals throughout the world are looking out for a fast-forward leap in the field of creation of bioethanol to give an efficient and eco-friendly fuel and researchers across the globe anticipate blending results.

References

Arokiasamy, W.J., Xavier, V.A.J., Sivasankaran, C., Kumar Ramanujam, P., Alagurajan, S., Rajkumar, R., 2016. Simultaneous saccharification and fermentation of rice bran and ground nut shell for the production of ethanol. J. Chem. Pharm. Sci. 9, 202–205.

Barakat, A., Monlau, F., Solhy, A., Carrere, H., 2015. Mechanical dissociation and fragmentation of lignocellulosic biomass: effect of initial moisture, biochemical and structural proprieties on energy requirement. Appl. Energy 142, 240–246. Available from: https://doi.org/10.1016/j.apenergy.2014.12.076.

Beig, B., Riaz, M., Raza Naqvi, S., Hassan, M., Zheng, Z., Karimi, K., et al., 2021. Current challenges and innovative developments in pretreatment of lignocellulosic residues for biofuel production: a review. Fuel 287, 119670. Available from: https://doi.org/10.1016/j.fuel.2020.119670.

Ben-Ghedalia, D., Shefet, G., Dror, Y., 1983. Chemical treatments for increasing the digestibility of cotton straw: 1. Effect of ozone and sodium hydroxide treatments on rumen metabolism and on the digestibility of cell walls and organic matter. J. Agric. Sci. 100, 393–400. Available from: https://doi.org/10.1017/S0021859600033542.

Bharathiraja, B., Sudharsanaa, T., Bharghavi, A., Sowmeya, G.S., Yuvaraj, D., Praveenkumar, R., et al., 2015. Biobutanol production from cellulose rich agricultural waste using *Clostridium* species. J. Chem. Pharm. Res. 7, 2463–2469.

Bharathiraja, B., Sudharsana, T., Jayamuthunagai, J., Praveenkumar, R., Chozhavendhan, S., Iyyappan, J., 2018. Biogas production – a review on composition, fuel properties, feed stock and principles of anaerobic digestion. Renew. Sustain. Energy Rev. 90, 570–582. Available from: https://doi.org/10.1016/j.rser.2018.03.093.

Boerjan, W., Ralph, J., Baucher, M., 2003. Lignin biosynthesis. Annu. Rev. Plant. Biol. 54, 519–546. Available from: https://doi.org/10.1146/annurev.arplant.54.031902.134938.

Cheah, W.Y., Show, P.L., Chang, J.-S., Ling, T.C., Juan, J.C., 2015. Biosequestration of atmospheric CO_2 and flue gas-containing CO_2 by microalgae. Bioresour. Technol. 184, 190–201. Available from: https://doi.org/10.1016/j.biortech.2014.11.026.

Cheah, W.Y., Ling, T.C., Juan, J.C., Lee, D.-J., Chang, J.-S., Show, P.L., 2016a. Biorefineries of carbon dioxide: from carbon capture and storage (CCS) to bioenergies production. Bioresour. Technol. 215, 346–356. Available from: https://doi.org/10.1016/j.biortech.2016.04.019.

Cheah, W.Y., Ling, T.C., Show, P.L., Juan, J.C., Chang, J.-S., Lee, D.-J., 2016b. Cultivation in wastewaters for energy: a microalgae platform. Appl. Energy 179, 609–625. Available from: https://doi.org/10.1016/j.apenergy.2016.07.015.

Chozhavendhan, S., Praveen Kumar, R., Elavazhagan, S., Barathiraja, B., Jayakumar, M., Varjani, S.J., 2018. In: Singhania, R.R., Agarwal, R.A., Kumar, R.P., Sukumaran, R.K. (Eds.), Utilization of Crude Glycerol from Biodiesel Industry for the Production of Value-Added Bioproducts BT - Waste

to Wealth. Springer, Singapore, Singapore, pp. 65–82. Available from: https://doi.org/10.1007/978-981-10-7431-8_4.

Chozhavendhan, S., Rajamehala, M., Karthigadevi, G., Praveenkumar, R., Bharathiraja, B., 2020a. A review on feedstock, pretreatment methods, influencing factors, production and purification processes of bio-hydrogen production. Case Stud. Chem. Environ. Eng. 2, 100038. Available from: https://doi.org/10.1016/j.cscee.2020.100038.

Chozhavendhan, S., Karthiga Devi, G., Bharathiraja, B., Praveen Kumar, R., Elavazhagan, S., 2020b. Assessment of crude glycerol utilization for sustainable development of biorefineries. Refining Biomass Residues for Sustainable Energy and Bioproducts. Elsevier Inc. Available from: https://doi.org/10.1016/b978-0-12-818996-2.00009-0.

Converse, A.O., Matsuno, R., Tanaka, M., Taniguchi, M., 1988. A model of enzyme adsorption and hydrolysis of microcrystalline cellulose with slow deactivation of the adsorbed enzyme. Biotechnol. Bioeng. 32, 38–45. Available from: https://doi.org/10.1002/bit.260320107.

Devi, G.K., Chozhavendhan, S., Jayamuthunagai, J., Bharathiraja, B., Praveen kumar, R., 2019. Conversion of Biomass to Methanol and Ethanol BT. In: Pogaku, R. (Ed.), Horizons in Bioprocess Engineering. Springer International Publishing, Cham, pp. 61–72. Available from: https://doi.org/10.1007/978-3-030-29069-6_4.

Dias, M.O., Ensinas, A.V., Nebra, S., Filho, R.M., Rossell, C., Maciel, M., 2009. Production of bioethanol and other bio-based materials from sugarcane bagasse: integration to conventional bioethanol production process. Chem. Eng. Res. Des. 87, 1206–1216.

Esteghlalian, A., Hashimoto, A.G., Fenske, J.J., Penner, M.H., 1997. Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. Bioresour. Technol. 59, 129–136. Available from: https://doi.org/10.1016/S0960-8524(97)81606-9.

Farzad, S., Mandegari, M.A., Guo, M., Haigh, K.F., Shah, N., Görgens, J.F., 2017. Multi-product biorefineries from lignocelluloses: a pathway to revitalisation of the sugar industry? Biotechnol. Biofuels 10, 1–24. Available from: https://doi.org/10.1186/s13068-017-0761-9.

Hamelinck, C.N., Van Hooijdonk, G., Faaij, A.P.C., 2005. Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term. Biomass Bioenergy 28, 384–410. Available from: https://doi.org/10.1016/j.biombioe.2004.09.002.

Hassan, N.S., Jalil, A.A., Hitam, C.N.C., Vo, D.V.N., Nabgan, W., 2020. Biofuels and renewable chemicals production by catalytic pyrolysis of cellulose: a review. Environ. Chem. Lett. 18, 1625–1648. Available from: https://doi.org/10.1007/s10311-020-01040-7.

Hasunuma, T., Okazaki, F., Okai, N., Hara, K.Y., Ishii, J., Kondo, A., 2013. A review of enzymes and microbes for lignocellulosic biorefinery and the possibility of their application to consolidated bioprocessing technology. Bioresour. Technol. 135, 513–522. Available from: https://doi.org/10.1016/j.biortech.2012.10.047.

Heaton, E.A., Dohleman, F.G., Long, S.P., 2008. Meeting US biofuel goals with less land: The potential of Miscanthus. Glob. Chang. Biol. 14, 2000–2014. Available from: https://doi.org/10.1111/j.1365-2486.2008.01662.x.

Hendriks, A.T.W.M., Zeeman, G., 2009. Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresour. Technol. 100, 10–18. Available from: https://doi.org/10.1016/j.biortech.2008.05.027.

Itoh, H., Wada, M., Honda, Y., Kuwahara, M., Watanabe, T., 2003. Bioorganosolve pretreatments for simultaneous saccharification and fermentation of beech wood by ethanolysis and white rot fungi. J. Biotechnol. 103, 273–280. Available from: https://doi.org/10.1016/s0168-1656(03)00123-8.

Karthiga Devi, G., Vignesh, K., Chozhavendhan, S., 2020. Effective utilization of sugarcane trash for energy production. Refining Biomass Residues for Sustainable Energy and Bioproducts. Elsevier Inc. Available from: https://doi.org/10.1016/b978-0-12-818996-2.00012-0.

Lari, Z., Ahmadzadeh, H., Hosseini, M., 2019. Chapter 2 - Cell wall disruption: a critical upstream process for biofuel production. In: Hosseini, M.B.T.-A. (Ed.), Woodhead Publishing Series in Energy. Woodhead Publishing, pp. 21–35. in F.C.T. for A.F. and B. Available from: https://doi.org/10.1016/B978-0-12-817937-6.00002-3.

Lee, J., 1997. Biological conversion of lignocellulosic biomass to ethanol. J. Biotechnol. 56, 1–24. Available from: https://doi.org/10.1016/s0168-1656(97)00073-4.

Levin, D.B., Pitt, L., Love, M., 2004. Biohydrogen production: prospects and limitations to practical application. Int. J. Hydrog. Energy 29, 173–185. Available from: https://doi.org/10.1016/S0360-3199(03)00094-6.

Levin, D.B., Islam, R., Cicek, N., Sparling, R., 2006. Hydrogen production by *Clostridium thermocellum* 27405 from cellulosic biomass substrates. Int. J. Hydrog. Energy 31, 1496–1503. Available from: https://doi.org/10.1016/j.ijhydene.2006.06.015.

Lewandowska, M., Kujawski, W., 2007. Ethanol production from lactose in a fermentation/pervaporation system. J. Food Eng. 79, 430–437. Available from: https://doi.org/10.1016/j.jfoodeng.2006.01.071.

Limayem, A., Ricke, S.C., 2012. Lignocellulosic biomass for bioethanol production: current perspectives, potential issues and future prospects. Prog. Energy Combust. Sci. 38, 449–467. Available from: https://doi.org/10.1016/j.pecs.2012.03.002.

Liu, Y., Cruz-Morales, P., Zargar, A., Belcher, M.S., Pang, B., Englund, E., et al., 2021. Biofuels for a sustainable future. Cell 184, 1636–1647. Available from: https://doi.org/10.1016/j.cell.2021.01.052.

Lynd, L.R., Weimer, P.J., van Zyl, W.H., Pretorius, I.S., 2002. Microbial cellulose utilization: fundamentals and biotechnology. Microbiol. Mol. Biol. Rev. 66, 506. Available from: https://doi.org/10.1128/MMBR.66.3.506-577.2002.

MacAllister, J., McCarthy, G., 2016. Renewable fuel standard program: Standards for 2017 and biomass-based diesel volume for 2018, Federal Register.

Menon, V., Rao, M., 2012. Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept. Prog. Energy Combust. Sci. 38, 522–550. Available from: https://doi.org/10.1016/j.pecs.2012.02.002.

Mes-Hartree, M., Hogan, C.M., Saddler, J.N., 1987. Recycle of enzymes and substrate following enzymatic hydrolysis of steam-pretreated aspenwood. Biotechnol. Bioeng. 30, 558–564. Available from: https://doi.org/10.1002/bit.260300413.

Murphy, J.D., McCarthy, K., 2005. Ethanol production from energy crops and wastes for use as a transport fuel in Ireland. Appl. Energy 82, 148–166. Available from: https://doi.org/10.1016/j.apenergy.2004.10.004.

Nauman Aftab, M., Iqbal, I., Riaz, F., Karadag, A., Tabatabaei, M., 2019. Different pretreatment methods of lignocellulosic biomass for use in biofuel production. Biomass Bioenergy - Recent. Trends Futur. Chall. 1–24. Available from: https://doi.org/10.5772/intechopen.84995.

Nazarpour, F., Abdullah, D.K., Abdullah, N., Motedayen, N., Zamiri, R., 2013. Biological pretreatment of rubberwood with *Ceriporiopsis subvermispora* for enzymatic hydrolysis and bioethanol production. Biomed. Res. Int. 2013, 268349. Available from: https://doi.org/10.1155/2013/268349.

Ojeda, K., Sánchez, E., Kafarov, V., 2011. Sustainable ethanol production from lignocellulosic biomass – application of exergy analysis. Energy 36, 2119–2128. Available from: https://doi.org/10.1016/j.energy.2010.08.017.

Palmqvist, E., Hahn-Hägerdal, B., 2000. Fermentation of lignocellulosic hydrolysates. II: inhibitors and mechanisms of inhibition. Bioresour. Technol. 74, 25–33. Available from: https://doi.org/10.1016/S0960-8524(99)00161-3.

Pérez, J., Muñoz-Dorado, J., de la Rubia, T., Martínez, J., 2002. Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. Int. Microbiol. Off. J. Span. Soc. Microbiol. 5, 53–63. Available from: https://doi.org/10.1007/s10123-002-0062-3.

Phillips, V.D., Kinoshita, C.M., Neill, D.R., Takahashi, P.K., 1990. Thermochemical production of methanol from biomass in Hawaii. Appl. Energy 35, 167–175. Available from: https://doi.org/10.1016/0306-2619(90)90066-M.

Prasad, A., Sotenko, M., Blenkinsopp, T., Coles, S.R., 2016. Life cycle assessment of lignocellulosic biomass pretreatment methods in biofuel production. Int. J. Life Cycle Assess. 21, 44–50. Available from: https://doi.org/10.1007/s11367-015-0985-5.

Rathore, D., Singh, A., Dahiya, D., Nigam, P.S., 2019. Sustainability of biohydrogen as fuel: present scenario and future perspective. AIMS Energy 7, 1–19. Available from: https://doi.org/10.3934/energy.2019.1.1.

Ravi, A., Gurunathan, B., Rajendiran, N., Varjani, S., Gnansounou, E., Pandey, A., et al., 2020. Contemporary approaches towards augmentation of distinctive heterogeneous catalyst for sustainable biodiesel production. Environ. Technol. Innov. 19, 100906. Available from: https://doi.org/10.1016/j.eti.2020.100906.

Rolz, C., de Leon, R., de Arriola, M.C., de Cabrera, S., 1986. Biodelignification of lemon grass and citronella bagasse by white-rot fungi. Appl. Environ. Microbiol. 52, 607–611. Available from: https://doi.org/10.1128/aem.52.4.607-611.1986.

Rosales-Calderon, O., Arantes, V., 2019. A review on commercial-scale high-value products that can be produced alongside cellulosic ethanol. Biotechnol. Biofuels 12, 240. Available from: https://doi.org/10.1186/s13068-019-1529-1.

Roy, S., Kumar, K., Ghosh, S., Das, D., 2014. Thermophilic biohydrogen production using pre-treated algal biomass as substrate. Biomass Bioenergy 157–166. Available from: https://doi.org/10.1016/jbiombioe201312006.

Sanderson, K., 2011. Lignocellulose: a chewy problem. Nature 474, S12–S14. Available from: https://doi.org/10.1038/474S012a.

Sarker, T.R., Pattnaik, F., Nanda, S., Dalai, A.K., Meda, V., Naik, S., 2021. Hydrothermal pretreatment technologies for lignocellulosic biomass: a review of steam explosion and subcritical water hydrolysis. Chemosphere 284, 131372. Available from: https://doi.org/10.1016/j.chemosphere.2021.131372.

Scagline-Mellor, S., Griggs, T., Skousen, J., Wolfrum, E., Holásková, I., 2018. Switchgrass and giant miscanthus biomass and theoretical ethanol production from reclaimed mine lands. BioEnergy Res. 11, 562–573. Available from: https://doi.org/10.1007/s12155-018-9915-2.

Sheehan, J., 2000. The road to bioethanol: a strategic perspective of the U.S. Department of Energy's National Ethanol Program. Glycosyl Hydrolases for Biomass Conversion. ACS Symposium Series. American Chemical Society, pp. 1–2. Available from: https://doi.org/10.1021/bk-2001-0769.ch001.

Singh, J., Suhag, M., Dhaka, A., 2015. Augmented digestion of lignocellulose by steam explosion, acid and alkaline pretreatment methods: a review. Carbohydr. Polym. 117C, 624–631. Available from: https://doi.org/10.1016/j.carbpol.2014.10.012.

Singh, M.V.P., Archana, A., Chozhavendhan, S., Prabhu, N., Rajamehala, M., 2021. In: Kumar, R.P., Bharathiraja, B.B.T.-N. (Eds.), Chapter 25 - A Nano-Based Biofuel: Remedy to Boost a Sustainable and Greener Environment. Academic Press, pp. 519–531. Available from: https://doi.org/10.1016/B978-0-12-822401-4.00020-9.

Soltanian, S., Aghbashlo, M., Almasi, F., Hosseinzadeh-Bandbafha, H., Nizami, A.-S., Ok, Y.S., et al., 2020. A critical review of the effects of pretreatment methods on the exergetic aspects of lignocellulosic biofuels. Energy Convers. Manag. 212, 112792. Available from: https://doi.org/10.1016/j.enconman.2020.112792.

Somerville, C., Youngs, H., Taylor, C., Davis, S.C., Long, S.P., 2010. Feedstocks for lignocellulosic biofuels. Science 329, 790–792. Available from: https://doi.org/10.1126/science.1189268.

Srivastava, R.K., Shetti, N.P., Reddy, K.R., Kwon, E.E., Nadagouda, M.N., Aminabhavi, T.M., 2021. Biomass utilization and production of biofuels from carbon neutral materials. Environ. Pollut. 276, 116731. Available from: https://doi.org/10.1016/j.envpol.2021.116731.

Sulfahri, Mushlihah, S., Langford, A., Tassakka, A.C.M.A.R., 2020. Ozonolysis as an effective pretreatment strategy for bioethanol production from marine algae. BioEnergy Res. 13, 1269–1279. Available from: https://doi.org/10.1007/s12155-020-10131-w.

Sun, Y., Cheng, J., 2002. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour. Technol. 83, 1–11. Available from: https://doi.org/10.1016/S0960-8524(01)00212-7.

Vidal, P.F., Molinier, J., 1988. Ozonolysis of lignin—improvement of in vitro digestibility of poplar sawdust. Biomass 16, 1–17. Available from: https://doi.org/10.1016/0144-4565(88)90012-1.

Vinardell, M.P., Mitjans, M., 2017. Lignins and their derivatives with beneficial effects on human health. Int. J. Mol. Sci. 18, 1219. Available from: https://doi.org/10.3390/ijms18061219.

Wang, X., Ruan, Z., Sheridan, P., Boileau, D., Liu, Y., Liao, W., 2015. Two-stage photoautotrophic cultivation to improve carbohydrate production in *Chlamydomonas reinhardtii*. Biomass Bioenergy 74, 280–287. Available from: https://doi.org/10.1016/j.biombioe.2015.01.024.

Weber, C., Farwick, A., Benisch, F., Brat, D., Dietz, H., Subtil, T., et al., 2010. Trends and challenges in the microbial production of lignocellulosic bioalcohol fuels. Appl. Microbiol. Biotechnol. 87, 1303–1315. Available from: https://doi.org/10.1007/s00253-010-2707-z.

Zheng, J., Choo, K., Bradt, C., Lehoux, R., Rehmann, L., 2014. Enzymatic hydrolysis of steam exploded corncob residues after pretreatment in a twin-screw extruder. Biotechnol. Rep. 3, 99–107. Available from: https://doi.org/10.1016/j.btre.2014.06.008.