Clean Energy Production Technologies
Series Editors: Neha Srivastava · P. K. Mishra

Neha Srivastava
Bhawna Verma
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Agroindustrial Waste for Green Fuel Application

Springer

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

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Preface

The book entitled *Agroindustrial Waste for Green Fuel Application* explores the feasibility of agroindustrial waste as promising substrate for various bioenergy production. Agriculturally available biomasses are renewable in nature, broadly available, highly rich in cellulosic content which can be further converted into different bioenergy options. Though various agroindustrial waste have been investigated for different bioenergy options, there are limitations of certain bioenergy options due to which it cannot be practically transformed commercially. Thus, this book is a potential trial towards the practical suitability of these bioenergy options, generated through agroindustrial waste. The specificity, availability, and structural details of cellulosic biomass play a key role in enhancing the various bioenergy production and focusing on these points the book also explores the different agroindustrial waste, specifically cellulosic rich and the potential waste options which are also less explored have been discussed in the book. The book is divided into 10 key potential chapters in which Chaps. 1 and 2 are targeted on wheat, maize, and pulses waste as potential biofuels producing substrates whereas Chaps. 3 and 4 are based on specific substrates of woody plants, agriculture residues, and manure potential as promising raw materials for bioenergy production. Further, Chaps. 5 and 6 evaluate the various available potential technologies and impact of pretreatment methods and advancement to improve biofuel production process generated using these wastes. Additionally, Chaps. 7 and 8 explore the impact of individual verses mixed lignocellulosic substrate influence to further improve bioenergy production process. While Chaps. 9 and 10 are based on the existing challenges and their remediation possibilities to increase biofuels production while applying different approach like mixed agroindustrial waste on practical ground. All these chapters in the book provide a further and even clearer road map towards practical utility of biofuels production using agroindustrial waste as most suitable, promising, and low-cost substrate to produce various bioenergy production options.

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The editors are thankful to all the academicians and scientists whose contributions have enriched this volume. We also express our deep sense of gratitude to our parents whose blessings have always prompted us to pursue academic activities deeply. It is quite possible that in a work of this nature, some mistakes might have crept in text inadvertently and for these we owe undiluted responsibility. We are grateful to all authors for their contribution to this book. We are also thankful to Springer Nature for giving this opportunity to editors and DST, New Delhi, for all technical support as well as providing Women Scientist-B project (DST/WOS-B/ER-3/2021). We are also thankful to the Department of Chemical Engineering and Technology, IIT (BHU) Varanasi, UP, India. We thank them from the core of our heart.

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Chapter 1
Pulses Waste to Biofuels

Ankita, Shruti Choudhary, Harmeet Singh Bakala, Loveleen Kaur Sarao, and Sandeep Kaur

Abstract Human dependency on fossil fuels has increased due to an unprecedented population growth rate. There is a dire need to propel our energy dependency from fossil fuels to renewable energy resources. Increased pollution and the growing energy demand make it necessary to look for greener alternatives. Biodegradable waste utilization like agricultural and forestry residue, nonedible plant material is promising, economical, and environment-friendly substitutes for fossil fuels. The biofuel production could significantly bring down the dependency of India on foreign oil and fossil fuels. Here, the efficient usage of legume residues obtained from agroindustrial and food processing has several benefits. This chapter summarizes the potential for valorization of legume residue linked to the generation of unavoidable waste. The basic outline of biofuel production includes preparation and degradation of carbohydrate content in the substrate using pretreatment methods. Pretreatment of the substrate is done for enhancing delignification. Pretreatment processes can encompass biological, physical/mechanical, chemical, and physicochemical treatments. This is followed by either saccharification and fermentation to yield bioethanol/biogas or esterification to yield biodiesel or biolubricant. Cellulose microfibrils (CMF) were successfully extracted from pea pods by using various chemical treatments. Enzymatic saccharification of the soybean hull was done by using cellulase, beta-glucosidase, and Viscozyme (cell wall degrading enzyme complex). Legume residues like pea pods, broad beans pods, pigeon pea wood, fava bean straw, and soybean hull are generated annually in huge amount and represent an interesting source for biofuel production. Lignocellulosic biomass has enormous potential for serving as a promising substitute for fossil fuels and satisfy the steadily increasing fuel demands. Efficient utilization of all agricultural residue

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can help in reducing environmental impacts. The residue extraction will lead to achieve, a zero-waste economy and sustainable biofuel generation.

Keywords Pulses waste · Biofuel production · Lignocellulosic biomass · Saccharification

1.1 Introduction

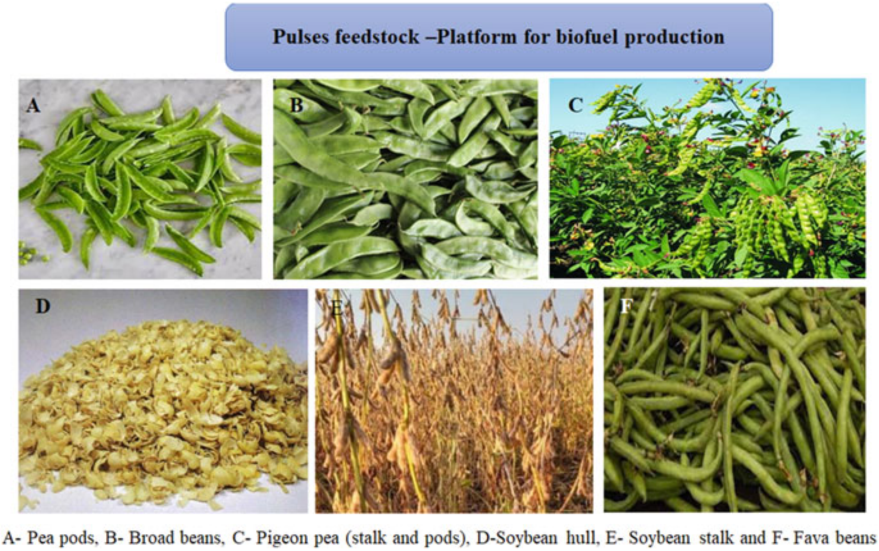
India is experiencing an unprecedented population growth. Continuously expanding global population coupled with industrialization lead to exhaustion of the natural fuel reserves already present in very less amount like natural gas, petroleum, and coal and energy consumption from these nonrenewable natural reserves release approximately 35 Mg of CO_2 annually, if this trend does not change emissions per year will exceed 43 billion Mg in the next 30 years (EIA 2019). The declining of fossil fuel reserves and their negative environmental impact leads to an increasing attention towards alternative fuels (Rezania et al. 2020a, b; Burkhardt et al. 2021). Biofuels blended with transportation fuels naturally reduces the dependency on India's foreign oil import. Hiking in fuel prices increases economic pressure, also one of the reason to look for alternative fuels. Energy is the major factor in the socioeconomic growth of the nation. Energy crisis can be a big problem for developing countries as well as developed countries. About 70% of diesel and 99.9% of petrol are utilized for transportation, making India the third largest consumer in the world (GoI, Press Information Bureau 2014). To mitigate climate change, as well as to reduce the dependence on natural reserves, biofuels from biomass have drawn focus on sustainable energy production. To feed the ever-increasing population, the researchers utilize advanced cultivation techniques for obtaining high-yielding varieties. Production of high-yielding varieties leads to the enhanced yield of food crops. This leads to proportional production of crop residues, viz., stalks, leaves, and seed pods as well. A huge quantity of this crop residue is rendered unused (Prasad et al. 2018; Kumar et al. 2016; Prasad et al. 2020). Disposal of this unutilized crop residues is a big challenge which is not handled properly. The burning of this crop residue pollutes the environment leading to emission of greenhouse gases (GHG). Declining fossil fuel reserves, increasing consumption of energy, and current environmental policies for the reduction of GHG emissions has created attention towards sustainable energy production. All these problems could be resolved via appropriate management of the use of this leftover crop residue (Rathore et al. 2019; Bhuvaneshwari et al. 2019). With the help of recent methodologies, this crop residue can become a viable and sustainable surrogate for petroleum-based fuels. Alternative biofuels like biogas, bioethanol, biodiesel, and biohydrogen are recognized as renewable and eco-friendly energy sources (Zivkovic and Veljkovic 2018). To maintain environmental sustainability, bioethanol produced from lignocellulosic biomass is thought of as an alternative to fossil-based fuels (Agarwal et al. 2021). For transportation, the best substitute is biofuel. To swamp the threat like depletion of fossil fuels, environmental pollution, GHG emission and

Table 1.1 Legumes production in the world (Data from FAOSTAT Food and agriculture database 2019)

S. No.	Legume	Yield (hg/ha)
1	Beans, dry	8741
2	Beans, green	163,555
3	Broad beans, dry	21,075
4	Chickpeas	10,384
5	Cowpeas, dry	6163
6	Peas, dry	19,791
7	Peas, green	78,249
8	Soybeans	27,690

fluctuating fuel prices, biofuel is thought of as the mandate of interest. According to the international energy agency report 2019, biofuel can contribute 6% of the total energy demand by about 2030 (Shi et al. 2018; Kumari and Singh 2019). Biofuel could be defined as fuel from the vegetal origin. The characteristics of vegetal fuels are similar to fossil fuels. This allows its use in spark engines with not many modifications required (Demirbas 2007).

Presently agriculture has become the biggest biological sector having high biomass production (European Commission 2015). Globally, 36% of the land area is apt for agricultural production and about 1.5 billion ha of arable land is presently under permanent crop cultivation (FAO (Food and Agriculture Organization of the United Nations) 2018). Pulses are an important crop and constitute an important part of the diet owing to their high protein content. Pulses belong to the Leguminosae family, which is the third largest family in the plant kingdom. According to FAOSTAT Food and agriculture database, 2019, green beans amounted to 163,555 hg/ha showed maximum production followed by green peas (Table 1.1). Pulses comprise annual and perennial leguminous crops having edible seeds that are used for both food and feed. Over the past decades, pulses are receiving a resurgence of interest because they require less water as well as low inputs and help to maintain soil fertility via biological N_2 fixation (Gupta et al. 2020). Pulses also help in mitigating greenhouse gases emission. Pulses crop residue can be put to use for the production of biofuels. Waste crop matter is a good source of biomass. They serve as a raw material for producing biofuels (Yang et al. 2015) (Fig. 1.1). Crop residues are the potential precursor to produce biofuels. Crop residues are wastes obtained at harvesting and processing (Ramprasad 2016). Crop residue is recognized as a potent cellulosic feedstock and used for biofuel production because crop residue is having a fixed carbon content (Lal 2005). If we consider this waste as a renewable source, this waste can be transformed into biofuel. This biofuel gives supplementary revenue to the farmers and creates employment too (Clauser et al. 2021). Black gram is used to make many dishes but we use only the inner portion and the peel is thrown as waste. This waste raw biomass containing lignin, hemicellulose, and cellulose could be utilized for producing biofuels (Rajeswari and Saravanathamizhan 2020). Pigeon pea is a minor crop, but it is utilized as a potent crop for producing biofuels. All parts of pigeon pea can be utilized as food, fodder/forage, and fertilizer, but the unutilized parts like stem/stalk, the hull, and leaves biomass could be utilized as



A- Pea pods, B- Broad beans, C- Pigeon pea (stalk and pods), D-Soybean hull, E- Soybean stalk and F- Fava beans

Fig. 1.1 Potential pulses-based raw material for producing biofuels

feedstock for biofuel generation. The wood of pigeon pea is also identified as a potential lignocellulosic resource for producing renewable energy. The chemical composition of pigeon pea wood is—cellulose (34.26 ± 0.29%), hemicellulose (34.83 ± 0.68%), and lignin (17.99 ± 0.22%). The major agricultural residue in pigeon pea is stalk (Tanquilut et al. 2019). According to statistical analysis based on vegetable production, India is the leading producer of pea and per year production of pea (*Pisum sativum* L.) is 3.56 million metric tons which result in over one million tons of pea pods. These waste pea pods were dumped into the open places. With the help of modern technologies, these pods can be converted into biobutanol (Sharma et al. 2015). The products derived from the soya bean and the soya itself are widely used by humans, fodder for animals, and as raw material for producing biodiesel (da Cesar et al. 2019).

The residual straw of soybean contains cellulose, hemicellulose, and could be utilized for producing biofuels (Abdulkhani et al. 2016). Faba bean (*Vicia faba* L.) straws are also thought of as the potent raw material to produce ethanol and biogas (Petersson et al. 2007). Legumes contribute the biggest amount to food waste at 44% followed by root and tubers (20%) and cereals (19%) (Nora et al. 2017). Legumes have no direct competition with land and food production. Legumes have multiple arrays of potential—these can be produced on degraded lands or marginal soils, having the ability to reduce greenhouse gases emission, increases carbon sequestration in soil, and provides a feedstock for sustainable biofuel production (Jensen et al. 2012). Biomass residue of peanut shell (*Arachis hypogea*) can be used as a source of energy-producing material. The amount of moisture content in peanut shell is quite low making this an ideal biofuel that can be used for heat production in industrial boilers and households. No drying treatment is necessary because the amount of moisture content in peanut shell is quite low (Moreno et al. 2018).

1.2 Biofuels

Biofuels are easily derived from biological resources like plants and organic waste, which are cheap and abundant in nature (Akhlaghi et al. 2015). Biofuels have a longer history and have been serving since we started burning firewood for cooking. In comparison to petrol or coal fuel burning, biofuels do not lead to carbon emission (Srivastava et al. 2020). According to the survey of the European union (EU 2021) biofuels serve as a renewable alternative to fossil fuels. Biofuels like biodiesel and bioethanol are the fuels used for transportation and are available in liquid or gas form. These are made up of biomass. These biofuels help in the reduction of greenhouse gas emissions without affecting environmental sustainability. Sustainability means without menacing the needs of future generations, by meeting the needs of the present generations. Biofuels play an important role to decarbonize our energy resources to mitigate the worst risk of climate changes.

1.2.1 Feedstocks for Biofuels: Lignocellulosic Biomass (LCB)

Biomass is a reliable source of energy. It is the only roadmap for producing biofuels to sustain the economy of the country. Biomass is a renewable resource of energy. Crop residues are the nonedible part generally the waste generated at the time of harvesting and processing (Ramprasad 2016). At the time of harvesting the crop residue is the leftover material which generally includes stalks, stems, seed pods, leaves, etc. (Sharma et al. 2018). Biofuels are obtained from various biological processes from waste organic matter of plants. These biofuels meet our energy requirements without carbon emission by considering environmental sustainability (Srivastava et al. 2020). With the help of photosynthesis, plants produce biomass. In photosynthesis, solar energy is transformed into chemical energy by plants in the form of $C_6H_{12}O_6$ (Fig. 1.2). Lignocellulose (LC), the forest residue and woody biomass represent an abundant, low-cost, truly carbon neutral and under-utilized biological resources. It is a potential source for biofuel production (Machineni 2019). These properties of lignocellulose make second-generation biofuels quite sustainable as compared to the first-generation biofuels (Sindhu et al. 2019). This

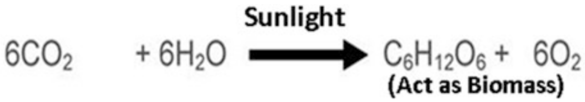


Fig. 1.2 The building blocks of Plant Biomass

$$6CO_2 + 6H_2O \xrightarrow{\text{Sunlight}} \underset{\text{(Act as Biomass)}}{C_6H_{12}O_6 + 6O_2}$$

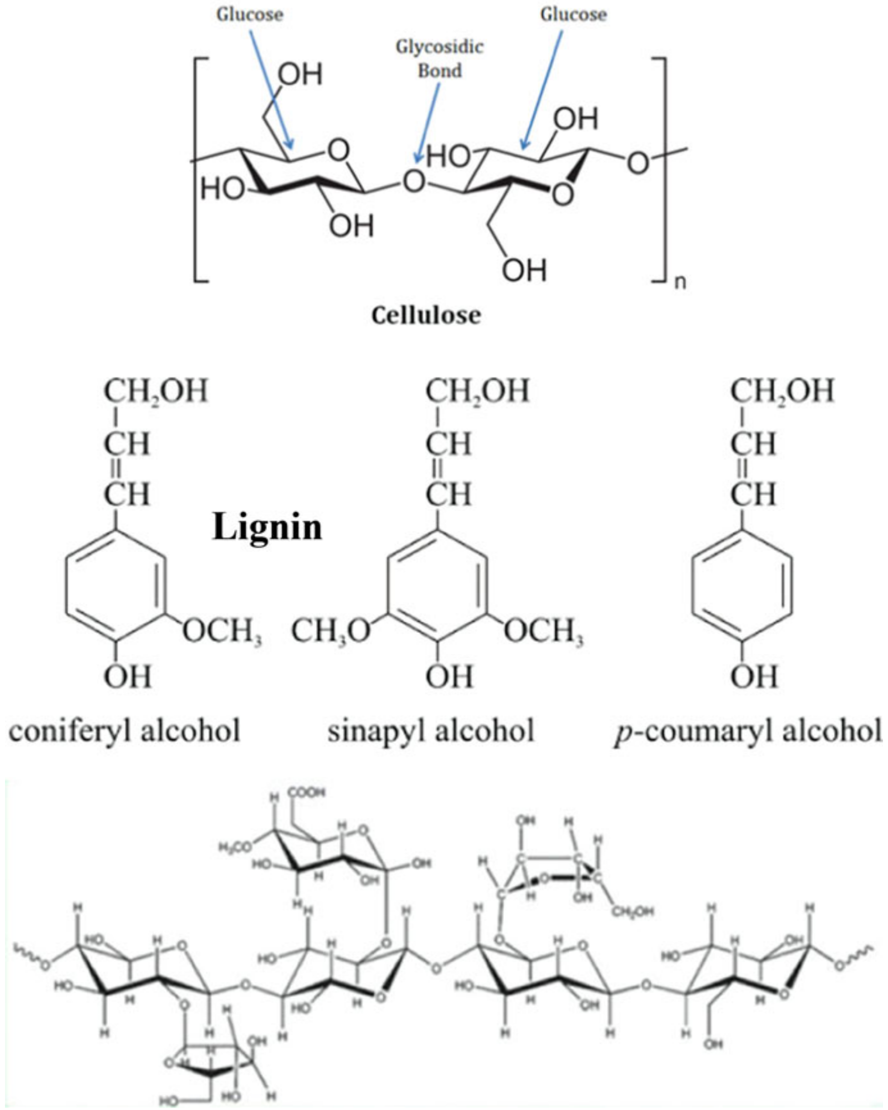


Fig. 1.3 Composition of Lignocellulosic biomass

waste brings no competition with food and is considered an ideal biomass feedstock. Lignocellulose is rich in cellulose (a potential source of sugar production), hemicellulose, and lignin (Fig. 1.3). Lignin, cellulose, and hemicellulose constitute the main limiting factors for biofuel generation through biochemical pathways. There will be a reduction in the cost of biofuels by using lignocellulose as a substrate which is an inevitable part of the plant cell. Approximately 90% of the total plant dry weight is constituted by cellulosic and non-cellulosic polysaccharides. Lignocellulosic biomass contributes a natural resource for renewable and economical bioenergy generation. Various pretreatments are required for converting lignocellulosic biomass to biofuel (Rezania et al. 2020a, b). The enzymatic treatment is very expensive. To overcome this hurdle, it is mandatory to look for a well-suited pretreatment method for the generation of biofuels. By combining one or two pretreatments, we can increase the production of biofuels but combining two pretreatments has some drawbacks. To fulfill the energy, it is important to maintain a balance between fossil fuel utilization, first- and second-generation biofuels (Kumari and Singh 2018). The complex nature of lignocellulose limits its transformation into value-added products and expensive pretreatments and enzymes are required for the conversion of lignocellulose. A fungus *Parascedosporium* genus was isolated from wheat straw, secrets a broad array of carbohydrate-active enzymes when allowed to grow on a lignocellulose-based substrate. The activity of enzyme breakdown the β-ether units in lignin, releasing flavonoid tricin and enhance the digestion of lignocellulose (Oates et al. 2021).

1.3 Classification of Biofuels

These days, biofuels have been in vogue. Biomass is a renewable energy source. Biofuels could be divided into two broad groups—bioethanol (alcohol) and biodiesel (oil). Biofuels are classified into primary and secondary biofuels on the basis of their direct or indirect use Fig. 1.4. The primary biofuels do not involve any type of processing. Solid material from forest waste is directly used as fuel for cooking, viz.,

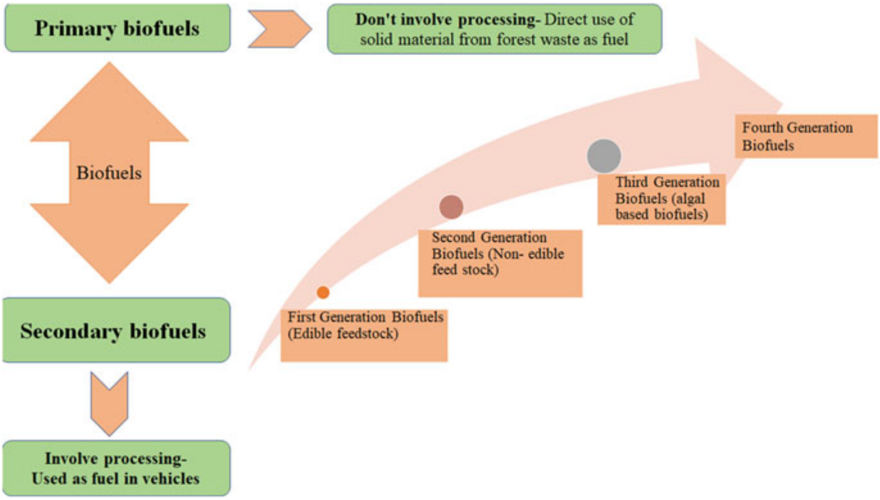


Fig. 1.4 Classification of biofuels on the basis of their use

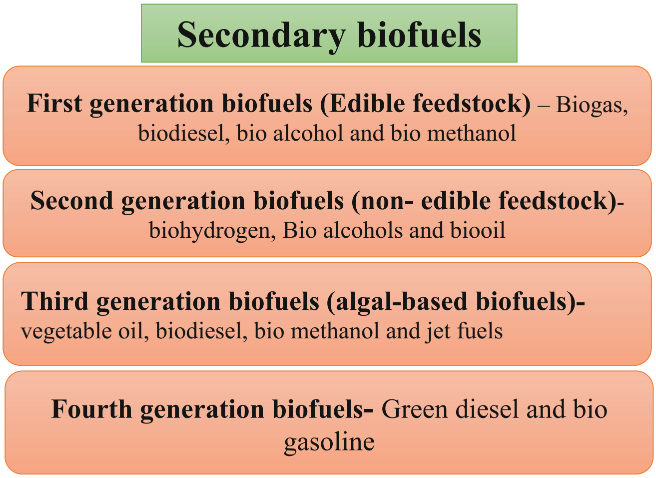


Fig. 1.5 Categorization of secondary biofuels into four generations

firewood, grass, wood pellets, wood chips, etc. On the basis of feedstock resources and generation technologies secondary biofuels are classified into first-, secon, and third-generation biofuels (Algayyima et al. 2018). Figure 1.5 represents the secondary biofuels on the basis of their generation technologies. Two main first-generation biofuels used extensively are ethanol (Fig. 1.6) and biodiesel (Fig. 1.7) mainly produced from edible biomass like corns, wheat, maize, soybeans, rape seed, sugar, and starch (Callegari et al. 2020). Through the fermentation process, starch and sugars obtained from edible food crops are converted into ethanol, and biodiesel is derived by the transesterification method (Lee and Lavoie 2013). The production of biodiesel is a chemical process. In biodiesel production, the oil extraction is done from feedstock and then extracted oil is transformed into biodiesel with the help of the transesterification process (Fig. 1.7). However, there are some conflicts about food security and environmental sustainability. This sets a limit on the increasing production of first-generation biofuels. The major shortcoming of the first-generation biofuels is the food versus fuel debate.

In third-generation biofuels, microalgae is thought of as the more potent and convenient feedstock. This is so owing to its low cultivation price, area, and enhanced growth rate (Yin et al. 2020). Microalgae can be grown under both fresh and wastewater. Due to their high photosynthetic ability microalgae can produce a high content of lipid (lipid-rich composition), which is used for producing biodiesel (Ananthi et al. 2021). Genetically modified microalgae can be used as a feedstock for fourth-generation biofuels. Genetically modified microorganisms are genetically modified to enhance CO_2 sequestration, superior productivity, and adaptability to grow in poor nutrient environments (Aron et al. 2020).

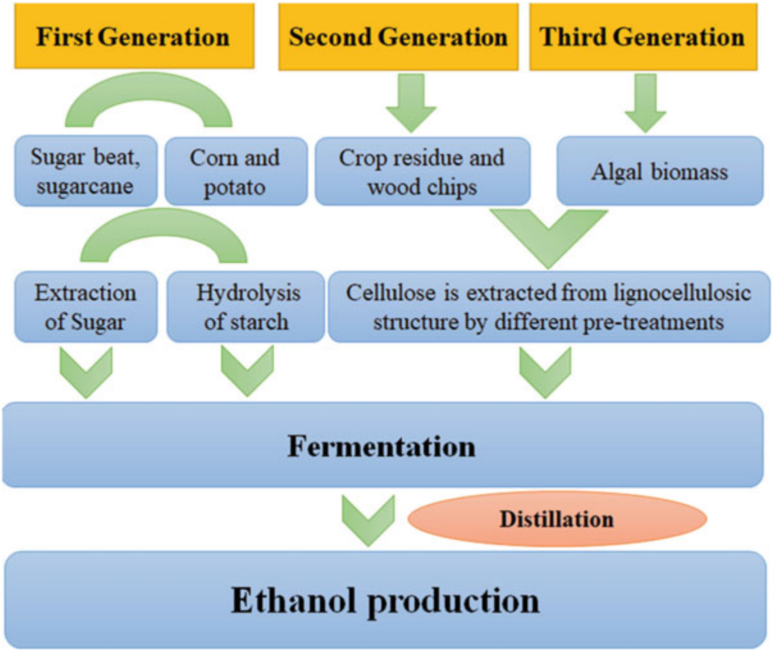


Fig. 1.6 Overview of Ethanol production pathway

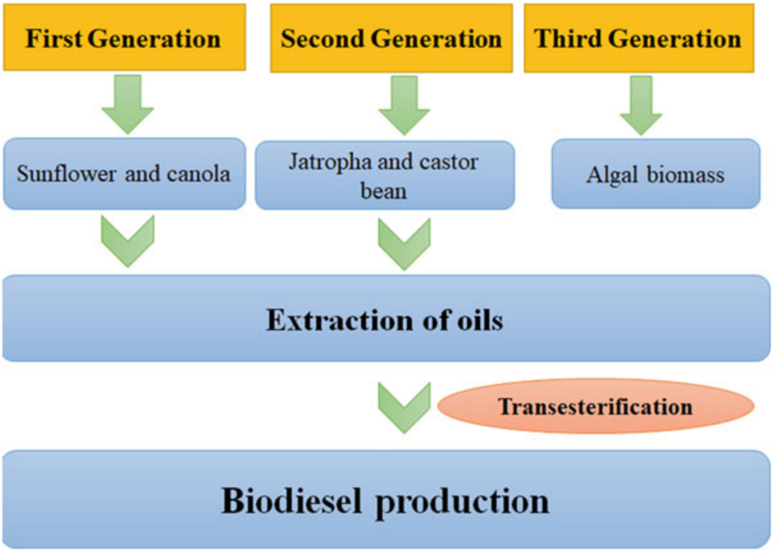


Fig. 1.7 Overview of Biodiesel production pathway

1.4 Biofuel Production from Pulses Waste

To decarbonize the energy sector biomass-based fuel is the only answer to the current issue. Biomass-based sources involved agricultural and forestry waste (Salleh et al. 2019). Biomass gained attention as sustainable nonconventional alternative renewable biofuels to conventional nonrenewable energy resources. LC waste is a type of agroindustrial biomass. It is an inexpensive source of energy. Agricultural waste/residue represents the abundant LCB as a feedstock to produce energy. The basic components of LCB are cellulose, hemicelluloses, and lignin (Kumara et al. 2020). The use of lignocellulosic biomass is a zero-waste approach in which a petroleum-based economy is replaced by bio-based economy with a mandate to develop environmental sustainability (Gallegos et al. 2017).

The demand for legume crops including peas and beans is increasing. This has led to high production not only of the main products but their by-products as well. Consequently, there is a rise in by-product recycling and its utilization as renewable energy. Root residues left after crop harvest are a good source of soil nitrogen and act as natural fertilizer while the rest of the plant parts can be sent for biofuel production. Raw material suitable for biofuel (bioethanol, biodiesel, biolubricants, biogas, etc.) production should contain high carbohydrate or nitrogen. With high biomass residues of 3.7–5.7 tons per hectare representing nearly 50% of total crop biomass, high polysaccharide (49–57% of the biomass fraction), and low lignin (13–14% of the biomass fraction), faba bean waste fulfills the basic requirements for biofuel production. Such resources have been actively investigated to synthesize alternate energy sources in form of bioethanol and biogas (Jasinskas et al. 2020; Frame et al. 1997; Alkhtib et al. 2016; Petersson et al. 2007). Similarly, pigeon pea stalks or wood have high cellulose and hemicellulose, but low lignin content relative to conventional crop wastes like sugarcane bagasse. Fermenting this waste for bioethanol can reduce dependency on oil and fossil fuels (Kirti et al. 2019; Tanquilut et al. 2020). Wastes from pea (26% cellulose, 20.5% hemicellulose, and 3.92% lignin) and soybean hulls (46–51% cellulose, 16–18% hemicellulose, and 1.4–2% lignin) are attractive sources of biofuel (Yoo et al. 2011; Nimbalkar et al. 2018). Synthetic oleochemical esters can replace mineral oil-based lubricants, both technically and ecologically. One such neopentyl glycol-base biolubricant derived from soybean is the best example (Aguieiras et al. 2020; Cavalcanti et al. 2018; Sharma et al. 2017; Nimbalkar et al. 2018). In the following section, we will discuss the methodology of biofuel production from legume waste as raw materials. These reports are from lab-scale experiments, the majority of which can be easily adapted and display the potential for large-scale production at industrial levels.

1.5 Procedure to Generate Biofuel from Legumes

The basic outline of biofuel production includes preparation and degradation of carbohydrate content in the substrate using pretreatment methods. This is followed by either saccharification and fermentation to yield bioethanol/biogas or esterification to yield biodiesel or bio lubricant (Fig. 1.8). Lignin can be depolymerized to produce aromatic compounds while cellulose and hemicellulose in the biomass are degraded to ethanol. In brief, bioethanol production is divided into:

1. Pretreatment of lignocellulosic substrate
2. Enzymatic hydrolysis of cellulose
3. Fermentation of glucose to bioethanol
4. Ethanol recovery by distillation

On the other hand, biogas production involves anaerobic breakdown of reducing sugars in the biomass into methane and carbon dioxide. For bio-oils, the fatty acids in the pretreated or untreated biomass are subjected to esterification using chemicals or enzymes as catalysts. These oils can be further processed to yield biodiesel or transesterified to get biolubricants.

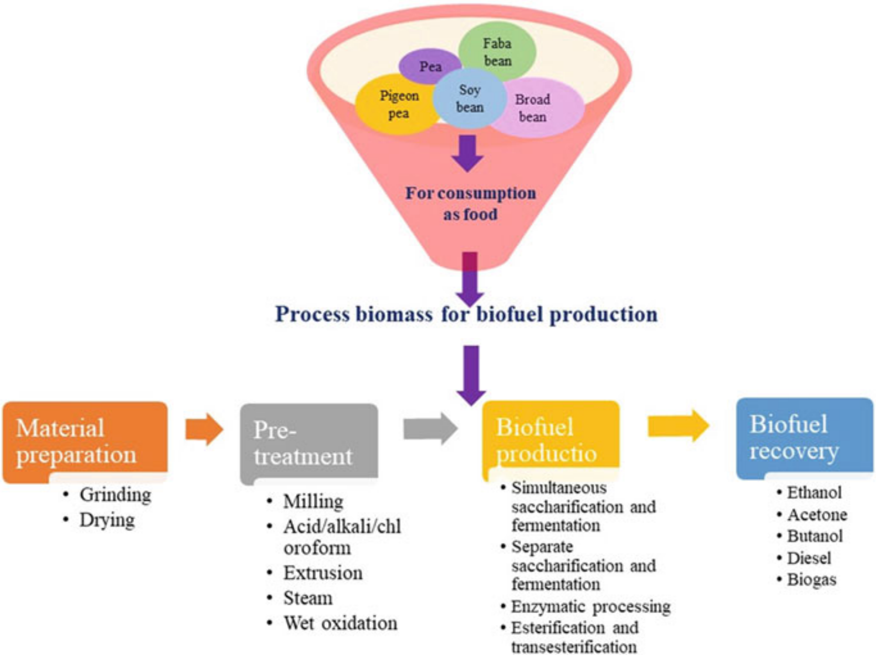


Fig. 1.8 Overview of Biofuel production from Pulses waste

1.5.1 Preparation of Raw Material

After harvesting of the crop at maturity, grains are separated while the rest of the plant parts can be utilized for waste treatment. Soil processing, planting, and cultivation method have been evaluated and demonstrated to affect biomass indicators (moisture and calorific value), and hence biofuel production quality (Jasinskas et al. 2020; Frame et al. 1997; Alkhtib et al. 2016; Petersson et al. 2007; Aguieiras et al. 2020; Cavalcanti et al. 2018; Sharma et al. 2017; Nimbalkar et al. 2018). For instance, conventional plowing yielded the best results in terms of pellet properties, harmful gas emissions, etc. No-till technology is suitable both for grain production and pellets processing (Jasinskas et al. 2020). Planting times determine pod yield, residual biomass, and, hence, saccharification potential. Lignin and pectin content decrease from the first to the last planting and increase for cellulose. Similarly, greenhouse-grown pods had high lignin, hemicellulose, and pectin while cellulose was the highest in the field-grown plants (Gomez et al. 2017).

Faba bean: Leftover and empty faba bean pods and straw after harvesting were milled together to <2 mm before pretreatment and further analysis. The raw material was dried at 70 °C to constant weight for pretreatment or stored at room temperature or at −20 °C to use later (Petersson et al. 2007; Gomez et al. 2017).

Soybean: Soybean hulls needed grinding with a roller mill that reduces the particle size to <1041 μm before pretreatment. Pretreatment methods such as thermo-mechanical extrusion and acid and alkali hydrolysis followed by enzymatic hydrolysis have been optimized. All these methods provided a comparable efficiency to yield high sugar and thus biofuel production (Yoo et al. 2011). The Other type of biofuel is also reported from soybean. Dried soybean seeds were used to extract biodiesel (Abideen Adeyinka et al. 2020). Soybean cooking oil waste was also used for biodiesel preparation by transesterification. Different blends of the resulting diesel were evaluated for performance characteristics of the engine (Sharma et al. 2017). Fatty acids from soybean have high linoleic acid which provide them good stability at low temperature. Considering this, soybean oil or biodiesel can be transesterified to get neopentyl glycol (NPG)-based biolubricant as a better alternate to oil. Now that soybean biodiesel is easily available due to its increased production worldwide (Aguieiras et al. 2020; Cavalcanti et al. 2018), its utilization for biolubricant production can become an extension of biofuel supply and sales.

Pea and broad beans: Pea peels have been used to produce biofuel from cellulose (Verma and Kumar 2011; Babbar et al. 2014). Pea pods were separated from kernels, cut into small pieces, and homogenized. The homogenized mass was dried at 60–120 °C for 1–4 h to 0.1 g moisture/g dry solid (Nimbalkar et al. 2018). It is demonstrated that drying enables long-term storage, eases the action of pretreatment processes, and more sugar is released from biomass than the wet substrate. Drying might give an effective structural distribution that facilitates good substrate accessibility during acidic hydrolysis and hence higher sugar release. Further, 100 °C was found optimum for drying because it required less time without accompanying any thermal degradation (Nimbalkar et al. 2018; Kassab et al. 2020).

In addition to pea, broad bean pods were also dried and ground to extract cellulosic mass and used for biofuel production (Kassab et al. 2020).

Pigeon pea: Pigeon pea stalks are among the abundant agricultural waste in certain regions of India. These were dried at 45–80 °C for 2 h to reduce moisture to level enough for effective saccharification. Dried stalks were then pulverized to fine particles (0.2–1 mm) (Kirti et al. 2019). The woody biomass from pigeon pea can also be reduced with a mill and dried until the moisture content reaches $<10\%$ followed by screening to a particle size of 1.3 mm (Tanquilut et al. 2020).

1.5.2 Pretreatment Processes

Successful conversion of cellulose to simple sugars and then to biofuel from lignocellulosic material requires the removal of the lignin component that hinders cellulose breakdown (Table 1.2). Therefore, before proceeding with biofuel production, pretreatment of the substrate is done to enhance delignification and as a result, biofuel productivity. Pretreatment processes can encompass biological, physical/mechanical, chemical, and physicochemical treatments or a combination of these. With the help of thermochemical, chemical, and biological approaches the lignocellulose can be converted to gaseous, liquid, and solid fuels (Wang et al. 2020). Depending on the method, pretreatment can utilize microbes, alkali, acid, pre-digestion, steam, pyrolysis, hot water, etc. Generally, all these methods act by reducing crystallinity and degree of polymerization while, increasing the surface area of biomass for the downstream enzymatic action leading to biofuel production. However, harsh pretreatment conditions may leave partially degraded hemicellulose and lignin in the substrate, which may affect biofuel productivity. Secondly, this degradation can also generate inhibitors of fermentation (furfurals, phenolics, etc.) and reduce the rate of fermentation and hence yield. This may further require specific pretreatment aids to get rid of toxic compounds. Overall, pretreatment can be the most expensive step, accounting for 33% of the total cost of biofuel production (Mtui 2009). Each method has its own benefits and disadvantages, and requires optimizations for maximizing yield, minimizing energy input, being economically efficient, and may change according to the nature of raw material. Combining different pretreatment methods is another strategy to improve the economy and yields of biofuel production. Here, we will discuss those pretreatment methods which have been successfully exhibited for biofuel production from legumes only.

1.5.2.1 Physicomechanical Pretreatment

The main goal during a physical or mechanical pretreatment is to enhance the surface area and decrease the degree of polymerization and crystallinity by reducing the particle size. The most common methods reported for legumes are mechanical comminution (chipping, milling, or grinding) and extrusion (passing the biomass

Table 1.2 A summary of chemical composition of the lignocellulosic material and biofuel productivity from distinct legume wastes based on studies referred in the text

	Faba bean straw (Petersson et al. 2007)	Soybean (Yoo et al. 2011, Aguieiras et al. 2020, Cavalcanti et al. 2018, Abideen Adeyinka et al. 2020)	Pigeon pea (Kirti et al. 2019; Tanquilut et al. 2020)	Pea pod (Kassab et al. 2020)
Cellulose composition (% of dry weight)				
Untreated	–	35.4	30–50	32.08
Acid treated	–	61.8	–	–
Alkali treated	–	66.7	–	–
No starch	–	36.7	–	–
Glucose yield (g per g of dry material)				
Untreated	–	0.16	–	–
Acid pretreated	–	0.27	0.2	–
Alkali pretreated	–	0.36	1.3	–
Steam pretreated	–	–	1.6	–
Ethanol yield (g per 100 g dry material)				
Untreated	–	–	–	0.15
Wet-oxidized	8.3	–	–	–
Dried	–	–	–	0.2
Methane yield (g per 100 g of dry material)				
Untreated	18.9	–	–	–
Wet-oxidized	18.4	–	–	–
Biolubricant yield (% of dry weight)				
Biodiesel	–	83	44–52	–
Biodiesel composition (%)				
Free fatty acids	–	13.8	–	–
Saturated fatty acids	–	55.8	–	–
Monounsaturated fatty acids	–	28.9	–	–
Polyunsaturated fatty acids	–	15.3	–	–
Neopentyl glycol diester	–	43–47	–	–
Neopentyl glycol monoester	–	5.7	–	–
Methyl ester	–	33.4	–	–
Trimethylolpropane diester	–	40	–	–
Trimethylolpropane triester	–	17.1	–	–

via cross-section die). These methods are eco-friendly and do not generate any harmful toxins, but on the other hand, are quite energy consuming. Milling was attempted for dried pigeon pea stalk (Kirti et al. 2019) and faba bean waste (Petersson et al. 2007; Gomez et al. 2017) to increase the saccharification yield.

1.5.2.2 Chemical Treatment

For biofuel production, high cellulose crystallinity and concentration in the lignocellulosic substrates are prerequisites. These features are often enriched chemically by pretreating the biomass with sulfuric acid, sodium chlorite, peracetic acid, etc. Besides acid or alkali treatment is also effective in hemicellulose removal and delignification (Yoo et al. 2011). Sulfuric acid or sodium hydroxide (both at a concentration of 1% w/w) was added to ground soybean hulls (10% w/w), followed by washing at 85 °C and then drying at 45 °C for 24 h (Yoo et al. 2011). Glucose yield from soybean hulls elevated by 69.6% and 128.7%, when pretreated with dilute acid and alkali, respectively as compared to the untreated biomass (Yoo et al. 2011). Similarly, alkali pretreated faba bean provided a higher glucose yield (60.7 g/kg/h) than water pretreatment (27.6 g/kg/h) (Gomez et al. 2017). For pigeon pea, acid and alkali were mixed to get 1:10 slurry and incubated overnight at 50 °C (Kirti et al. 2019). For cellulose microfibril extraction (CMF) from pea and broad bean pods, the fine powder was washed for 1 h at 60 °C. Then treatment with 4% sodium hydroxide was followed by bleaching with acetate buffer and aqueous sodium chlorite. Finally, the CMFs were hydrolyzed with 64% sulfuric acid for 30 min at 50 °C to get cellulose nanocrystals (Kassab et al. 2020).

For bio-oils extraction, methanol and chloroform are used. The powdered soybean seeds were incubated in 2:1 mixture of methanol and chloroform for 24 h to dissolve the oils (Abideen Adeyinka et al. 2020). The lower phase was separated and incubated again in chloroform followed by potassium chloride. After this, the lower chloroform phase that contained most of the extracted lipids was collected and kept for chloroform evaporation at 80 °C for 24 h. For transesterification, the crude oil obtained from the previous step was dissolved in chloroform–methanol mixture (2:1, v/v), to which methanol and 95–97% sulfuric acid were added as chemical catalysts (Abideen Adeyinka et al. 2020). The mixture was shaken, incubated at 100 °C, and cooled to room temperature. Distilled water enables phase separation, where the upper aqueous layer has methanol, glycerol, and sulphuric acid, while the lower layer contains chloroform and esters. Finally, ester-rich layer was filtered and kept for chloroform removal at room temperature.

1.5.2.3 Physiochemical Pretreatment

Advanced oxidation processes are so far the best physiochemical pretreatment methods reported for biofuel production in legumes. Oxidation is beneficial in terms of enhancing the transesterification and posttreatment of bioenergy effluent.

For oxidation and pretreatment, legume wastes are treated with steam, wet air, high temperature, high pressure, speed, or a combination of these.

1.5.2.4 Steam

This pretreatment was recommended for pigeon pea stalks. The dried solid and water were mixed in a ratio of 1:10 and heated to 121 °C for 30 min. This could yield 1.6 and 0.9 mg/mL of reducing sugar and pentose, respectively (Kirti et al. 2019).

1.5.3 Thermochemical or Pyrolysis

Pyrolysis was used to convert lignocellulose in pigeon pea wood to bio-oil (Tanquilut et al. 2020). The biomass ground to 1.3 mm was processed in a semi-continuous reactor at 466 °C. The heating rate was controlled to 10 °C/min with a continuous nitrogen flow rate of 14 mL/min for 15 min. These conditions provided a 52% yield that was found comparable to the theoretical yield. The resulting bio-oils had low ash (0.2%), high heating value (29 MJ/kg), and high value-added phenolics. Additionally, a scaled-up pyrolysis was performed in a fluidized bed reactor yielding 44% bio-oil productivity with ~100 g of feed/h, 475 °C, and nitrogen flow rate of 1.5 L/min. It was further recommended to process this bio-oil to produce biofuels because high water content in bio-oil lowers its heating value, and, therefore, limits its utility (Tanquilut et al. 2020).

1.5.4 Extrusion

Extrusion is a method where thermo-mechanical action of the screw induces high pressure, temperature, and speed that eventually breaks cell wall structures and frees the cellulose microfibrils in substrates. This pretreatment method is also adapted at industrial scales and offers both high product stability and throughput. This method is well-suited for continuous operation as it allows simultaneous mixing and has less residence period and generates less effluent waste without extra energy input (in terms of temperature, washing, or conditioning). However, the compression ratio, temperature, and screw speed should be carefully controlled to achieve good pretreatment efficiency (Karunanithy and Muthukumarappan 2011). In addition, extrusion can be integrated with alkali or acid pretreatments to further increase sugar recovery. Alkali treatment is preferred as it is more efficient in degrading ester and glycoside chain of lignin and hemicellulose than acids and the latter can also be corrosive in action. For acid treatment, different alloys can be used for the barrel and extruder screw fabrication to prevent corrosion.

A continuously stirred thermochemical reactor environment was employed for the extrusion of soybean waste (Yoo et al. 2011). In this design, a twin-screw extruder with a six-head configuration, screw diameter of 18 mm, L/D ratio of 30: 1, and 2.4 mm circular die opening was used. Before extrusion, soybean hulls were mixed with 0–20% corn starch to ease the flow of hulls, hydrated, and kept for 24 h at room temperature. Without starch as a processing aid, the substrate can burn and even block the die during extrusion. These problems can also be avoided by adjusting the in-barrel moisture upto 40%. Low in-barrel moisture can also make the hulls difficult to extrude. The extruder screw regularly removes softened portions of the substrate, exposing the interior to chemical and/or thermal action and hence improves the overall rate of cellulose conversion (Lamsal et al. 2010). To achieve 95% cellulose to glucose conversion, barrel temperature is set to 80 °C, with extruder screw speed of 350 rpm, providing a feed rate of 0.48–2.0 kg/h under controlled moisture and starch levels (Yoo et al. 2011). Extrusion increased cellulose crystallinity in soybean hulls by 82% without any significant effect on lignocellulose composition. Extruded soybean hull pellets can be dried at 45 °C for 24 h to reduce the moisture content to 9–10%, which can then be stored at room temperature prior to enzymatic hydrolysis.

1.5.5 Wet oxidation

Wet oxidation for biofuel generation subjects the biomass to high temperature (170–200 °C) and high pressure (500–2000 kPa) for 10–15 min (Petersson et al. 2007). Here, water acts as an acid to hydrolyze the biomass at >170 °C oxidizing lignin and generating pentose monomers from hemicellulose, while cellulose is least affected. Temperature, incubation time, and oxygen pressure are the major factors governing the competence of wet air oxidation. However, energy and capital cost are some disadvantages of the method. Chemical agents, such as sodium carbonate and alkaline peroxide, can be supplemented to decrease reaction temperature, improve hemicellulose degradation, and decrease inhibitor production.

Faba bean straw (including pods) is suspended in water and heated at 195 °C under 12 bar oxygen pressure and 2 g/L of sodium carbonate for 15 min (Petersson et al. 2007). Solid and liquid fractions were separated or processed together for bioethanol production. Pretreated materials can also be stored at -20 °C until further use. The solid fraction or filter cake can be dried at 20 °C and 65% relative humidity. For biogas production, pretreatment conditions, including microbial acclimatization were further optimized to increase sugar recovery, lower the inhibitor formation, and, hence, enhance productivity (Petersson et al. 2007).

1.6 Saccharification and Fermentation

Saccharification is the next step where reducing sugars are liberated from the pretreated cellulosic biomass and become available for fermentation. Saccharification ability is enumerated based on the ability of biomass hydrolysis to fermentable sugars. This ability of biomass is inversely related to lignin, hemicellulose, and pectin content but directly to total and crystalline cellulose. This value can also be used to determine the effect of various parameters such as agricultural practices on biomass quality. Saccharification is done with the aid of enzymes and can be performed stand-alone referred to as, separate hydrolysis and fermentation (SHF) or can be combined as simultaneous saccharification and fermentation (SSF) to balance the production economy.

1.6.1 Simultaneous Saccharification and Fermentation (SSF)

After wet oxidation, faba bean filter cake was mixed with filtrate or water (pH 4.8) at 50 °C with cellulase for 24 h (Petersson et al. 2007). Commercial yeast and urea (24%) were added after cooling the mixture to room temperature. The headspace was flushed with nitrogen gas, sealed with a yeast lock filled with glycerol, and incubated at 32 °C. The quantity of ethanol generated is determined as weight loss caused by carbon dioxide discharge.

For biogas, inoculum (69% of the volatile solid content) can be taken from another plant where manure is utilized as raw material for biogas generation. Bioreactors producing a high concentration of methane from bean shells and peas with sediments were designed. Finally, the vessels were flushed with nitrogen, a seal with a rubber septum, and incubated at 42 °C with continuous stirring (Petersson et al. 2007). The methane content in the flasks is measured regularly for 67 days and gas is collected.

1.6.2 Separate Hydrolysis and Fermentation (SHF)

Saccharification of dried pea pods was done with sulfuric acid (1.3% v/v). Then the biomass was hydrolyzed at 121 °C for 15 min and filtered (Nimbalkar et al. 2018). Some sugar degradation products such as furfurals, weak acids, or phenolics are generated after saccharification that can negatively affect fermentation and subsequently, reduce the solvent yield and productivity. Activated charcoal is used to remove these inhibitors in a process known as detoxification. For pea pods, detoxification was done by adding activated charcoal (5% w/v) to hydrolysates with a continuous stirring for 2 h at 60 °C and pH 10. Finally, filtration was done to get rid of activated charcoal. This step can remove 95% of phenolics and up to 30% acetic acid with only 10% sugar loss.

For fermentation, the inoculum of *Clostridium acetobutylicum* was prepared and incubated for 18–20 h at 37 °C (Nimbalkar et al. 2018). The detoxified slurry from pea pod waste was inoculated with inoculum (5% v/v) together in a production medium and kept at 37 °C for 96 h for fermentation. Nutritional components of this medium were carefully controlled to suit maximum product formation in this type of batch fermentation (Nimbalkar et al. 2018). Similarly, the saccharified biomass from pigeon pea stalk was inoculated with *Saccharomyces cerevisiae* for solid-state fermentation (Kirti et al. 2019).

1.6.3 Enzymatic Aids for Biofuel Production

Commercial enzymes have been utilized as biocatalysts in the conversion of cellulose or fatty acids in biomass for biofuel production. Cellulase, beta-glucosidase, and Viscozyme (cell wall degrading enzyme complex) were used for enzymatic saccharification of the pretreated soybean hull (Yoo et al. 2011). Cellulase breaks cellulose into glucose, cellobiose, and higher glucose polymers. The beta-glucosidase hydrolyzes cellobiose and impede the initial stage of cellulose hydrolysis. While viscozyme is a cocktail of carbohydrases, arabinase, cellulase, b-glucanase, hemicellulase, and xylanase that breaks branched pectin-like substances of cell walls. All enzyme solutions are prepared in 0.05 M sodium acetate buffer (pH 5) and incubated at 50 °C before adding the pretreated biomass (Petersson et al. 2007). Similar treatment with cellulase was suggested for steam pretreated pigeon pea stalks (Kirti et al. 2019). The ground faba bean subjected to water, acid, or alkali saccharification was also hydrolyzed using an enzyme cocktail (Petersson et al. 2007; Gomez et al. 2017).

1.6.4 Enzymatic Aids for Biolubricant Production

Using enzymes over chemical catalysts in a biolubricant synthesis from biodiesel is also preferred. Enzymatic treatment avoids high energy demands, side product formation due to thermal degradation, nonspecific reactions, and the need for purification compared to when chemical catalysts are utilized that in turn reduces the cost of biomass conversion. One such biocatalyst, lipase enabled >95% conversion rate in 24 h from soybean biodiesel or oil by transesterification and esterification, respectively (Aguieiras et al. 2020; Cavalcanti et al. 2018). Lipase hydrolyses triacylglycerol in long-chain fatty acid to produce free fatty acid (FFA), diacylglycerol, monoacylglyercol, and glycerol. To obtain target polyol esters, FAME (fatty acid methyl esters) transesterification (Aguieiras et al. 2020) or FFA esterification were (Cavalcanti et al. 2018) performed. In these conversions, enzyme properties (viz., activity, stability, selectivity, specificity, recovery, reuse, inhibitor resistance, etc.) can influence the final constitution of the product by controlling the position of polyol modification and recognition. Therefore, enzyme kinetics and immobilization are major players in conversion reactions. Commercially available immobilized lipases Lipozyme, Novozyme, and Lipomod from *Rhizopus* and *Candida* species provide good conversion efficiency in case of soybean.

Soybean oil (50% v/v) and lipase (1–4% w/v) were incubated in 100 mM sodium phosphate buffer (pH 7.0, 50% v/v) at 40 °C for 4–24 h for hydrolysis. The hydrolyzed oil or FFA was extracted with hexane, which was later removed with a rotary evaporator (Cavalcanti et al. 2018). Similarly, NPG synthesis from soybean diesel was done in a reactor under controlled temperature with regular stirring (Aguieiras et al. 2020). Methanol is the by-product of transesterification reaction that can compete with NPG as a nucleophile and inactivate the lipase and therefore needs continuous removal. Different batch reactors with small and large outlets were tried to get better methanol evaporation with the latter showing high (100%) conversion (Aguieiras et al. 2020). For esterification and transesterification, oil/biodiesel and water (3.75:1) can further aid the NPG solubility (Aguieiras et al. 2020; Cavalcanti et al. 2018). Besides NPG diesters, trimethylolpropane (TMP) esters were obtained with this methodology (Cavalcanti et al. 2018).

The enzyme reutilization can compensate for using expensive enzymatic aids. Therefore, reusing the biocatalysts can be an economical idea here. After completion of one reaction cycle, immobilized lipase was washed with hexane or ether, vacuum filtered, and dried in a desiccator for 24 h and reused (Aguieiras et al. 2020; Cavalcanti et al. 2018). Observing six consecutive 24-h reactions exhibited 56–100% of the first reaction conversion rate after 6 reaction cycles. This operational stability of lipase was highly dependent on the solvent used for washing and whether methanol is produced as a by-product during transesterification.

1.6.5 The Chemical Aids for Bio Lubricant Production

As explained in the pretreatment section, crude oil is generated from soybean. Instead of enzymes, the oil was incubated with methanol and sulfuric acid as catalysts for transesterification (Abideen Adeyinka et al. 2020).

1.6.6 Recovery or Yield Calculator

Pretreatment frees the cellulose for saccharification. Saccharification liberates more reducing sugars after enzymatic hydrolysis of cellulose. Upon fermentation, these sugars then yield biofuel. Ultimately, the effectiveness of pretreatment and saccharification is evaluated in terms of reducing sugars released that in turn will determine the biofuel yield.

To evaluate the efficiency of pretreatment, sugar recovery in filtrate or solid was calculated. This is equal to the percentage of the ratio of sugar in the filtrate to that in raw material (Petersson et al. 2007).

$$\text{Recovery}_{\text{filtrate/solid}} = \left[\text{Sugar}_{\text{filtrate/solid}}(\text{g}/100\text{g})/\text{Sugar}_{\text{raw material}}(\text{g}/100\text{g})\right]100\%$$

Cellulose yield after enzymatic hydrolysis is calculated as a percentage of the ratio of the mass of glucose after hydrolysis to that in the biomass before hydrolysis with 0.9 as the conversion factor. Similarly, for hemicellulose hydrolysis, the mass of xylose and arabinose to that of hemicellulose in the raw material is considered (Petersson et al. 2007).

$$\begin{aligned}&\text{Hydrolysis yield}_{\text{cellulase}}\\&\quad = \left(\text{Mass of Glucose}_{\text{after hydrolysis}} \times 0.9/\text{Mass of glucose}_{\text{raw material}}\right)100\%\end{aligned}$$

$$\text{Hydrolysis yield}_{\text{hemicellulase}} = \begin{aligned}&\left(\text{Mass of xylose} + \text{arabinose}_{\text{after hydrolysis}}\right.\\&\left.\times 0.88/\text{Mass of hemicellulose}_{\text{raw material}}\right)100\%\end{aligned}$$

Ethanol yield is reported as g ethanol produced per 100 g of raw material or as volume per g of volatile solids. Biogas yield is given in g methane produced per 100 g of dry material or volume of methane per unit weight of volatile solid. The quantity of biogas resulting from inoculum only is subtracted from the total biogas formed before yield is calculated. Theoretically, it is assumed that all glucose of raw material will be converted into ethanol—0.51 g ethanol per g $C_6H_{12}O_6$. While for methane, the entire volatile solid in the raw material having the empirical formula (CH_2O) will be converted into CH_4 and CO_2 (Petersson et al. 2007).

Reducing sugar and glucose yield (Y_{RS}) can also be calculated as g per g of the extruded biomass as in the case of soybean hulls (Yoo et al. 2011). The degree of conversion to reducing sugars (C_{RS}%) is based on total cellulose and hemicellulose content in 1 g of pellet (g/g) in soybean hulls (Yoo et al. 2011). While the degree of conversion from cellulose to glucose (C_{CG}%) is the ratio of glucose obtained (Y_G) to theoretical yield based on cellulose content in 1 g of pellet (g/g) in soybean hulls. Here, 1.1 is the conversion factor for polymer to monomer sugar. Also, reducing sugar and glucose yields are corrected for starch contribution, assuming 100% conversion.

$$C_{\text{RS}}\% = [Y_{\text{RS}} \times 100]/[(C + H) \times 1.1]$$

$$C_{\text{CG}}\% = (Y_G \times 100)/(C \times 1.1)$$

Slurries from the dried batch of pea pod yielded 5.94 g/L of solvent from 50% of the utilized sugar (Nimbalkar et al. 2018) and 7–8% ethanol from pigeon pea (Kirti et al. 2019). These studies also claimed that this yield can be further enhanced.

For biolubricants, NPG ester synthesis is measured in terms of substrate (FAME) consumption by gas chromatography and discounting the side product (FFA) formation by the product acidity. If initial and final FAME content and acidity are Ei and Ef, and Ai and Af, respectively, then the percentage of hydroxyl groups in NPG that were converted to esters is the conversion percentage. Furthermore, the FAME/NPG molar ratio (MR) and the number of hydroxyl groups in the polyol molecule (H) were 3.75 and 2, respectively (Aguieiras et al. 2020; Cavalcanti et al. 2018).

$$\text{Conversion}(\%\text{hydroxyl groups}) = [100 \times (\text{Ei} - (\text{Ef} + (\text{Af} - \text{Ai}))) \times MR]/(H \times \text{Ei})$$

As quoted earlier, lipase allowed nearly 100% conversion of oil and biodiesel. The resulting NPG esters from soybean biodiesel showed a viscosity index of >198, more than the required value for a lubricant (150). High viscosity index for lubricant is desirable as its viscosity is less likely to change with temperature. This property of oil ensures that there will be good lubrication in colder climates or during power failure. At last, the NPG derived from soybean had a pour point from −3 to −9 °C and oxidative stability of >25 min that can be further improved by using chemical additives/fluids, distillation, etc. (Aguieiras et al. 2020).

1.7 Conclusion

Urbanization, industrialization, and unprecedented population growth are considered to be vital source for the economic development of the country. The crisis of limited fossil fuels is actually a major issue in the context to ever-growing energy demand. To mitigate climate change, as well as to reduce the dependence on natural reserves and to decrease carbon emissions, biofuel from renewable sources are considered to be the best alternative. Biofuel represents a significant potential for sustainability and economic growth of the developing as well as a developed country. Agriculture practices result in a vast amount of waste residues, especially in a country like India which has one of the largest arable lands in the world. For an annual legume production ranging from 1.61 to 11.23 million tons for lentils, pigeon pea, groundnut, soybean, and grams, an equivalent amount of waste is expected. One way to manage this waste is through their utilization for biofuel production. Moreover, with the rapid depletion of nonrenewable fossil fuels, alternate sources are required to meet the ever-increasing energy demands. Several studies have shown the use of legume waste and optimized reaction conditions for biomass conversion to biolubricant, bioethanol, and biogas. These investigations report that pretreatment is crucial for an efficient fermentation or conversion reaction. Prior treatment of the raw material with chemical, physical forces, extrusion, steam, wet oxidation, or a combination of these can enrich the cellulose content and/or ease the downstream processes and consequently ensure maximum productivity of biofuel from the biomass. All these processes have also displayed the possibility of scaling up the extraction protocols to a commercial scale and clearly indicate that the legume waste is a good candidate for biofuel production.

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Chapter 2
Utilization of Wheat and Maize Waste as Biofuel Source

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Abstract Greater use of fossil fuels, especially in metro areas, has led to the production of amplified levels of pollution during the recent decades. Renewable biomass fuels such as bioethanol, biogas, biodiesel, and biohydrogen may replace the use of petroleum-derived fuels. Straw is one of the several agricultural residues of major crop plant production including cereals. It majorly contains dried stalks, leaves, and corn cobs, which are left behind after harvesting. Agricultural waste like straw or stover is a prospective lignocellulose-based feedstock with an advantageous greenhouse gas balance for biofuel, and hence bioenergy production. Wheat straw and Maize stover are such plentiful agricultural residues with low commercial value. Being lignocellulosic in nature, straw is recalcitrant, and thus requires the physical, chemical, or biological pretreatment to provide better accessibility to three major biopolymer compounds of straw, viz., the polysaccharides cellulose, hemicellulose and lignin. Both wheat straw and corn stover have the potential to be efficiently explored for producing ethanol, biogas, and biohydrogen commercially. Decent research efforts have been put in for the production of biobutanol, biodiesel, and biochemicals using this feedstock, but to exploit them on a commercial scale, greater research insights and technologies are needed. The prime obstacle for generating industrial biofuel production using lignocellulosic raw material is the greater operational cost required for biomass feedstock pretreatment. The development of genetically engineered microbial strains, improved production as well as extraction techniques along with the generation of valuable by-products are some promising means of establishing cereal straw as feedstock for efficient and economic biofuel and chemical production.

Keywords Lignocellulosic feedstock · Biofuels · Pretreatment · Wheat straw · Corn stover · Bioethanol · Fermentation

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2.1 Introduction

In today's environment, energy is an incredibly valuable resource. Energy can be generated in a variety of ways. The burning of fuel is one method of generating energy. When people think of fuel, they usually think of automobiles, furnaces, and fireplaces. Fuel is burnt during a chemical process known as combustion which produces energy that can be used to power a variety of technologies. Fossil fuels are the most common fuel forms used by humans to power vehicles, furnaces, and a lot more. Fossil fuels are derived from deposits of biological matter that have been compressed for millions of years, and hence termed fossils. Some examples of these fuels are coal, natural gas, and oil that can be refined into petroleum and diesel. These fossil fuels can be found in huge quantities all around the earth along with a drawback that they are not 100% sustainable. Yeah, we might wait a few millennia for more fossil fuels to be created, but that is not feasible.

As the population grows rapidly along with developing society and the rise of industrial prosperity in developing countries, the energy demand over the globe is also growing continuously. The population of the world is expected to reach 9.7 billion in 2050. Along with this population burst, world's energy consumption and dependency is also anticipated to go up. This demand is still met using mostly conventional fossil fuels such as coal, natural gas, and oil. The levels of greenhouse gases are greatly elevated in the atmosphere of our planet by excessive utilization of fossil fuels over recent decades (Ballesteros et al. 2006).

Globally, oil is a prominent energy source for both the transport as well as for the production of materials. As per estimates, each day 84 million barrels of oil is consumed and it is expected to reach up to 116 million barrels by 2030. Of this quantity, the significantly expanded sector in the USA and Europe, i.e., the transport sector, alone accounts for about 60% (International Energy Agency (IEA) 2007). The use of oil in India and China is on a rising trend and increasing at least 3% yearly. Moreover, the generation of numerous chemicals as well as plastic materials is greatly relied on fossil fuels, globally contributing to about 4% of the refined oil (Nossin 2009). In addition to these facts, the unavoidable decline in the energy supply of the world, along with an unsteady oil market, has moved society's focus to renewable energy sources as a viable alternative.

Biofuels are carriers of energy that store biomass-derived energy. A large variety of biomass sources can be exploited for the production of bioenergy in several ways. For instance, food, fiber, and wood process residues (industrial sector); energy crops, crops, and their wastes (agriculture sector and forestry sector). These can all be utilized for the generation of electricity, heat, combined heat, and power along with other bioenergy forms. Biofuels are also known as *renewable* energy due to their transformed solar energy form.

Biofuels, for example, reduced liquid/gaseous compounds coming from renewable organic biomass are viewed as a way to reduce reliance on fossil resources and decrease greenhouse gas (GHG) emissions. All fuels which are petroleum-based can be supplanted by sustainable biomass/biofuels, viz., bioethanol, biodiesel, and biohydrogen.

Wheat along with rice and maize is one of the prominent cereals which dominate the world's agricultural production. Cereal straw/stover, especially of wheat (*Triticum* spp.) and maize (*Zea mays*) may offer a good resource for manufacturing biofuels. This is because it is a by-product of food production, and therefore its generation does not interfere with food production (Townsend et al. 2017). Over the course of this chapter, we are presenting an overview of biofuels especially utilizing wheat and maize waste i.e. straw and stover, respectively. Also, the major bio-products along with their potential applications in different sectors are discussed. Finally, the impact of biofuel production on soil productivity and environment is presented in a descriptive manner with some future prospects.

2.2 Biofuels and History

Biofuel is generated from biomass using contemporary processes, rather than the relatively slow geological phenomena that lead to the development of fossil fuels like oil. Since biomass (for example, wood logs) can potentially be used as a fuel directly, few individuals use the terms biomass and biofuel conversely. However, most of the time, the term biomass simply refers to the biological raw material used to make the fuel, or some thermally or chemically altered solid end product forms, such as briquettes or torrefied pellets.

Biofuel may be referred to fuel that is obtained directly from plants or indirectly from domestic, agricultural, industrial/commercial waste materials. Plants along with microalgae use photosynthesis for carbon fixation, ultimately leading to the production of biofuel. On the other hand, biomass could be transformed using thermal, chemical, or biochemical conversion into biofuels. It will result in the production of solid, liquid, or gaseous fuel. The newly produced biomass thus can also be used directly in the form of biofuel. The term "biofuels" is commonly used to refer to a liquid or gaseous transportation fuels. Though humans are using biofuels since they first burned wood in a fireplace, some of the first biofuels to be used commonly in our modern day were with the world's first automobile designs. Henry Ford, the man who founded the car company Ford Motor Company, planned to power his popular Model-T with a form of biofuel made from peanut oil. Huge reserves of oil were gradually discovered, and Ford converted his car fuel to petroleum due to its intense abundance and therefore low price tag. Gasoline became the new standard for all vehicles and has stayed that way since.

Since the 1970s, when gas prices began to rise sharply, searching for alternative sources of fuel for automobiles has become a common area of research. The use of biofuels is being rediscovered for potential use in not just automobile engines, but as a general power source. Though 100% biofuels cars are still uncommon to find, it is common to have everyday diesel fuel including a small percent of ethanol which is a type of biofuel. At the moment, normal fuel will contain up to 10% ethanol.

2.3 Types of Biofuels

Biofuels can basically be categorized as (Alavijeh et al. 2019) primary and secondary or (Arai et al. 2006) liquid and Gaseous biofuels

1. (a) *Primary biofuels* (raw) are those in which the organic material is utilized mostly in its natural state such as firewood, wood chips, and pellets. These fuels are directly combusted. It generally includes supplying cooking fuel, heating, or electricity generation required for industrial utilizations. (b) *Secondary biofuels* (processed) are utilized for a broader spectrum of applications. It includes transportation and industrial processes (at high temp.). These can be utilized as solids (charcoal), liquids (ethanol, biodiesel, and butanol), or gases (biogas and biohydrogen).
2. **(a) Liquid biofuels:**

   Ethanol: Biologically, ethanol is produced by the combined action of enzymes and microbes by the process of fermentation of starches (easiest) or sugars or cellulose (complex). Biobutanol (biogasoline) is generally regarded as a direct substitute for gasoline. This is because it might be used straightway in a gasoline engine.

   Bioethanol is widely used in the United States, Europe, and Brazil. It is an alcohol produced through fermentation, mainly from carbohydrates manufactured in sugars or starch obtained from wheat, maize, sugar beets, sweet sorghum, sugarcane, and any sugar/starch from which alcoholic beverages like brandy may be manufactured. Nonfood sources derived cellulosic biomass, e.g., grasses and trees, is also being explored as an ethanol production feedstock.

   Plant waste-derived ethanol may be utilized as a gasoline substitute in petrol engines in its pure form (E100). This may be blended with gasoline to any desirable percentage(%). Several existing petrol engines of automobiles can support blends of petroleum/gasoline with ≤15% bioethanol (Tibaquira et al. 2018). Because of low energy density of ethanol than gasoline, it needs more fuel for generating same amount of work. A benefit is evident from its higher octane rating than ethanol-free gasoline. It facilitates a rise in the compression ratio of an engine leading to enhanced thermal efficiency. In the regions with greater altitudes, a mixture of gasoline and ethanol is compulsory to lower atmospheric pollution emissions (Shankar 2017).

   Ethanol is also utilized to power bioethanol fireplaces. It is "flueless" and does not demand a chimney. Hence, they are actually advantageous for newly constructed houses and apartments without a flue. One drawback of such fireplace is that they have slightly less heat output when compared with gas fires or electric heat and precautions must be taken into consideration to keep them away from poisoning from carbon monoxide.

   Biodiesel: Biodiesel is among the most regular biofuel used in European nations which comprises of monoalkyl esters of long chain fatty acids obtained from biomass-based oils, viz., vegetable oils or animal fat. It can be obtained from a transesterification reaction between fatty acid and alcohol, mainly methanol, to generate a fatty acid alkyl ester. Biodiesel is also called “neat” biodiesel, when present in its pure form, i.e., B100; therefore, used as a vehicle fuel which presently minimizes emissions $\leq$60% compared to diesel. However, it is most commonly utilized as a diesel additive to minimize the hydrocarbon levels, carbon monoxide and other particulates generated through diesel-powered vehicles. Chemically, biodiesel primarily comprises fatty acid methyl (or ethyl) esters (FAMEs). Feedstock for biodiesel contains vegetable oils, animal fats, jatropha, rapeseed, mahua, mustard, sunflower, palm oil, algae, hemp, *Pongamia pinnata,* and field pennycress. When combined with mineral diesel, it can be used in any diesel engine, although some maintenance and performance issues can arise during winter usage, because lower temperatures make fuel slightly more viscous. It generally depends on the type of feedstock used for its production.

During the late 1990s, just biodiesel mixed with traditional diesel fuel could be used for electronically operated “common rail” and “Unit Injector” style systems. These engines are well equipped with metered and atomized multistage injection systems, extremely sensitive to the fuel’s viscosity. Today’s several diesel engines of the present generation are designed to operate on B100 without requiring any modifications to the engine, but this is dependent on the fuel rail configuration. Biodiesel act as an effective solvent as it dissolves old deposits present in pipes and fuel tank. Hence, it cleans residues which are accumulated by mineral diesel therefore the engine filters might need to be changed with greater frequency. It also removes carbon deposits from the combustion chamber of the engine, allowing it to run more efficiently. A 5% biodiesel blend is commonly used in many European countries which can be found at a number of gas stations. Being an oxygenated fuel (comprising less C and more H_2 and O_2 than conventional diesel), it increases biodiesel combustion and lowers particulate emissions from unburned carbon. Nevertheless, pure biodiesel, on the other hand, can increase NO_2 emissions.

Moreover, biodiesel is biodegradable, nontoxic substance having high flash point of ~148 °C (300 °F) compared to petroleum diesel fuel, having a flash point of 52 °C (125 °F) making it more safer for handling and transportation.

2. **(b) Gaseous biofuels**

Biogas and Biomethane: Basically, biogas is methane released by anaerobes during anaerobic digestion of organic matter. It can be generated either by using energy crops or from biodegradable waste materials fed into anaerobic digesters to increment yield of gas. Digestate, solid co-product obtained during biogas formation, can be utilized as a fertilizer or as a biofuel. Carbon dioxide and other impurities when removed from biogas are referred to as biomethane. Biogas could be retrieved using mechanical biological treatment waste processing systems. Also, by feeding cattle manure into anaerobic digesters, farmers can generate biogas effectively.

Syngas: It is a combination of CO, H_2, and other hydrocarbons formed by incomplete combustion of biomass, i.e., to fully transform the biomass into CO_2 and water, combustion of biomass with an inadequate amount of oxygen is done. Biomass is dried and often pyrolyzed prior to partial combustion. The resulting combination of gas is called Syngas, which is more effective than the direct combustion of the original biofuel. This is because it brings out greater energy present in fuel. It can be burned directly in internal combustion engines (ICE), greater temperature fuel cells, or turbines. A gasification reactor which is wood-fuelled called wood gas generator could be attached to ICE producing hydrogen and methanol. Otherwise, it may be transferred via Fischer–Tropsch process to generate a diesel replacement or a combination of alcohols (to be blended into gasoline).

Other forms of bioalcohols: Methanol is presently generated from natural gas, a nonrenewable type of fossil fuel. In times to come, it is believed to be generated from biomass as **biomethanol**. It seems to be technically practical yet current production is being delayed for the economic viability concerns which are still pending. Such an economy using methanol is a possible substitute for the hydrogen-based economy.

Biobutanol: Butanol (C_4H_9OH) obtained through fermentation from a biomass feedstock is known as biobutanol. The isomer of butanol which is produced is influenced by the production process. As a biofuel currently two main isomers n-butanol and isobutanol are mainly used. One more isomer named t-butanol cannot be used as a fuel considering it degrades much more slowly in the atmosphere. Biobutanol has the properties of both a fuel and an oxygenate, used for blends with gasoline in spark-ignition engines. Biobutanol is volatile; evaporated butanol can form butyraldehydes in the atmosphere upon reacting. Because both n-butanol and isobutanol have soil mobility, they can pollute groundwater and evaporate from soil and water surfaces. The half-life of these isomers of biobutanol are estimated to be of several days, and hence are readily biodegradable. Like ethanol, rapid biodegradation of biobutanol at spill sites contaminated with petroleum hydrocarbons could potentially exhaust aqueous oxygen which results in methane production and prolonged contamination of petroleum aromatic compounds. Some advantages of butanol over ethanol are butanol can generate more energy owing to its low oxygen content, can be burned "straight" in the currently available gasoline engine (without any engine transformation). It is also not much corrosive as well less water soluble compared to ethanol making it safer for distribution through existing infrastructures.

Green diesel: It is generated through hydrocracking biological oil feedstocks, viz., vegetable oils as well as animal fats. Hydrocracking can be defined as a refinery process which utilizes high temperatures and pressure to break down large molecules present in vegetable oils, into short hydrocarbon(HC) chains utilized in diesel engines in the presence of a catalyst. Renewable diesel, hydrotreated vegetable oil (HVO fuel), or hydrogen-derived renewable diesel are all terms that have been used to describe it. Green diesel, unlike biodiesel, has identical chemical properties to conventional diesel. It does not need any new engines, pipelines, or facilities to export and use. However, it has not been generated at a price comparable with petroleum. It is being generated in Louisiana (the USA) and Singapore by Conoco Phillips, Neste Oil, Dynamic Fuels, and Honeywell UOP along with Preem in Gothenburg, Sweden (as Evolution Diesel).

Straight vegetable oil (SVO): While straight edible vegetable oil (unmodified) is generally not utilized normally as a fuel source but for this purpose, low-quality oil is utilized. Prior to using as fuel, already used VO is gradually converted to biodiesel or (much less frequently) being washed of water and particulates. Hydrogenation of oils and fats may be used to make diesel replacement. The end product is a straight-chain HC having greater cetane number, lower aromatics, and S-content without any oxygen. Hydrogenated oils could be mixed in any proportion with diesel. They have many advantages over biodiesel which include acceptable lower temperature efficiency, no stability issues for storage, and no microbial susceptibility.

Bioethers (Fuel ethers): These, also known as oxygenated fuels, are low-cost compounds which increase the octane rating of gasoline. Wheat or sugar beets are used to make bioethers. They also improve engine efficiency while lowering engine wear and harmful exhaust emissions significantly. In the UK, petroethers are likely to be replaced with bioethers but their low energy density makes them unlikely to become a fuel in and of themselves. They also help to improve air quality by significantly reducing ground-level ozone emissions.

Biohydrogen: Hydrogen is the most plentiful element present in the whole Universe. It is also very common on earth. It has the simplest atomic structure as it is made up of just one proton and one electron and has high energy content (120–142.9 MJ/k). Pure hydrogen (H_2), which is diatomic, is rarely found in nature because it readily interacts with other elements. Water, biomass, and fossil fuels are the most common chemically bound sources of hydrogen. It must be extracted from one of these compounds before it can be used in a reasonable way and energy is needed in this process. In view of that, renewability and cleanliness of such energy has great significance. Although hydrogen fuel cells do not emit any carbon, the production of hydrogen can result in significant greenhouse gas emissions and other harmful co-products. However, once obtained, hydrogen is a near-zero-emissions/ideal energy carrier which may be a useful alternative to fossil fuels. Hydrogen is now a preferred fuel for space programs; it protects the atmosphere and helps to combat climate change. However, current production utilized commercial methods are not environment friendly as they need a major energy input and entail high costs. The production of biohydrogen provides a better substitute which is environment friendly. As compared to thermochemical and electrolysis processes, it utilizes organic wastes efficiently and requires lesser input of energy (ambient temperature and atmospheric pressure).

Biohydrogen is H_2 that is produced biologically. This technology is gaining popularity because it is a renewable kind of fuel which could be easily extracted from biomass of several types. The gasification of solid biomass as well as digestion of biomass (generally water-rich), both with subsequent purification and transformation of the resulting syngas into hydrogen, are the two routes of conversion for hydrogen from biomass. The direct use of biomass faces stiff competition in both conversion routes.

2.4 Generations of Biofuels

Biofuels are classified into four major generations (Fig. 2.1) on the basis of their biomass sources, advantages, disadvantages, and technical advancement.

(a) **First-Generation Biofuels**

It is effectively documented as conventional biofuels because it is produced from food crops grown around the world. The first-generation biofuels' raw materials are primarily starch, sugar, or vegetable oil-rich crops like corn, cassava, and sugar cane, which are converted into ethanol or biodiesel through transesterification or yeast fermentation. These feedstocks are primarily made up of glucose polysaccharides linked by α-glycosidic linkages, which are easily hydrolyzed into monosaccharides and used by microbes. In addition, these feedstocks contain a significant amount of fatty acids, protein, trace elements, and other ingredients that aid microbial fermentation. The fermentation processes mainly generate ethanol, with small amounts of butanol and propanol. Ethanol is generally opted as a fuel additive in so many countries. The prime objection associated with these first-gen biofuel is that the feedstock majorly put into use is food crops, posing a food versus fuel dilemma. Another issue associated with these biofuels is the loss of biodiversity due to the possibility of monoculture, rivalry for land vs water, and noneconomic manufacturing.

Example: bioalcohol, bidiesel, syngas, biogas

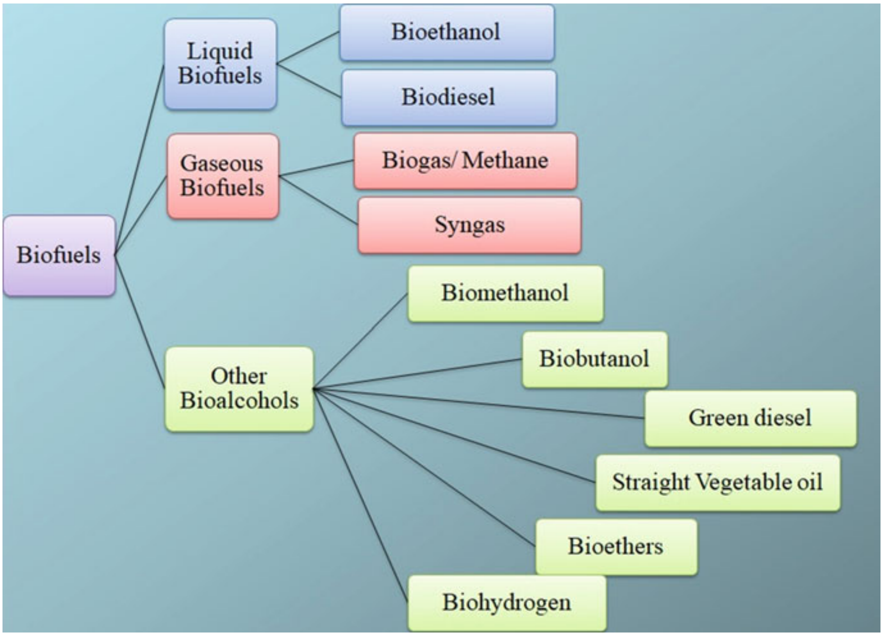

Fig. 2.1 Major types of biofuels based on different molecular states

(b) **Second-Generation Biofuels**

This is majorly produced from nonfood crops, lignocellulosic biomass (LCB) or woody crops, agricultural residues(ARs), or wastes. Chief biochemical constituents of LCB are cellulose, hemicellulose, and lignin with a three-dimensional complex structure. To disorder the lignin-carbohydrate complex structure, biomass must be pretreated (Tarasov et al. 2018). They efficiently utilize the leftovers of food crops grown on arable land or specialized nonfood crops raised on land unsuitable for raising food crops. Hence, the SGBs provide an amazing solution to the food versus fuel controversy. Nonfood feedstock includes grasses, other crops, waste vegetable oil, municipal solid waste, etc., for the production of second-generation biofuels. Ethanol is extracted from fast-growing trees using enzymatic hydrolysis of biomass to remove sugars from the plant's lignin fibers. However, straw and other residues are subjected to thermo-chemical pretreatments like gasification to generate Syngas. The H_2 generated is typically utilized as a fuel, while the other HCs may be exploited as gasoline additives. There are some limitations associated with the generation of SGBs such as high capital costs, difficulty in extracting sugars, and nutrients from the soil and fuel crops.

Example: cellulosic biofuels, biohydrogen, biomethanol.

(c) **Third-Generation Biofuels**

Biofuels in this generation are produced from algae that naturally contained oil content which is more than 50%. In general, wastewater is used for growing algae and biodiesel can be produced through extraction and processing of its oil content. Also, the residue left after oil extraction could further be exploited to generate ethanol. This algae feedstock provides a cheap, high-energy renewable raw material having a high ignition point, is biodegradable, and is relatively safe for the environment if spilled. It also reduces land and water limitations since it eliminated the need for soil or freshwater. Constraints of such biofuel technology include greater capital finance. It is so because its production requires greater energy and fertilizer, fuel generated degrades rapidly than other biofuels. Also, it does not run fine in winter.

Example: Algae fuel

(d) **Fourth-Generation Biofuels**

During the growth period, biomass that has absorbed carbon dioxide is typically used to make this form of fuel. The fourth-generation biofuels (FGBs) production process happened as the CO_2 is caught using practices like oxy-fuel combustion (Moravvej et al. 2019). CO_2 may then be geo-sequestered by storing it in aged oil and gas fields. This generation of biofuels is produced using non-arable land and does not require any biomass to be broken down. This consists of electrofuel sand photobiological solar fuels. Electrofuels are generated by electrical energy which is stored in liquid and gas chemical bonds. The main targets are butanol, biodiesel, and H_2 while methane and butane are also included. Solar fuel is of chemical nature and is synthesized from solar energy. Light is normally transformed into chemical energy by reducing protons to H_2 or CO_2 to organic compounds. For developing FGBs, the technology is still in its

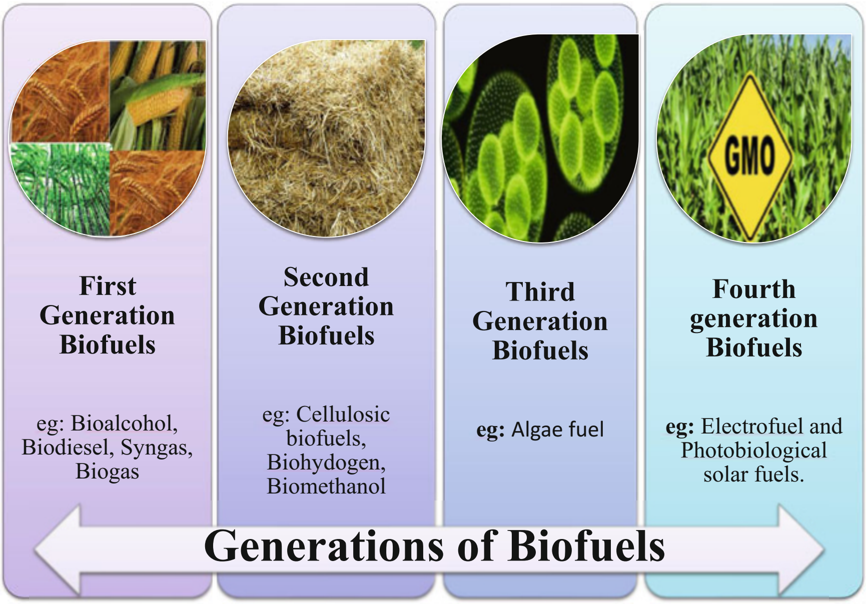

Fig. 2.2 Different generations of biofuels along with corresponding examples

early stages, necessitating a large upfront investment and longer processing times, both of which should be improved in the future to make it a viable biofuel alternative.

Example: electrofuel and photobiological solar fuels (Fig. 2.2).

2.5 Global Scenario of Biofuel Production

Global biofuel production had been on a rising trend until the pandemic struck adversely last year. Global transport biofuel production in 2020 is estimated to be 144 billion liters (International Energy Agency (IEA) 2020) (Fig. 2.3).

The United States is the leader in biodiesel production followed by Brazil (Fig. 2.4a). Ethanol and biodiesel are two chief biofuels which have a great possibility for substituting gasoline and diesel (Fig. 2.3), the key contributors to greenhouse gases and particulate matter, respectively. Some attention is also being received by biohydrogen due to its environmental welcoming by-product, i.e., water.

Presently, approx. 64% of ethanol is generated using maize, 26% from sugarcane, 3% from molasses, 3% from wheat, and the remaining from other grains and sugar beets. On the other hand, 77% of biodiesel is derived from vegetable oils-VOs (37% rapeseed oil, 27% soybean oil, and 9% palm oil) or used cooking oils (23%).

In 2020, an estimated 98 billion liters of bioethanol was produced, with the US contributing 52 billion liters, Brazil 30 billion liters, and China with 4 billion liters (International Energy Agency (IEA) 2020) (Fig. 2.4a). Also, the bioethanol

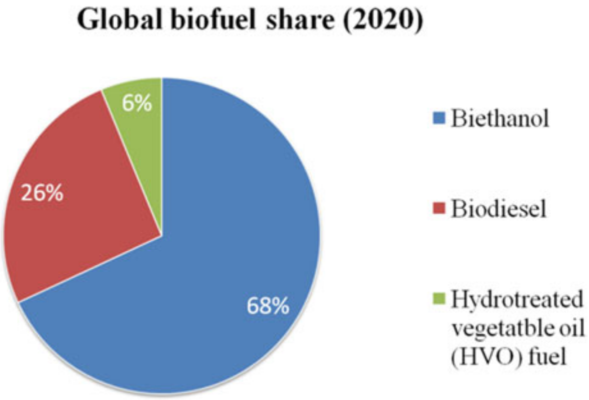

Fig. 2.3 Major Biofuels' production scenario over the globe (IEA 2020)

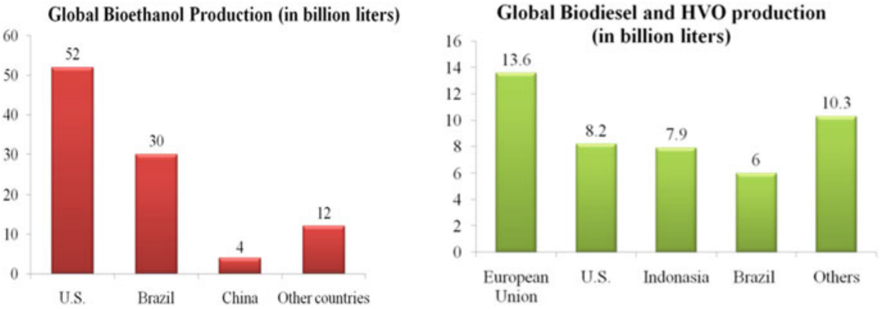

Fig. 2.4 (**a**) Major Bioethanol producing countries (International Energy Agency (IEA) 2020); (**b**) Major Biodiesel and HVO producing countries around the globe (International Energy Agency (IEA) 2020)

production in India has plummeted to 1.8 billion liters alongside global trend. The US mainly depends on maize for bioethanol production. About 37 billion liters of biodiesel is expected to have been produced last year all over the world in addition to 6 billion liters of hydrotreated vegetable oil (HVO)-based fuel (Fig. 2.4b). Globally, major current biofuel production is FG-conversion pathways-based, which involved the use of sugar, starch, or VO constituents of crop plants.

2.6 Biofuel Production from Agricultural Wastes

For providing a sustainable resource in terms of renewable energy for global usage, generation of biofuels from accessible glut of LCB has been the focus of exploration since the late twentieth century (Limayem and Ricke 2012). LC materials are renewable, inexpensive, and plentiful including agricultural residues (wheat straw, corn stover, etc.), solid waste, woody feedstock, etc. As such energy crops are

Table 2.1 Major biofuels produced all over the world along with their respective agricultural feedstock generally used

S. no.	Biofuel	Commercial feedstock
1.	Biodiesel	Lignocellulose, Oilseeds (rape seed, soya oil)
2.	Bioethanol	Lignocellulose (Wheat straw, Maize stover, Rice straw, Sugarcane bagasse)
3.	Furfural	Lignocellulose (straw, stover)
4.	Biomethane	Lignocellulose (straw, stover)
5.	Biohydrogen	Lignocellulose (straw, stover)
6.	Biobutanol	Starchy material (sugarcane, wheat, rice)

mostly grown in low fertility land giving rise to lower production thus making the cost of production much higher. Several factors could be put into consideration while deciding the type of crop (food or energy) to be cultivated on a piece of land (Glithero et al. 2015) (Table 2.1).

Energy crops generally include crops rich in starch and sugar such as maize and sugarcane as well as oilseed species such as soybean and sunflower. Above-mentioned sugar-starch crops are generally consumed as human food as well as animal feed. Such crops with their unique products may easily be converted into biofuel, such as ethanol by fermentation to be used as fuel. Grass grown as hay and pasture are generally included in this group. These crops are used as feedstock for energy production since they contain more fibers, such as cellulose, hemicellulose, and lignin and less carbohydrates, proteins, and oils. The methods such as direct burning for heat or power, ethanol synthesis (from cellulose fermentation), thermo-chemical procedures, or anaerobic digestion for biogas generation can be efficiently utilized to produce energy from these crops.

Despite the fact that a number of crop species are good candidates for biofuels, maize, and wheat wastes/residues have gained maximum consideration owing to low cost and greater availability (Battaglia et al. 2021). Straws and/or stover of cereals such as wheat and maize/corn are the finest ideal ingredients which can be utilized for biofuel manufacturing as it is the co-product of food crops. Hence, such kind of production of cereals does not lead to face off with food production (Tenenbaum 2008).

Bioconversion of wheat straw to different bio-products, viz., bioethanol, biohydrogen, butanol and biomethanol has substantial practical success. However, a number of limitations including prolonged pretreatment timings, methods, enzymolysis efficiency as well as fermentation are yet remaining to be resolved. A number of studies have been indicated for bioengineering of wheat straw, among the production of bioethanol (Maehara et al. 2013), biohydrogen (Cheng et al. 2011a, b; Kaparaju et al. 2009), and other bio-products (Ribbons 1987) have gained public interest with considerable success in the field.

2.7 Composition of Wheat and Maize Waste

Wheat straw contains three most important polymeric components, viz., cellulose, hemicelluloses, and lignin. The first two, i.e., cellulose and hemicelluloses are hydrolyzed into fermentable sugars (García et al. 2013). Nevertheless, hemicelluloses (heterogeneous polysaccharides like hexoses, pentoses, and sugars), cellulose (β−1, 4-glucan), and lignin together form a complex cross-linked structure. Such kind of recalcitrant arrangement helps to protect the carbohydrates from degradation by different microorganisms or enzymes (Sanderson 2011). Therefore, various pretreatment methods are deployed for wheat straw hydrolysis in order to rupture that recalcitrant arrangement (Feng et al. 2016; Talebnia et al. 2010).

Hemicelluloses in wheat or maize straw cell wall connect with lignin by chemical bonds and with cellulose by hydrogen bonds. Interestingly, hemicellulose is one of the most copious polysaccharides in the environment. That is why it happens to be tricky to part hemicelluloses from the cell wall. Lignin connects two major constituents, viz., hemicellulose and cellulose. It thus provides a physical barrier as an impervious wall in such biomass, i.e., wheat straw (Shirkavand et al. 2016). Although it is degradable in the environment, the presence of lignin in the structure provides quite strong impermeability along with protection from microbial attacks (Table 2.2).

Maize residues or Corn stover are the stalks, leaves, cobs, and husks that are left behind in the field after maize grains are harvested. Stover has the benefit of not being used as a food source as corn itself, and as a co-product of maize production, has lesser production costs. However, the corn stover is not typically "waste" as it is incidental to the corn production system. The relative distribution of stover yield components of whole maize plant dry matter is as follows: 22% stalk, 5.3% sheaths, 7.5% cobs, 10.6% leaves, 4.3% husks, 1.5% shanks, 0.5% lower ears, 0.5% tassels, and 0.2% silks. Corn stover is mainly composed of cellulose (as glucan) (~35% w/w), hemicellulose (as xylan), (~20% w/w), lignin (~12% w/w), ash (~7% w/w), and 26% of others. It is one of the most researched cellulosic feedstocks for bioethanol production due to its abundant supply and important lignocellulosic feedstocks for biofuel generation because of its high carbohydrate content (Saini et al. 2015) (Table 2.3).

Table 2.2 Biochemical composition of wheat straw (Panagiotopoulos et al. 2011a, b; Passoth and Sandgren 2019)

S. no.	Composition	Amount (%)
1.	Cellulose	35–40
2.	Hemicellulose	23–28
3.	Lignin	12–18
4.	Ash	1–3
5.	Protein	6–7

Table 2.3 Biochemical composition of corn stover (Ruan et al. 2019)

S. no.	Composition	Amount (%)
1.	Lignin	12
2.	Cellulose	35
3.	Hemicellulose	20
4.	Ash content	7
5.	Others	26

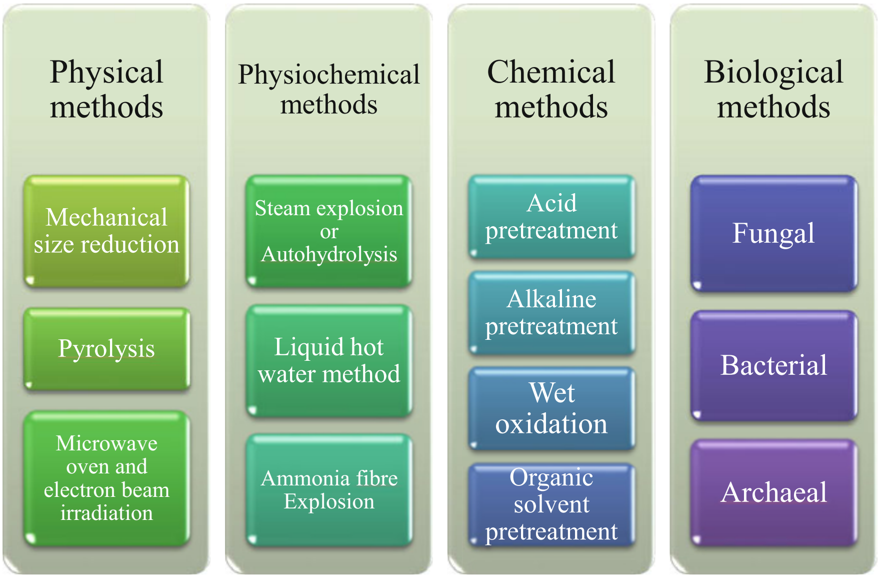

Fig. 2.5 Key techniques for pretreatment of lignocellulosic feedstock for biofuel generation

2.8 Pretreatment Process

The structural barriers such as lignin and hemicellulose lower the conversion of agricultural biomass up to 20% only of the original cellulose to fermentable sugars. Hence, to increase the production by bioconversion process, it is of paramount importance to break down hemicellulose and lignin shielding actions beforehand. In other words, to efficiently utilize the lignocellulosic feedstock like wheat straw and corn stover, pretreatment is required to hydrolyze the hemicelluloses to make the celluloses increase availability to the enzymes.

A number of different pretreatment ways (Fig. 2.5) have been investigated in the past times (Wi et al. 2015; Zabed et al. 2016), among which the ultrasonic (Liyakathali et al. 2016), physical procedures (milling) (Schneider et al. 2016), chemical processes, i.e., acid (Zhang et al. 2016a, b), alkaline, ionic liquid (Sathitsuksanoh et al. 2013), and biological organisms like *Phlebia radiata* (Bule et al. 2016) have shown promising results.

2.8.1 Physical Pretreatment

For producing bioethanol using wheat straw, the foremost step is reduction in size through milling, grinding, or chipping. The size reduction and extent of polymerization in addition to crystallinity of lignocellulosic feedstock reported to be decreased from different physical pretreatments of wheat straw. Hence, to increase the accessible area of biomass, various types of physical pretreatments, viz., ultrasonic, extrusion, and microwave can be explored. However, the major benefit of physically pretreating lignocellulosic biomass is that the co-product of toxic reagents is usually insignificant in this method (Fig. 2.6).

The straw materials become fine after the ball mill grinding is done and specific surface area is improved. The cellulase availability may be enhanced for more efficient hydrolysis. This amorphous structure being quite unstable in nature, takes a while to reform a new crystalline structure, making it a shortcoming of the physical method. Nevertheless, such mechanical grinding technology could help loosen the structure of cellulose in order to make microfiber structure and microfiber crystal area subsists in H-bond fracture. This pretreatment requires greater energy consumption along with higher production cost (Ghaffar and Fan 2013).

Another technique known as microwave processing has been also utilized for pretreating wheat straw materials to ferment them for efficient biofuel production. During the processing, microwave radiation (MR) is used for pretreating wheat straw for a considerable time duration. The orientation of the polarity will be altered with the change in external electric field. So, a mutual frictional effect will be generated due to fast molecular movement. Then, the field energy could be transformed into heat energy in the medium, in order for raising the temperature of the raw material, and hence a chain of physical as well as chemical reactions (viz., heating and puffing) take place (Coimbra et al. 2016a, b). The xylan recovery of up to 73% could be attained. The average microwave energy input was found to be ranging from 120 to 735 J/g dry mass (depending on the treatment severity), for the suspensions of 10% wheat straw dry biomass. Determined by the decline of lignin (acid insoluble) in biomass, the lignin clearance was reported to be largely dependent on the MEI, i.e., Microwave energy input. Cheng et al. (2011a, b) found that the maximum amount of hemicelluloses (>80%) and lignin (90%) can be extracted from the solid wheat straw material without solubilizing high amounts of cellulose or intensive saccharide degradation. Hence, MR could be among the effective pretreatment techniques for biomass like wheat straw.

In another pretreatment method called extrusion processing; cutting, mixing as well as heating of wheat straw materials is required. Such processed active sites are convenient to hydrolyze comparing to non-pretreated matter. It is evident from the report that the reagent with hydrolases dose of 6.92 FPU (which is the lowest) results in a superior lignocellulose hydrolysis yield as compared to theoretical. Hence, the resultant glucose yield and xylose yield were found to be 73.8% and 82.8%, respectively. With 20% substrate loading and 20 FPU/g of biomass substrate, the

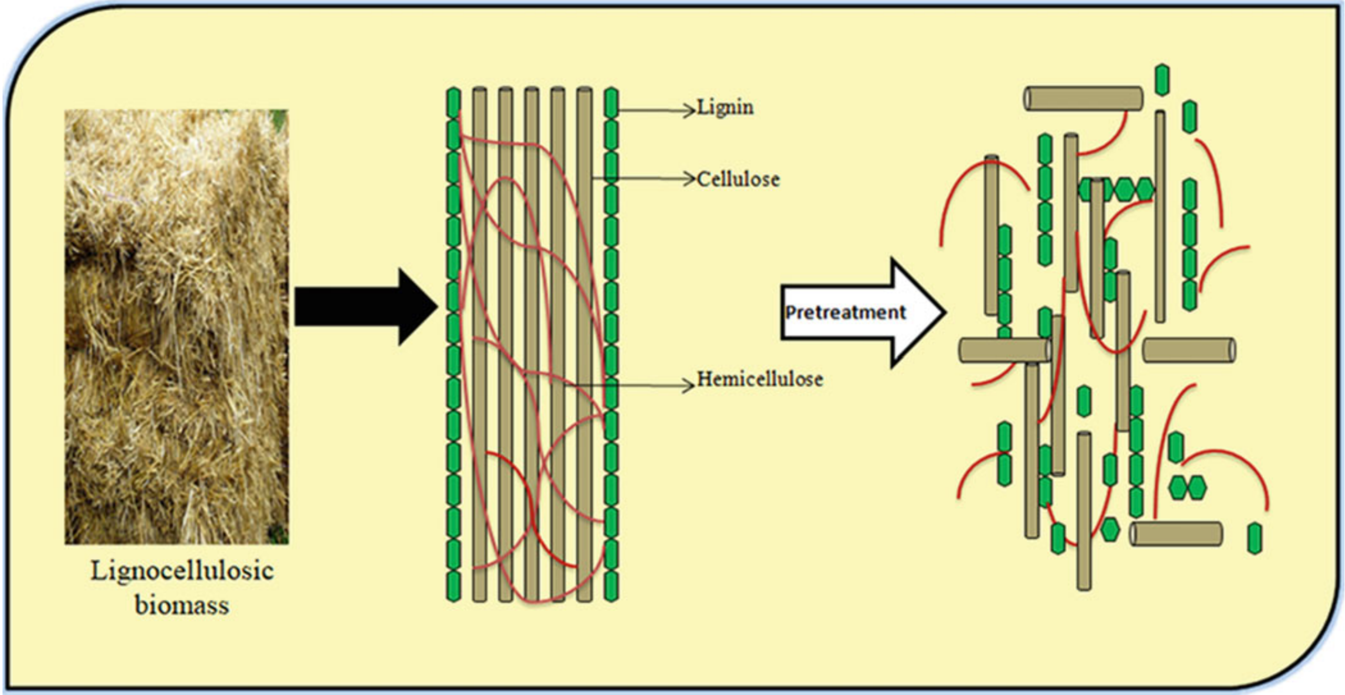

Fig. 2.6 Schematic representation depicting the action of pretreatment on lignocellulosic biomass

end product comprising 100 g/L of fermentable sugars was obtained (Mood et al. 2013).

For lowering the bioethanol production cost, it is of prime importance to overcome the biomass degradation barrier. This makes bioconversion of LCB to bioethanol highly efficient, remunerative, and effective. Such cellulosic barriers can be efficiently broken by CO_2 laser plasma (CLP) catalysis, which could be helpful for reducing the particle size of straw cellulose (Janker-Obermeier et al. 2012; Tian et al. 2015). For the delineating mechanism of CLP catalysis, straw cellulose-surface catalyzed by Carbon dioxide laser was analyzed by Fourier transform infrared spectroscopy (FTIS) and scanning electron microscopy$(SEM). Outcomes indicated that CLP can efficiently increase the bioconversion of straw cellulose to bioethanol (Janker-Obermeier et al. 2012). Compared with ultrasonic pretreatment of straw cellulose, CLP pretreatment may considerably enhance the rate of saccharification, i.e., up to 27.75% (134% of the saccharification rate of ultrasonic pretreatment). These results demonstrated that CLP was notably more effective than ultrasonic method of pretreatment (Tian et al. 2011, 2015).

2.8.2 *Physicochemical Pretreatment*

Auto-hydrolysis or Steam explosion using steam burst is a fine technique to pretreat lignocellulosic biomass thus enhancing its availability to cellulase hydrolysis. In this method of lignocellulosic pretreatment, wheat straw or corn stover biomass is transformed into levulinic acid, xylitol, and alcohol (no catalyst required). Then, it is heated using highly pressurized steam (160–290 °C and 20–50 bar) for a couple of mins to facilitate water molecules to penetrate the structure of the substrate. After that, a stopping reaction takes place with unexpected degradation to atm. pressure facilitating the water molecules to escape explosively. When steam expands inside the lignocellulosic matrix, the matrix's individual fibers get separated. The chemical breakdown of glycosidic bonds (in both cellulose and hemicelluloses), as well as cleavage of hemicellulose-lignin bonds, takes place when lignocellulosic biomass is pretreated with steam explosion (Chen and Liu 2015). The hemicellulose hydrolysis into monomers of glucose and xylose results in the production of acetic acid, which further catalyzes hemicellulose hydrolysis and therefore the mechanism is referred as auto-hydrolysis (Singh et al. 2015). When compared to other pretreatment processes, steam explosion has many benefits, including a low environmental impact, zero recycling cost, minimal chemical usage, maximum sugar recovery, and higher energy efficiency (Pielhop et al. 2016).

In another technique, compressed hot liquid water (LHW) is utilized for hydrolyzing hemicellulose, liberating the majority of oligomeric sugars from hemicellulose over a 20-min period at 170–230 °C and pressures greater than 5 MPa. LHW breaks down hemicellulose by releasing its acetyl groups and removing lignin, exposing cellulose fiber (Zhuang et al. 2016). Since no acid or solvent is used, this approach is both environmentally and economically appealing. Furthermore, since the particles get broken down with procedure, the size of biomass has no impact, making the method more appealing for industrial applications (Bhutto et al. 2017). Imman et al. (2018) showed that corn cobs when pretreated with LHW method at 160 °C for 10 min results in a maximum sugar recovery of 58.8% (derived from hemicellulose) and a 73.1% enzymatic hydrolysis yield with more than 60% lignin elimination.

In Ammonia Fiber Explosion or AFEX method, lignocellulosic feedstock is heated using liquid NH_3 (1:1 ratio) under high temperature (60–100 °C) and pressure for 5–30 min (Shirkavand et al. 2016). After that, the pressure is spontaneously released. Such conditions make lignocellulose swell with a quick release of pressure interrupting the fibrous structure of straw/stover, lowering cellulose crystallinity and hence improving enzyme accessibility. Since there is no need for small particle size in this approach, the inhibitors of downstream processing are not released. The process has drawbacks, such as lower efficiency for biomass with more lignin content and the potential to solubilize just a fraction of solid material such as hemicellulose. This approach has the advantage of being simple and time-saving. This mechanism does not allow for the direct release of sugars; rather it facilitates the enzymatic hydrolysis of polymers for producing sugars. Ammonia loading, high pressure, biomass moisture content, and temperature are the main limiting factors affecting the procedure. As compared to other pretreatment ways, 90% cellulose and hemicellulose transformations could be achieved under ideal conditions and fewer enzymes would be required (Brodeur et al. 2011). Ammonia Fiber Explosion pretreatment is more suitable for agricultural wastes like rice/wheat straw and corn stover, i.e., with low lignin content. Several experiments have been carried out to assess optimal Ammonia Fiber Explosion conditions for various lignocellulosic biomasses. Zhao et al. (2014) found that a 5:1, i.e., ammonia to biomass feeding, 70% moisture content and 170 °C temperature were perfectly optimal for greater enzymatic digestibility of maize stover. The same team also discovered that presoaking the maize feedstock before this kind of pretreatment improves delignification from 15.74 to 24.07%, resulting in an improvement from 82.13 to 87.78% in glucan digestibility. Mathew et al. (2016), when compared the effects of dilute acid pretreatment and AFEX on maize stover observed that hydrolyzate treated with AFEX produced more ethanol than dilute acid treated hydrolyzate.

2.8.3 Chemical Pretreatment

For improving the efficiency of lignocellulosic pretreatment, a number of chemical methods were devised including alkaline, acidic, organic solvents as well as ionic liquid methods, etc., for processing the wheat straw for bioconversion (da Costa Lopes et al. 2013). The chemical reagents help break down the polymerization and crystallinity of the corn stover as well as wheat straw. These techniques are exceptionally effective at destruction. Despite that, the generation of toxic intermediary compounds, higher cost, and carbohydrate polymer loss are some of the major drawbacks of chemical pretreatment.

Among these, acid pretreatment is a primitive process of wheat straw pretreatment. Recently, this method in combination with other techniques shows promise with good suitability for industrial biofuel production. Lignocellulosic feedstock can be pretreated by applying chemicals like HCl and H_2SO_4, which however are highly corrosive and with adverse environmental impacts (Schneider et al. 2014). Some of the most critical factors in this method include acid concentration, temperature, particle size and liquid to solid (LS) ratio. The wheat straw is added to the pretreatment reactor after proper grinding. In several studies, maximum hemicellulose (about 90%) was transformed into xylose at 190 °C along with 1.1% H_2SO_4. After that, the removal of matter from the cooled reactor takes place. Next, to separate fermentation inhibitors, liquid fraction is used alongside additional lime. *Cellulase* enzyme is then used for enzymatic hydrolysis of the pretreated feedstock. Recently, the traditional acid method has been improved by studying dilute acid treatment (DAT). Dilute sulfuric acid spray (DSAS) approach is used to treat corn stalks, with dilute H_2SO_4 (2%) at 95 °C, sprayed on wheat straw for 1 h 30 min, resulting in pentose recovery rate, glucose recovery rate, and lignin removal rate ranging from 90–93%, 90–95%, and 70–75%, respectively. So far, acid treatment is reported to be the best method for pretreatment; however, its biggest concern is the environmental and feed pollution and production of more gas and other by-products, leading to decline in nutritional value (Zhang et al. 2016a, b; Chen et al. 2011).

Wheat straw acidification using H_2SO_4, HCl, formic acid, phosphoric acid, etc., can smash up the physical structure of such materials hence improving digestion as well as utilization. Nevertheless, owing to greater cost, this way of pretreatment is usually not preferred and rarely used all over the world.

The alkaline pretreatment method is efficient in removing yield hemicellulose and lignin. This method facilitates the amplification of exposed surface area for the reaction sites, which is later beneficial during enzyme hydrolysis (García et al. 2013). Alkaline solutions, e.g., sodium hydroxide and sodium carbonate facilitate the interruption in esterification reaction along with rupturing of glycosidic causing structural alteration and biomass degradation, cellulose swelling with limited decrystallization of shielding action (Li et al. 2010). After carrying out the NaOH pretreatment, the impacts of β-glucanase and wheat straw concentration on the degradation products of straw were investigated. Later, the optimal alkali treatment straw concentration was found and major constituents of degradation products were also examined. Wheat straw was hydrolyzed after it got treated with several concentrations of NaOH. Then, using HPLC, glucose and xylose content in acid degradation products was estimated and after that, cellulose and hemicellulose were deduced. After pretreatment of β-glucanase using wheat straw, best degradation conditions were estimated qualitatively using HPLC. The outcomes indicated the optimal wheat straw concentration of 1% and cellulose and hemicellulose content in wheat straw were found to be 44.13% and 21.34%, respectively (Coimbra et al. 2016a, b). Some basic shortcomings of alkaline pretreatment methods involve longer time duration and inescapable salt formation.

Also, organic solutions pretreatment methods could be used to remove biochemical barriers for efficient wheat straw bioconversion. Such methods can directly rupture the bonds between lignin and hemicelluloses (Koo et al. 2011). As a result, the accessibility of cellulase to straw biomass increases significantly, which means there are greater attack sites by barrier function removal. However, the main problems with these techniques include solutions recovery, sometimes huge costs as well as ignitability and volatility. Organic solutions, e.g., acetone, methanol, ethylene, and glycerol are explored for wheat residue pretreatment for bioconversion. It has been reported that glycerol organosolv pretreatment or GOP may help to efficiently increase the hydrolyzability of wheat straw feedstock (Sun et al. 2015), making it a promising means of wheat straw organic solution pretreatment. More recently, different pretreatment methods were explored for enhancing the enzymatic hydrolysis rate using wheat straw including hot water pretreatment, sodium hydroxide, and sulfuric acid pretreatment. A maximum cellulose conversion rate of 87.2% was obtained with NaOH (4%) pretreatment at 121 °C, which efficiently removed lignin and hemicellulose as well (Zheng et al. 2018).

Other than first-generation reagents for wheat and maize residue pretreatment, the second-generation solutions, i.e., ionic liquids have captured worldwide attention during the last decade for pretreating wheat straw materials (Sathitsuksanoh et al. 2013). The ionic liquid (a salt generally melting at room temp.) possesses some major properties such as strong polarity, hard to oxidize, nonvolatileness, good solvent, easy synthesis and recovery. It is also an environment-friendly method due to the utilization of conventional organic solvents. This is referred to as a green solvent that substitutes volatile organic solvents in various areas of application. The wheat straw or corn stover pretreated using N-methylmorpholine-N-oxide results in lowering the crystallinity of cellulose. Hence, it considerably improves bioethanol production efficiency. The studies demonstrated that these approaches offer a significantly high digestibility of the lignocellulose-based materials along with high glucose yields. During the processing however such liquids may become highly viscous adding to their drawbacks. Another difficulty involved with this method is that most ionic liquids are toxic for cellulose (Sathitsuksanoh et al. 2013).

2.8.4 Biological Pretreatment

As far as pretreatment methods are concerned, high energy consumption and input is required in physical pretreatment methods whereas chemical pretreatment tools demand chemical reagents/additives. However, biological or microorganism-based pretreatment methods possess an upper hand of lower energy requirements. Several microorganisms including fungi (white rot fungi, brown rot fungi, soft rot fungi) have properties of strong biodegradability for removing lignin from lignocellulosic feedstock matter for bioconversion.

White rot fungi (WRF) has significantly greater lignin decomposition capacity (LDC) but it also consumes a part of the cellulose and hemicellulose during the process of decomposition. As a result, for selective pretreatment various genetic engineering-based methods were adopted. After the transformation of white rot fungi was performed, the strains which were having a higher concentration of lignin oxidase without cellulase and hemicellulase were finally selected (Sánchez 2009). Their powerful biodegradability is derived from strong oxidative activity and greater efficiency substrate specificity of their ligninolytic enzymes (Dias et al. 2010). Such vital characteristics facilitate fungi specifically degrade lignin. Degradation of lignin is regulated by three key enzyme systems, viz., lignin peroxidase, laccase and manganese peroxidase system (Cianchetta et al. 2014).

On the other hand, brown rot fungi (BRF) exclusively decompose cellulose and pectin, and finally, hemicellulose, while modifying the lignin over this course of degradation. As BRF does not degrade ligninase directly, it is not feasible in the initial stages of the degradation to have enzymatic reactions, but to use LMW degradable substances, which are supposed to be through the extracellular Fenton reaction system (Ferrous iron and H_2O_2) to produce hydroxyl radicals (OH)/strong oxidizing agent for lignocellulosic wheat straw (Lopez-Abelairas et al. 2013). There are three layers constituting wheat straw (Kumar et al. 2009),

1. Superficial layer
2. Primary wall
3. Three secondary layers namely S_1, S_2, and S3

Prior investigations presented that BRF-based pretreatment in straw takes place in S2 (middle secondary) layer, with no effect on S3 (inner secondary) layer. To analyze the pretreatment ability of BRFs using cultured substrate (i.e., wheat straw), seven BRF were assessed both individually and in various combinations. *Phanerochaete chrysosporium* showed a highest reduction in the total fermentable sugars (26.45%) and also in the content of lignin (28.93%) when measured individually. Comparisons among different rot fungi combinations, viz., WR plus BR, WR plus WR, and WR plus SR fungi showed that in some combinations, the delignification role was enhanced significantly. The best combination comprising *Deadalea flavida* and *P. chrysosporium* was able to cause a lignin reduction of 36.27%.

2.9 Enzymatic Hydrolysis (EH)

Enzymatic breakdown is a crucial step during the production of plant biomass-based biofuels. The saccharification event converts complex carbohydrates into simple monomers, which is a decisive step for the production of bioethanol. Due to its low energy demand, low corrosion, low toxicity, and lack of toxic by-product formation; enzyme hydrolysis is generally a desirable method over acid and alkali hydrolysis. The major enzyme "cellulase" performs best within the temperature range of 40–50 ° C, whereas the enzyme "xylanase" works best at 50 °C (both with pH 4–5). During this process of hydrolysis, the glycosidic bonds (among cellulose and hemicelluloses polymers) are broken down by the action of cellulolytic enzymes (Yang et al. 2011). Such enzymes are usually categorized into three distinct sections, viz., exoglucanase, endoglucanase, and β-glucosidase. Exoglucanase attacks cellulose outer bonds while the endoglucanase breaks down the inner cellulose regions thus generating free chain ends. Eventually, due to the action of β-glucosidase, this chain is degraded to glucose (Jayasekara and Ratnayake 2019).

Enzyme-based hydrolysis is indeed quite effective way to liberate simple sugars from complex lignocellulosic biomass. "Callulases," the enzymes which efficiently catalyze this hydrolysis process, can be formed by several fungi namely *Trichoderma reesei* and *Aspergillus niger* (Linde et al. 2008) and/or bacteria like *Clostridium cellulovorans* (Arai et al. 2006). Using cellulase enzyme in combination with other hydrolyzing enzymes may substantially enhance enzymatic hydrolysis (EH) rate. This is documented that the conjugated action of cellulases along with hemicellulase leads to elevated production of sugar. Belkacemi and Hamoudi (2003) showed that from corn stalk, the hydrolysis of hemicellulose (pH of 5) may release 90% sugar at 30 °C after 10 h. It is also proposed that during EH of corn straw by cellulase of *T. reesei* ZU-02 and cellobiase of *A. niger* ZU-07, the inclusion of Tween 80 at 5 g per liter can increase the rate of saccharification by 7.5% (Chen et al. 2008). In another study, alkaline peroxide pretreated wheat straw led to 96.75% decomposition after EH, whereas using wet wheat straw, >75% yield was obtained when pretreated with autocatalytic organic solvent (Saha and Cotta 2006).

2.9.1 Fungal Cellulase Production

For the commercial production of cellulose, the focus has been on fungi mostly, because most of the desirable bacterial species are anaerobes having quite low growth rates. *Aspergillus terreus* M11 (thermoacidophilic fungus) was isolated by Gao et al. (2008) for cellulase production optimization. With solid-state fermentation (SSF) method at 45 °C, they achieved 243 U filter paper activity, 128 U β-glucosidase activity and 581 U endoglucanase activity (for each g of carbon) (pH 3) with 80% moisture content. Gupta et al. (2015) exploited 23 fungal strains extracted from the soil for the synthesis of cellulase. They determined enzymes' activity generated from those fungal strains was approximately 4.59 IU/g for Filter paper cellulose (FPase) and 29.04 IU/g for Carboxymethyl cellulose (CMCase) using SSF technique (Table 2.4).

2.9.2 Bacterial/Yeast Cellulase Production

A number of bacterial species such as *Pseudomonas fluorescens*, *B. subtilis*, *E. coli* and *Serratia marcescens* have been isolated. These species later standardized the cellulose production (Sethi et al. 2013). The best temperature was reported to be 40 °

Table 2.4 Different fungi used for enzymatic hydrolysis of lignocellulosic feedstock with their respective enzyme(s)

S. no.	Fungus	Nature	Enzyme(s)
1.	*Trichoderma reesei*	Mesophilic	Cellulase
2.	*Aspergillus niger*	Mesophilic	Xylanase, cellulase, cellobiase
3.	*Myceliophthora thermophila*	Thermophilic	Carbohydrate-active enzymes (CAZymes), e.g., Glycoside hydrolases
4.	*Termoascus aurantiacus*	Thermophilic	Cellulase
5.	*Talaromyces emersonii*	Thermophilic	Alpha amylase, beta amylase, glucoamylase
6.	*Malbranchea cinnamomea*	Thermophilic	Xylanase, mannanase

C (pH of 10) and *Pseudomonas fluorescens* was shown to be the best among all species for the production of cellulase. More recently, Touijer et al. (2019) attempted cellulase enzyme production with cellulotyic yeast and process optimization for maximum activity as well as productivity. During the investigation, *Trichosporon* genus bacteria were isolated to be utilized on several substrates such as cellulose fiber, carboxymethyl cellulose (CMC), and filter paper (FP). The suitable temperature for CMCase and FPase was 55 °C (pH of 4) and 60 °C (pH of 6) respectively giving the activity of 0.56 for the FPase and 0.52 for the CMCase and fiber (10 min incubation). Nandimath et al. (2016) further studied bacteria-derived cellulase enzyme for enhancing its production. Among 40 distinct isolates under investigation, two isolates, i.e., one each from *Pseudomonas spp* and *Bacillus spp* were identified. The optimal production temp. showed to be 30 °C (pH 5). Moreover, higher activity was observed in *Pseudomonas spp* (22.11) as compared to *Bacillus spp* (14.6).

After completing this step, the hydrolyzate is finally relocated for carrying out the process of fermentation process to achieve lignocellulose-based biofuel production.

2.10 Fermentation

Major process in biofuel production is fermentation, which occurs through the metabolic activity of microbes. Microorganisms are unable to ferment efficiently (with greater yield as well as enhanced rate) all sugars released during pretreatment and hydrolysis. It is a prime factor thwarting commercial utilization of lignocellulose-based bioethanol generation.

For producing bioethanol commercially, the ideal microorganism must have characteristics such as broad substrate utilization, greater yield of ethanol along with productivity, cellulolytic activity, tolerance to inhibitors present in the hydrolyzates and to high concentrations of ethanol as well as the ability for sugar fermentation at a higher temp. (Hahn-Hagerdal et al. 2007). The yeast-like *Saccharomyces cerevisiae* and bacterium such as *Zymomonas mobilis* are a few best-known microbes for producing ethanol from hexoses, (Claassen et al. 1999) providing greater ethanol yield (theoretically 90–97%). It also shows enhanced tolerance of ethanol up to ca. 10% (w/v) in fermenting medium. Native strains of *Saccharomyces cerevisiae* strain yield 99% ethanol (Jorgensen 2009). *S. cerevisiae* and *Z. mobilis* are unable to use xylose (Rogers et al. 2007), which is the main drawback of these native strains. Some other microbes which ferment xylose to ethanol including enteric bacteria as well as yeasts *Pichia stipitis*, *Candida shehatae* and *Pachysolen tannophilus* (Chandel et al. 2007; Lin and Tanaka 2006) are distinguished by less ethanol yields along with their affinity to reassimilate ethanol generated (Karakashev et al. 2007). GM strains of such yeast are able to ferment both hexoses and pentoses (Karhumaa et al. 2007). Despite that, such strains exhibited less productivity in terms of transformation of xylose to ethanol (Watanabe et al. 2007). Additionally, the major realistic shortcoming for the broad adoption of GM ethanologens is that plasmids harboring xylose conversion genes are generally not welcomed by native/host cells (Krishnan et al. 2000). The advantages of fermentation at greater temp. such as higher production rates, quite easier product recovery, using a range of substrates and reduced contamination risk (Torry-Smith 2002), ethanol fermentation using some strict anaerobic thermophilic bacteria like *Clostridium* sp. (Claassen et al. 1999) and *Thermoanaerobacter* sp. (Larsen et al. 1997) have been documented. Low tolerance to ethanol is the major drawback of thermophilic ethanologens, i.e., <30 g/L (Claassen et al. 1999).

Ethanol fermentation using feedstock such as wheat straw as well as corn stover hydrolyzates has been broadly investigated using a number of microorganisms such as yeasts, bacteria, and fungi, generally raised as pure cultures (Table 2.5).

Research attempts with respect to ethanol fermentation are under progress. Construction of new promising genetically modified organisms (GMOs) or new wild-type ethanologens having greater ethanol tolerance, yield, and productivity will be required for further development of commercial bioethanol production from lignocellulose-derived wheat and maize waste.

2.11 Separation of Biofuels from Fermentation Broth through Distillation

The distillation of ethanol produced during fermentation from an ethanol-water solution results in hydrous (azeotropic) ethanol (theoretical maximum 95.5% ethanol and 4.5% water). Molecular sieves/additives are essential for breaking down the azeotrope to obtain ethanol in pure form. The energy balance of bioethanol production evaluates that the distillation process demands more energy, also because ethanol concentration in the fermented broth is low. This step necessitates high energy and works with just 4% initial ethanol conc. making it more economical

Table 2.5 Major microorganisms utilized in fermentation of wheat straw and corn stover-based hydrolyzates, their sugar substrates, respective ethanol yield as well as features

S. no.	Microorganism	Group	Sugar (s) substrate	Ethanol yield	Features/Conditions	References
1.	*S. cerevisiae*	Yeast	Glucose, Xylose	UWS: 99%	Mesophilic, facultative anaerobic	Jorgensen (2009)
2.	*Saccharomyces cerevisiae* 590. E1	Recombinant Yeast	Glucose, Xylose	UWS: 63%	Ferment cellulose without additional enzymatic hydrolysis process	
3.	*S. cerevisiae* (cellulose utilizing) + *P. pastoris* (Xylan utilizing)	Recombinant Yeast	Glucose, Xylose	UWS: 0.42 g g^{-1} (82.6%)	Simultaneous saccharification and co-fermentation (SScF)	Zhang et al. (2017)
4.	*Thermoanaerobacter mathranii* BG1L1	Recombinant Bacteria	Glucose, Xylose	UWS: 76%	Extreme thermophilic (70 °C), strict anaerobic	Georgieva et al. (2008)
5.	*Kluyveromyces marxianus* CECT 10875	Recombinant Yeast	–	UWS: 65%	Thermotolerant (42 °C), facultative anaerobic	Tomas-Pejo et al. (2009)
6.	*S. cerevisae* + *Fusarium oxysporum*	Fungus	Glucose, Xylose, Cellulose	UWS: 0.44 g g^{-1} (80%)	Simultaneous saccharification and co-fermentation (SScF)	Paschos et al. (2015)
7.	*S. cerevisiae* strain CR01	Recombinant Yeast	Xylose, Glucose	UWS: 0.43 g g^{-1} UCS: 0.41 g g^{-1}	Mesophilic; Short-term adaptation + vitamin mixture	Dijk et al. (2020)
8.	*Hohenbuehelia sp.* ZW-16	Fungus (white rot)	Glucose, Xylose, and Arabinose	UCS: 4.6 g/L (from 50 g/L corn straw hydrolyzate)	Thermophilic	Liang et al. (2013)
9.	*Pichia stipitis* A	Recombinant Bacteria	–	UWS: 0.41 gp/gs	Adapted at hydrolyzate elevated conc.	Nigam (2001)
10.	*Pichia stipitis* NRRL Y-7124	Recombinant Bacteria	–	UCS: 0.35 gp/gs	Adapted at hydrolyzate elevated conc.	Nigam (2001)

(continued)

Table 2.5 (continued)

S. no.	Microorganism	Group	Sugar (s) substrate	Ethanol yield	Features/Conditions	References
11.	*Micor indicus*	Fungus	Glucose, Xylose, and Mannose	UCS: 0.43 g g^{-1} (84.3% theoretical)	Anaerobic fermentation	Alavijeh et al. (2019)
12.	*E. coli* strain FBR5	Bacteria (recombinant)	–	UWS: 90%	Mesophilic, semianaerobic	Saha and Cotta (2006)

UWS Using wheat straw, *UCS* Using corn stover

(Zentou et al. 2019). During the distillation process, energy usage could be minimized if lower heating is required; this could be achieved by consuming residual thermal energy from other processes to steam fermented broth. Various biofuels that are not soluble in water are being considered by researchers as a way to avoid the distillation process.

2.11.1 Bioethanol

The major application of lignocellulosic feedstock is ethanol production. The most established and efficient organism for producing ethanol is the yeast *Saccharomyces cerevisiae*, converting hexose sugars to ethanol. Moreover, under industrial conditions, the yeast *Brettanomyces bruxellensis* and bacterium *Zymomonas mobilis* may generate ethanol (Blomqvist and Passoth 2015; Gupta et al. 2016) (Fig. 2.7).

However, hemicelluloses-derived xylose and other pentoses cannot be assimilated by these microorganisms. Lignocellulosic feedstock produces economically feasible ethanol. This is equally important to produce ethanol from hemicellulose sugars. Considerable attempts have been carried out to produce inhibitor-tolerant *S. cerevisiae* strains, which ferment xyloses (Passoth 2017). Eventually, the resultant strains by combining the metabolic and evolutionary engineering of industrial yeast isolates could ferment glucose and xylose in straw. The world's first second-generation commercial ethanol plant is in Crescentino (Italy). About 40,000 metric tons of ethanol is produced there each year, from 270,000 tons of biomass including wheat as well as rice straw (http://www.biochemtex.com/en/references/crescentino, accessed 18/04/2021). Using straw as a feedstock, second-generation ethanol plants have been installed in the USA and Brazil. They have a total annual capacity of approx. 530 million liter ethanol. The second-generation bioethanol are expensive in price than fossil resources derived fuels and first-generation ethanol. With the use of second-generation bioethanol, there is a considerable decline in GHGs compared to fossil fuels but still, bioethanol production is difficult. The rise in cost is majorly due to the requirement for extensive pretreatment of biomass in addition to greater equipment cost (Lantz et al. 2018).

Extensive pretreatment costs can be resolved by adjusting the feedstock handling. Blending wood chips from short rotation coppice and wheat straw led to greater monomeric sugar yields after pretreatment compared to treatment of just feedstocks. Mixing may moreover resolve the supply uncertainty in case of biomass scarcity (seasonal). Theoretically, if all processes (pretreatment, hydrolysis and fermentation) were fully efficient (100%), the average composition of corn stover with respect to glucan (36.2%) and xylan (22.7%) could yield, ethanol corresponding to 20.6% and 13.1%, respectively, i.e., a highest ethanol yield by mass of 33.9% of the dry solids in stover. Taken as a whole for corn stover, ethanol yield from raw glucan content normally fluctuates between 35 and 85%.

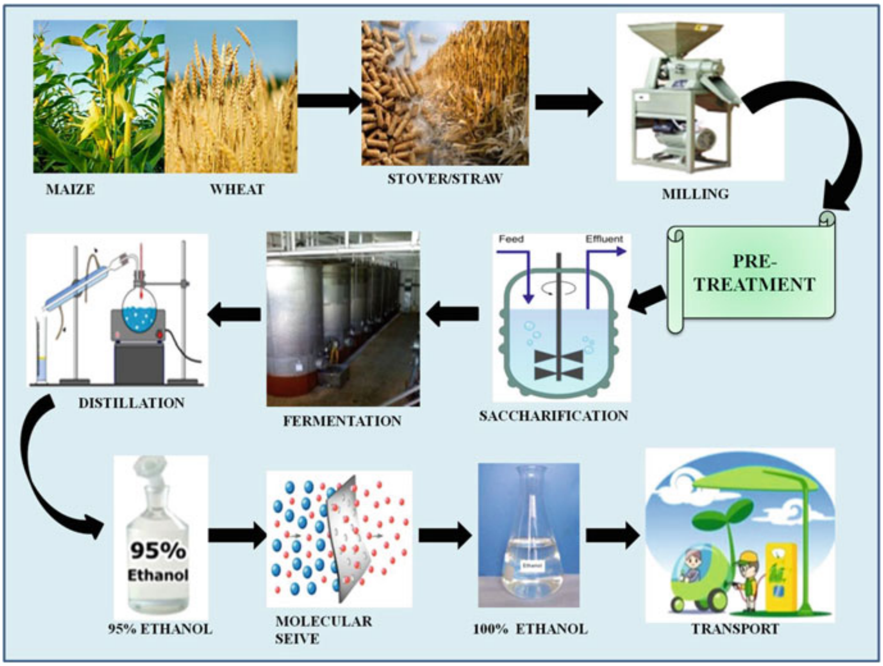

Fig. 2.7 A general scheme involved in the production of bioethanol from Wheat or Maize residue

2.11.2 Methane (Biogas) Generation

A promising application of agricultural waste like wheat straw is the production of methane. Production of biogas using anaerobic digestion shows greater energy efficiency, GHG emissions, and biomass transformation compared to ethanol generation (Borjesson and Mattiasson 2008). By such degradation of lignocellulosic biomass using wheat straw, biogas with high energy efficiency is produced. The anaerobic degradation of agricultural residue (biomass) is divided into four steps:

1. Degradation or hydrolysis of biopolymers
2. Acetogenesis
3. Acidogenesis
4. Methanogenesis

During anaerobic digestion, hydrolytic bacteria constitute a portion of the microbial consortium thus making biomass pretreatment nonmandatory for biogas production. The major restrictive factor for methane production using lignocellulose is the hydrolysis step due to its complexity and recalcitrant structure. Thus, various physical, thermochemical as well as biological treatments of such feedstock have been researched. Overall, pretreatment may pose positive or negative effects on eventual biogas generation (Carrere et al. 2016). Therefore, optimization for specific material and production technique is needed. Recently, a novel gas biofuel, hythane, consisting hydrogen and methane has been introduced. The GHG emissions of methane are decreased by the addition of 10–25% (v/v) H_2 to CH_4 with a better fuel efficiency of compound biofuel. This makes hythane a potential fuel source (Liu et al. 2013). A promising way to produce hythane utilizing agricultural waste is two-stage dark fermentation process. Hydrogen produced from corn stover from hydrogen fermentation and the end products may be further exploited by methanogens (i.e., methane fermentation—MF). To minimize the effect of lignin in lowering biogas production, best ligninolytic fungal strains were explored to treat the wheat straw. With active generation of lignin peroxidases and laccases, these cultures helped in reducing lignin content by 48.2%. This pretreatment leads to enhancing biogas yield by 500% compared to control (untreated) in addition to making the biomass more digestible, and thus rendering it an economic method (Shah and Ullah 2019).

Major problematic substrate for biogas production is lignocellulose. Lignocellulose has a recalcitrant structure, having greater C/N ratio and lack of essential trace elements like Fe, Co, Ni, Mo, Se, and W. The C to N ratio of 20–30 is critical for the efficient production of biogas. The C/N ratio for wheat straw and corn stover feedstock is 60 and 63, respectively. This specific issue can be solved by deploying co-digestion of lignocellulosic feedstock and animal waste (Sawatdeenarunat et al. 2015).

2.11.3 Butanol from Wheat Straw

Using wheat straw, there are several methods for producing butanol. Both the forms of butanol; isobutanol as well as n-butanol exhibit the behavior of fuels. Acetone-butanol-ethanol is generated from wheat straw from *Clostridium beijerinckii* P260 can be categorized into five key steps (Alavijeh et al. 2019) hydrolysis and fermentation of straw individually, (Arai et al. 2006) simultaneous hydrolysis and fermentation of lignocellulosic straw (no mixing), (Ballesteros et al. 2006) fermentation and hydrolysis through supplementation, (Battaglia et al. 2021) fermentation and hydrolysis of straw with mixing by gas stripping, and (Belkacemi and Hamoudi 2003) Lastly, more attractive as well as cheaper process, i.e., fermentation and hydrolysis of wheat straw (Qureshi et al. 2008).

2.11.4 Biohydrogen Production

Production of biohydrogen through dark fermentation in CSTR, wheat straw hydrolyzate (xylose) may be utilized as a substrate (Kongjan et al. (2008). Previously, *Caldicellulosiruptor saccharolyticus* (thermophile) (Blumer-Schuette et al. 2008) was utilized for hydrogen production. *C. saccharolyticus* is a cellulolytic bacterium, which grows at 70 °C (optimum temp.) and yields high hydrogen (van Niel et al. 2002; Panagiotopoulos et al. 2011a, b). It is advantageous over other microorganisms and it uses hexoses and pentoses (de Vrije et al. 2009; Kengen et al. 2009) simultaneously. Wheat straw-based biohydrogen production was explored through fermentability tests within the biorefinery framework. The EH of wheat straw and dilute acid pretreatment results in hydrolyzate having relatively less sugar conc. (23.0 g/L) and relatively good fermentability. In a biorefinery, fermentative hydrogen production has shown to be improved by blending wheat grain along with wheat straw hydrolyzate (Panagiotopoulos et al. 2013). The MF-process has been broadly investigated and optimized. Therefore, using corn stover, two-stage fermentation can be improved by enhancing the H_2 production rate as well as yield in MFP. A mixture of the *Clostridium cellulolyticum* (cellulolytic bacteria) and H_2-producing bacteria (non-cellulolytic) produced biohydrogen using steam-exploded corn stover (Zhang et al. 2016a, b). The highest yield up to 51.9 L H_2/kg total solid (TS) of coculture system having *C. cellulolyticum* and *Citrobacter amalonaticus* was achieved.

2.12 Biotechnology for Efficient Biofuel Production

Over the world, lignocelluloses derived from plant biomass are promising sources for sustainable production of biofuel. Nevertheless, transformation of lignocellulosic feedstock to biofuel is quite expensive owing to the costs of chemical or physical pretreatment processes and EH for degrading plant cell wall (PCW). Resistance of PCWs through enzymatic degradation has been significantly lowered in a number of plant species by altering PCWs using various molecular and biotechnological tools (Quanzi et al. 2014). This objective has been achieved by modifying the composition and structure of lignin along with reducing its content. Recalcitrance reduction of plant cells has also been obtained by manipulation of hemicellulose biosynthesis and overexpressing the bacterial enzymes in plant cells to interrupt linkages found in the lignin-carbohydrate complexes. Such GM (genetically modified) plants usually showed enhanced both saccharification yield as well as ethanol production. The enzymes derived from bacteria and fungi, which are responsible for cell wall degradation, have been over-expressed in plants to raise the saccharification efficiency than exogenous incorporation of cellulolytic enzymes. Auto-hydrolysis has been made possible through in-planta expression of thermostable CWD enzymes derived from thermophilic bacteria. Genetically modified plants can efficiently reduce recalcitrance simultaneously avoiding yield loss, signifying that successful cell wall modification could be explored without any effect on plant development/cellular integrity. In maize, p-coumaroyl CoA: hydroxycinnamyl alcohol transferase (pCAT), leading to the production of pCA-monolignol conjugates, was suppressed using RNAi technique, resulting in substantially lowered pCA levels (Marita et al. 2014). As pCA is not involved in the radical coupling reactions of lignification, modifying acyltransferases can produce desirable lignin (lower pCA and higher monolignol conjugates), which could be cleaved by alkaline/acidolytic processes, providing a promising tool for enhanced saccharification yield in crops such as wheat and maize.

2.13 Environmental Impacts and Sustainability Issues

Although there are a number of crop species available as good biofuel candidates, residues/waste derived from wheat and maize have received relatively greater attention due to lower cost and higher availability, especially in countries like the US and India. Biofuels derived from lignocellulose may assist to solve issues about utilizing food grain crops for manufacturing biofuel. In some cases, removing stover will result in more serious water and wind erosion. Soil organic matter and carbon levels can also be lower by removing corn stover. As of now, different prediction models are being prepared to determine how much stover needs to remain in the field for preserving soil quality. According to a report, sustaining soil carbon level is generally a huge constraint for harvesting stover as compared to the amount of stover required to prevent wind and water erosion. This needful amount to sustain soil carbon level varies as it depends on certain factors. Harvesting corn stover could offer a few benefits. Large quantities of stover will obstruct no-till planting, forcing farmers to bury part of the residue with one or more tillage operations. It also has a cooling and wetting effect on soil in spring, favoring insect and pathogens, leading to more requirements of pesticides. Nevertheless, there are many possible drawbacks to eliminating corn stover, including potential effects on facilitating soil erosion, soil organic matter, and soil nutrient removal that must be taken into consideration before its wider adoption. There might be a possibility to enhance the sustainable rate of removal, provided other regulatory practices are executed. It may comprise narrower row spacing, greater plant population, establishing cover crops, zero tillage, and elevated fertilization rates or deployment of organic amendments. One major advantage of using biofuels is that its adoption significantly lowers greenhouse gas emissions. Using pure bioethanol (100%) results in a 50–60% reduction than conventional fuels. As obvious, the benefits obtained from the use of blends would be smaller. Regarding biodiesel, the advantage of changing climate will depend on the kind of feedstock or raw material for generating bioethanol. If cellulosic materials such as wheat and maize residues are used, the greater net reduction in greenhouse gas emission up to 75–80% may be achieved. This is due to lower energy requirement for the cultivation of such plants and the energy-efficient processes also take place during the production stage, which further encourages the use of renewable energy sources. It is noteworthy that biofuel production, being itself an energy-intensive process, needs substantial amounts of conventionally produced energy. Deployment of biofuels could also effectively lower emissions of other pollutants from vehicles, not to forget its dependence on vehicle type as well as fuel specifications.

In annual cropping systems, the use of residues may enhance and diversify the farmers' income. They could efficiently bring down the use of fossil fuel and GHS emissions, considering the desired end products. There are several benefits of residue harvest such as the decline of insect pest and disease pressure (Wilhelm et al. 2004). Despite that, there are issues about potential adverse effects as they operate both as sink and source of soil carbon (C) that offers vital ecosystem services (Su et al. 2020). Many crop residues act as a boost for agricultural productivity (Raffa et al. 2014; Wilhelm et al. 2007) such as diminishing soil erosion and improving physical properties of soil owing to their positive impacts on soil organic carbon, bulk density (BD), water holding capacity, nutrient availability as well as infiltration (Kenney 2011; Zhang et al. 2020). Nevertheless, there are a number of tradeoffs and uncertainties about the reliance on agronomic (such as residual management and fertilization rate) and abiotic (e.g., nutrient availability, soil properties, weather conditions) factors.

So far, there is hardly any evidence which shows that crop residue management (CRM) has an effect on grain yield over a longer period in case of inadequate water availability (Battaglia et al. 2021). During periods of optimum water availability, wheat and maize residue removal rates (RRR) of at least 90% results in almost equal or higher grain yield than without removal. Reduction in organic fractions occurred majorly in case of absolute removal of stover. It was observed that with up to 30% of crop residue removal, the water runoff, soil erosion and nutrient leaching such as total N and extractable K in the soil were also reduced. The effects of stover management on soil BD fluctuated significantly, depending on soil layer along with residue and tillage management, with RRR of $<50\%$ for maintaining the stability of soil aggregates. Decrease in CO_2 and N_2O fluxes generally happened in case of 100% removal of residue. Using wheat straw often led to an increase in CH_4 emissions and regardless of N rates, ≥ 8 Mg/ha of wheat straw led to highest CO_2 and N_2O emissions. Prior to using CRs, it is hence advisable to check, whether positive (or at least neutral) sustainability impacts could be retained under the given location-specific conditions of the agro-ecosystem.

2.14 Major Challenges

Presently, scientists and researchers around the globe are looking for possible alternative fuels from inexpensive and abundantly available sources such as agricultural wastes. This goal also has some serious challenges as it is very easy to use energy crops for production of bioethanol, but it is economically infeasible since these are majorly consumed as human food. Another issue is that during pretreatment of feedstock, few inhibitory compounds, viz., weak acids from derivatives and phenolic compounds hinder the succeeding processes of saccharification as well as fermentation. Such yield limiting compounds eventually affects the cost of the whole process thus making it non-remunerative. High expense is owing to few technological impediments involved in all distinct steps during the procedure. According to an estimate, pretreatment alone covers about 33% of the whole cost of production. The currently available methods for this process are capital intensive.

Moreover, it is also expensive to maintain a consistence performance of the GM yeast fermentation processes commercially. Developing highly efficient PRT methods for LC biomass and combining the optimal factors into more economic bioethanol production systems are also concerns.

As reported, demand for food as well as transport fuels is likely to rise manifolds (about >50 times) over the globe. Hence, there is a huge requirement for a renewable supply of energy by omitting any impacts on food supply. Biofuels generated from underexplored CRs, viz., cellulosic feedstock are expected to be greatly valuable and economically feasible. Hence, it is of paramount importance to regulate the manufacturing of such products, analyzing the cost of the pretreatment, and encouraging the utilization of agricultural wastes for ecosystem sustainability.

2.15 Conclusion and Future Prospects

The swift development of technology and accelerated explosion in the global population in addition to the environmental pollution necessitates the requirement of finding new energy resources. These sources must be environmental friendly as well as efficient and cheaper. The advent of biofuels in transportation is regarded a vital and crucial role in lowering the reliance of the present world on fossil energy. Bioethanol has already arrived as an alternative to gasoline in a few nations namely USA, Brazil, and India.

Taking into consideration the significant reliance of the world's economy on fossil fuel resources, looking for unconventional tools and techniques for the production of fuel in addition to chemicals and food is immensely needed. Also, the production of value-added compounds using agricultural waste or residues will put greater value on the agricultural industry. It will also be enhancing the economic charisma of green/ecosystem-friendly technologies. Opportunities will be created by developing tools and technologies to generate a variety of fuels as well as chemicals using residue/straw for producing products, which are best suited to native conditions as well as market demands. Normally, the production of more than one lignocellulosic biofuel, viz., ethanol or biogas can be combined. For meeting the continuously elevating need for transportation fuels, biofuel is one of the best option to be investigated and adopted globally. Starch-derived biofuels are a great choice of bioethanol generation, but it is not feasible for large-scale manufacturing, keeping in view the even greater requirement for such food grains for human and livestock consumption. Keeping in view the sustainability aspect, bioethanol must be manufactured using secondary biomass derived primarily from agricultural waste (such as wheat and maize residue). It has the benefits of both utilizing waste as resource recovery and avoid in using biomass with the potential to be used as human food. The residue from agricultural crops (i.e., lignocellulosic biomass) is a promising feedstock for commercial generation of various biofuels such as bioethanol and biohydrogen because of its natural abundance and moreover separate land, water, and energy are not a compulsion. Currently, several technologies for transforming agricultural plant residues into biodiesel are under progress, development and exploration. Umpteen issues faced during the establishment of various biofuel production technologies must be tackled by modern scientific and technological advancements. It will be of great help to develop more efficient as well as economic processes required for generating second-generation bioethanol. In this way, it would provide a generous way out of the currently prevailing energy crisis owing to draining oil and gas. A deliberate analysis of agricultural and environmental along with economic outcomes needed to be carried out for any kind of practical application to achieve a sustainable replacement for conventional fossil fuels.

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Chapter 3
Agricultural Residues and Manures into Bioenergy

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Abstract The mandate for energy has upsurged with the increase in population worldwide. Exploiting fossil fuels for energy has directed the exhaustion of fossil fuel assets. Thus, substitute sources of energy are required. Biomass is a renewable source and an alternative feedstock for providing eco-friendly and sustainable energy. Biofuels obtained from different biomass are grouped into three distinct groups: first-generation biofuels (obtained from wheat, sugarcane, barley, potato, soybean, corn, coconut, and sunflower), second-generation biofuels (produced from lignocellulosic materials like cassava, switchgrass, Jatropha, straw, and wood), third-generation biofuels (obtained from algae). The biofuel produced with the help of first-generation energy crops poses threat to biodiversity and food supply. But the use of lignocellulose as a biofuel does not contend with that of food production as it is nondigestible for humans. The principle advantage of algal biomass is higher oil production and it can convert all of the feedstock energy into various kinds of biofuels. Apart from this, it is useful for amputation of CO_2 from the industrial chimney (algae bio-fixation), food products, animal feed, and energy cogeneration after extraction of oil and treatment of wastewater. Thus, it is one of the world's most valuable, renewable, and sustainable source of the fuel which also helps in controlling environmental pollution. Thus, bioenergy crops and biofuels are considered as sustainable sources of energy production as waste products such as forest waste and agricultural residues, manures, industrial waste, and municipal solid waste are used for producing biofuels and bioenergy.

Keywords Bioenergy crops · Biofuels · Lignocellulose · Algae · Agricultural residues

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3.1 Introduction

The world has seen an increase in energy demand due to unceasing rise in the global population. The accomplishment of energy petition is typically done by ignition of fossil gases. But the use of these fuels poses many environmental hazards as the concentration of harmful gases (nitrogen oxide, greenhouse gases, and carbon dioxide) increases. For instance, greenhouse gases such as sulfur-containing compounds, particulate soot, and carbon dioxide are produced due to coal burning which results in acidification of the soil. Moreover, the energy which is produced from nuclear fission needs huge infrastructure and it also leads to hazardous effects on the environment in addition to human health (Gresshoff et al. 2017). Many long-term effects on the environment are related to the use of fossil fuels which include desertification and degradation of fertile soil (Karp and Shield 2008). The consequences of increased usage of fossil fuels are noticeable as diseases associated environmental pollution and drastic changes in climate such as torrential rains.

In addition to this, there has been increasing concern of depleting crude oil resources all over the world. As per the report of the renewable energy policy network (Mohr 2013), it was found that nearly 78% of the energy all over the world comes from fossil fuels, 3% is obtained from nuclear energy while another energy comes from resources which are renewable, i.e., hydrothermal, wind, biomass, and solar. At present, about 85 million barrels of oil from fossil fuels are refined each year. At the current rate, about 116 million barrels of crude oil will be needed every year by 2030. This increase in energy demand may lead to the exhaustion of fossil fuel assets. Thus, there is a need for substitute sources of energy (Lee and Lavoie 2013).

Due to increased concern about climate change all over the world, there is a need to evaluate the crops which are capable of producing higher biomass for the generation of energy (Lemus and Lal 2007). Biofuels and bioenergy crops are sustainable sources for the reason that these decrease carbon releases and dependency on fossil fuels along with providing habitat and ecosystem services (Fargione et al. 2010; Searchinger et al. 2008). Hence, the production of bioenergy will increase globally in near future (OECD-FAO (Organisation for Economic Co-operation and Development and the Food and Agriculture Organization) 2017).

Biomass is a renewable source and an alternative feedstock for providing eco-friendly and sustainable energy. Waste products such as forest waste and agricultural residues, manures, industrial waste, and municipal solid waste are used for producing biofuels and bioenergy. Different kinds of bioenergy can be produced from biomass. However, it is not competitive with respect to cost in comparison to petro fuels and other sources of renewable energy. Biofuels obtained from different biomass are grouped into three distinct groups. The first-generation biofuels are obtained from edible food crops like wheat, sugarcane, barley, potato, soybean, corn, coconut, and sunflower. While the second-generation biofuels are those which are obtained from lignocellulosic substances like cassava, switchgrass, Jatropha, straw, and wood. The third-generation biofuels are attained from algae

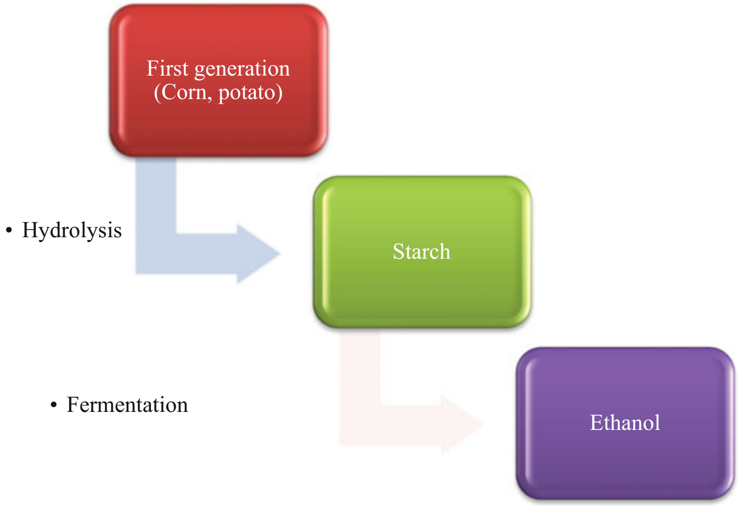


Fig. 3.1 Elementary steps for making of first-generation biofuels

produces huge quantities of lipids that are appropriate for the production of biodiesel.

Bioenergy crops provide several advantages over traditional fuels such as decrease in the level of greenhouse gases and emission of CO_2, reduction in soil erosion along with increased transpiration and content of soil carbon (Adler et al. 2007; Wang et al. 2012; Kim et al. 2013). Resultantly, attention of scientific community is being continuously drawn towards the use of bioenergy crops because they are eco-friendly and renewable. However, the use of bioenergy crops results in an increased race for nutrient requirement, agricultural land, and water resources with food crops. Apart from this, the use of bioenergy crops can result in more dispersal of dominant plant species and destruction of wildlife habitat (Dipti and Priyanka 2013). So, in this chapter various kinds of bioenergy crops in addition to their features are discussed in detail (Fig. 3.1).

3.2 First-Generation Biofuels

Biofuel generation was started with first-generation bioenergy crops that are crops of global or local source (Yadav et al. 2019). They are made of starch, vegetable oil, and sugar. Fuels such as propanol, ethanol, and butanol are obtained biologically due to the action of enzymes and microorganisms by the fermentation of cellulose, starch, or sugar.

Production of ethanol is done primarily from cane sugar or corn starch. In 2014, nearly 14 billion gallons of ethanol from corn starch were produced in the US. In the US, around 40% of the corn crop is used for the production of ethanol. Higher than

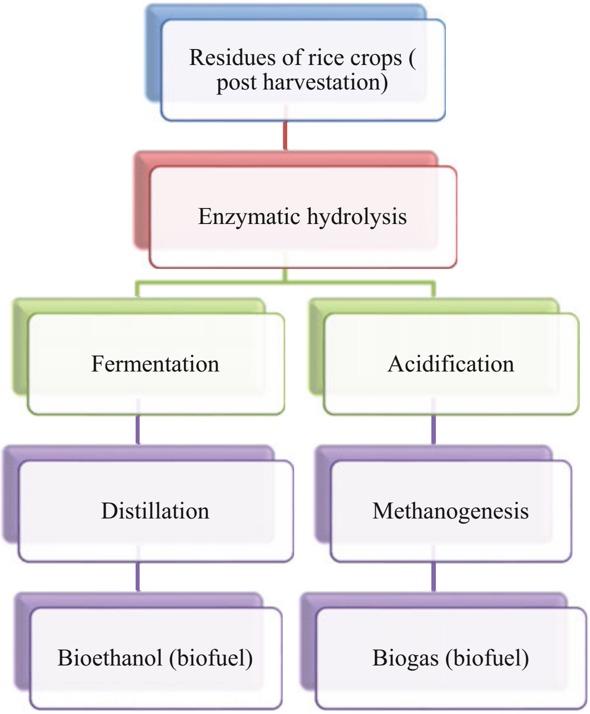


Fig. 3.2 Using rice postharvest residues for the manufacture of biofuels

90% of the world's ethanol supply is made by the US and Brazil (Renewable Fuels Association 2015).

Rice straw is an abundant lignocellulosic biomass having the potential for use as a feedstock for the production of bioethanol. Enzymatic hydrolysis is important to make ethanol from biomass for degradation of straw of rice into sugars like xylose and glucose. Since each biomass has diverse enzyme going-on therefore enzyme substances appropriate for all biomasses essential should be carefully chosen. Ethanol production can be done from treated straw through the process of simultaneous fermentation and saccharification (SSF) in the presence of xylose-fermenting fungus (*Mucor circinelloides*) and an optimized enzyme cocktail (Takano and Hoshino 2018).

Apart from this, biodiesel is also used as an alternative. Eventhough the cost of biodiesel production is higher, it is a copious source of renewable energy as it is eco-friendly. Producing biodiesel from coconut oil is more in comparison to rapeseed and soybean. Lubrication properties of coconut oil are much better compared to other biofuels (Hossain et al. 2012) (Fig. 3.2).

Coconut shell is most commonly used as a source for making charcoal. By using the traditional pit method, nearly 25–30 of charcoal can be produced from dry shells. Calorific value of coconut shell is higher (20.8 MJ/kg) and it is used for the production of biochar, energy-rich gases, bio-oil, steam, etc. Due to high volatile matter content, low content of ash, and cheap cost, coconut shell is more suitable for

Table 3.1 Biofuel production from rice straw

Pretreated source	Biofuel	Outcomes	References
Husk mixture	Pellets of fuel	Combustion properties are better and the quality of pellets of fuel; leading to the production of sustainable biofuel	Rios-Badran et al. (2020)
Straw pretreated with sodium hydroxide (NaOH)	Bioethanol from *Bacillus spp*	Better yield of sugars which are fermentable Capability of replacing enzymes which are traditional	Tsegaye et al. (2019)
Valorized straw	Bioethanol	Production of sustainable and eco-friendly biofuel	Kaur and Chander (2019)
Straw of pretreated rice	Biomethane	Production of biomethane is better and biogas after pretreatment resulting in higher net energy outputs	Elsayed et al. (2019)

pyrolysis process. It can be collected easily from the places where coconut meat is used for food processing. Other crops which are used for the production of first-generation biofuels include Corn, Sugarcane, Vegetable oils, Soybean, rapeseed, wheat, peanuts, and sugar beet (Table 3.1).

3.3 Second-Generation Biofuels

The second-generation biofuels, recognized as unconventional biofuels, refer to those biofuels which are formed from lignin, cellulose, and hemicellulose. Such kind of biofuels are either merged with petroleum-based fuels, ignited in the current engines, or can be used in slightly adapted vehicles such as vehicles for dimethyl ether. These biofuels are used because first-generation biofuels have certain limitations. With the help of first-generation biofuels, enough biofuel cannot be produced without posing threat to biodiversity and food supply. Also, such biofuels are less cost-competitive when compared with the prevailing fossil fuels (Anonymous 2021) (Fig. 3.3).

3.3.1 Characterization of Lignocellulosic Biomass: Components and Structure

Lignocellulose is the most copious natural biomasses in the world with 200 billion tons yield (Zhang and Percival 2008). It is stored in the plant's cell wall and it constitutes 60–80% of the woody tissues in plant stems, 15–30% in plant leaves, and 30–60% in the herbal stems (Moller et al. 2007). Use of lignocellulose as biofuels do

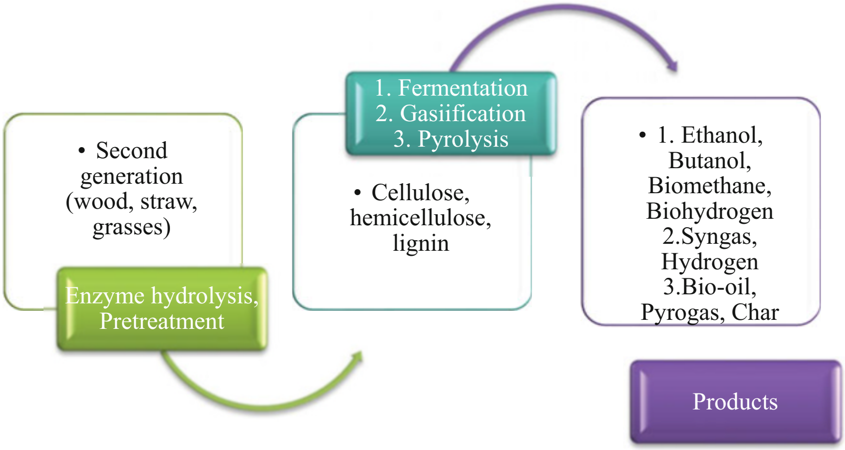


Fig. 3.3 Elementary steps for the manufacture of second-generation biofuels

not contend with that of food production (as in first-generation biofuels) because it is nondigestible for humans. Lignocellulose is made up of three polymeric compounds that are lignin, cellulose, and non-cellulosic carbohydrates (mainly hemicellulose).

Cellulose is a long chain homo-polymer that consists of a unit of glucose with a repeat unit of cellobiose (Zhang et al. 2019). It has 500–1,000,000 D-glucose units linked to β-1,4-glycosidic bonds (Volynets and Dahman 2011). In cellulose, a semi-crystalline structure is created due to interchain H-bonds present between hydroxyl groups (glucose residues) in the radial position and hydrogen atoms (aliphatic) in the axial position. This structure makes cellulose unaffected by enzymatic hydrolysis and the weaker interactions (hydrophobic) between the cellulose sheets promote the formation of a layer of water near the surface which results in production from acid hydrolysis (Bessou et al. 2011). The chemical structure of cellulose built from different plants is identical. However, cellulose molecules derived from different plants differ from each other in interconnections with other biomass molecules and crystalline structure.

Hemicellulose belongs to polysaccharide groups containing chains which are branched and shorter. As hemicellulose accounts for 35% of the biomass weight, these are considered important for biofuel production (Limayem and Ricke 2012). Hemicellulose are not chemically homogenous like cellulose and the chemical structure depends upon the kind of material as the hardwood mainly consists of xylans while the softwood constitutes glucomannans (Agbor et al. 2011; Vidal et al. 2011).

Lignin is an amorphous hetero polymer which constitutes three phenolic monomers—phenyl propionic alcohols, sinapylalcohol, p-coumaryl, and coniferyl. Covalent cross-linking (lignin with cellulose and hemicellulose) forms a strong matrix which provides protection to the polysaccharide from microbial degradation, thwarts its extraction with aqueous solvents which are neutral, and makes it oxidative stress resistant (Vidal et al. 2011). The highest lignin is present in forest biomass (30–60% in softwoods and 30–55% in hardwoods) while it is present in lesser quantity in agricultural residues (3–15%) and grasses (10–30%) (Limayem and Ricke 2012).

3.3.2 Lignocellulosic Biomass for Liquid Fuels by Thermochemical Conversion

The controlled oxidation or heating of the feedstock for the purpose of generating heat and energy products is defined as thermochemical conversion (Wang et al. 2021). With the help of thermochemical conversion, there is an acceleration of deoxygenation reactions in lignolytic biomass. The basic hypothesis behind thermoregulation is that these reactions can lead to the rearrangement of the fundamental structure of lignocellulosic biomass for producing high-grade biofuels in comparison to petroleum fuels (Jiang et al. 2015). It constitutes several techniques such as

- Pyrolysis
- Gasification
- Combustion
- Liquefication (Tables 3.2 and 3.3)

The process of heating biomass in anaerobic conditions so that the chemical compounds like lignin, cellulose, and hemicellulose that make the material decompose thermally into charcoal and combustible gases is called pyrolysis. When it is performed in the aerobic condition, then gasification takes place at a higher temperature ensuing formation of gaseous fuel along with solid residue termed as ash. Higher temperature during gasification prevents the formation as well as condensation of the liquid products (Wang et al. 2021) (Fig. 3.4).

During gasification, carbon monoxide, methane, carbon dioxide, and syngas are produced. As compared to pyrolysis, it requires lesser posttreatment. Gasification takes place in three stages that are drying (up to the temperature of 120 °C), devolatization, i.e., removal of volatile matter, and creation of char followed by gasification (at the temperature above 350 °C). For complete gasification, a temperature above 500 °C is required (Kuzhiyil et al. 2012). The gases formed throughout gasification are used for the indirect production of liquid fuel. This process differs from pyrolysis as they are performed at the higher pressure of hydrogen gas in the presence of a catalyst. Liquefaction is the process of direct creation of liquid fuel from solid or gas. It takes place at a high temperature (200–370 °C) and pressure of 4–20 MPa (Fig. 3.5).

Table 3.2 Lignocellulosic biomass composition

Biomass	Cellulose	Hemicellulose	Lignin	Reference
Rice straw	32–47	15–27	5–24	Sarkar et al. (2012), Van Dyk and Pletschke (2012), Saha (2003)
Rice hulls	24–36	12–19	11–19	Van Dyk and Pletschke (2012)
Rye straw	30.9	21.5	25.3	García-Cubero et al. (2009)
Straw of wheat	30–49	20–50	8–20	Sarkar et al. (2012), García-Cubero et al. (2009), Van Dyk and Pletschke (2012)
Corn cobs	35–45	35–42	5–15	García-Cubero et al. (2009), Saha (2003)
Corn fiber	15	35	8	Saha (2003)
Straw of corn	42.6	21.3	8.2	Sarkar et al. (2012)
Corn stover	39–42	19–25	15–18	García-Cubero et al. (2009), Saha (2003)
Softwood	40–45	25–29	30–60	Limayem and Ricke (2012), Balat (2011)
Hardwood	45–47	25–40	20–55	Limayem and Ricke (2012), Balat (2011)
Seed hair of cotton, flax	80–95	5–20	0	Balat (2011), Van Dyk and Pletschke (2012)
Bagasse (Sugarcane)	40	24–30	12–25	Sarkar et al. (2012), Van Dyk and Pletschke (2012), Saha (2003)
Switchgrass	30–50	10–40	5–20	Limayem and Ricke (2012), Saha (2003), McKendry (2002)
Bermuda grass	25–48	13–35	6–19	Van Dyk and Pletschke (2012), Saha (2003)

Table 3.3 Composition of other lignocellulosic sources

Biomass	Cellulose	Hemicellulose	Lignin	Reference
Fiber separated from municipal solid waste	49	16	10	Li and Huang (2010)
Municipal sludge (Primary)	29.3	Unknown	Unknown	Champagne and Li (2009)
Thickened waste (activated sludge)	13.8	Unknown	Unknown	Champagne and Li (2009)
Sawdust	45.0	15.1	25.3	Van Dyk and Pletschke (2012)
Waste paper (Chemical pulps)	50–70	12–20	6–10	Limayem and Ricke (2012)
Newspaper	40–55	25–40	18–20	Wang et al. (2012), Limayem and Ricke (2012)
Used office paper	55.7	13.9	5.8	Wang et al. (2012)
Magazine	34.3	27.1	14.2	Wang et al. (2012)
Cardboard	49.6	15.9	14.9	Wang et al. (2012)
Paper sludge	33–61	14.2	8.4–15.4	Peng and Chen (2011), Yamashita et al. (2008)
Chemical pulps	60–80	20–30	2–10	Balat (2011)

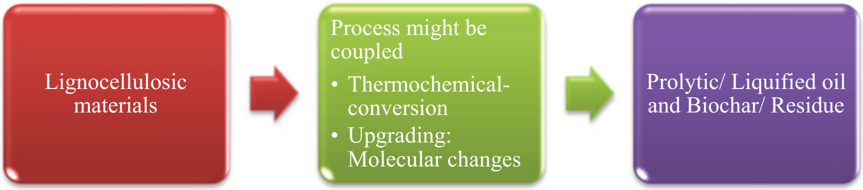
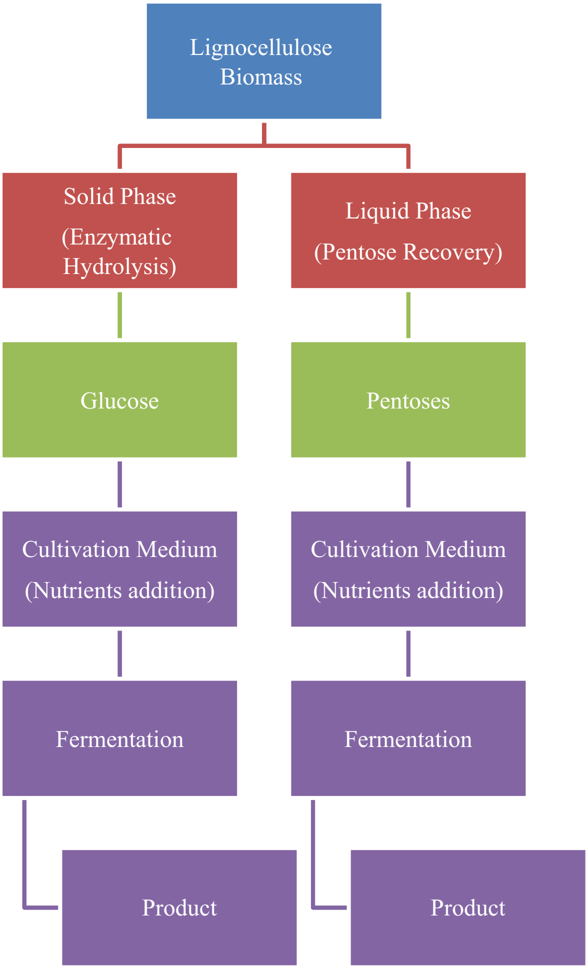


Fig. 3.4 Pathway for thermochemical conversion of lignocellulosic biomass (Jiang et al. 2015)

Fig. 3.5 Using lignocellulose biomass for making of liquid biofuels



3.4 Third-Generation Biofuels

The third-generation biofuels are the fuels that are formed from algal biomass (Brennana and Owendea 2010; Chen et al. 2011). These biofuels are advanced renewable fuels which are obtained from algae through various processes. Algal biomass is rich in oils which are attributed to its ability to photosynthesize abundantly (Anonymous 2014). Algae is an aquatic species with nearly 3000 breeds. Algae possess greater diversity in comparison to land plants because of their ability to reproduce at a faster rate (Suganya et al. 2016). Algae obtain CO_2 from the atmosphere during photosynthesis and convert it into oxygen (Laamanen et al. 2016). Oil from algae is extracted by breakage of the cell structure (Hallenbeck et al. 2016). The principle advantage of algal biomass other than higher oil production is that it can convert nearly all of the feedstock energy into various kinds of biofuels (Suganya et al. 2016). Apart from this, it is useful for the removal of carbon dioxide from the industrial chimney; the process known as algae bio-fixation, animal feed, food products, energy cogeneration after extraction of oil, and treatment of wastewater. Freshwater, brackish water, or even wastewater can be used to grow algae. They can grow at a rapid rate and do not require many nutrients for growth (Guiry 2012) (Fig. 3.6).

Using algae biomass for biofuel production offers several advantages which include:

(a) More tolerance to higher content of carbon dioxide
(b) Lesser consumption of water
(c) No use of pesticides or herbicides for the cultivation of algae
(d) Can be grown throughout the year

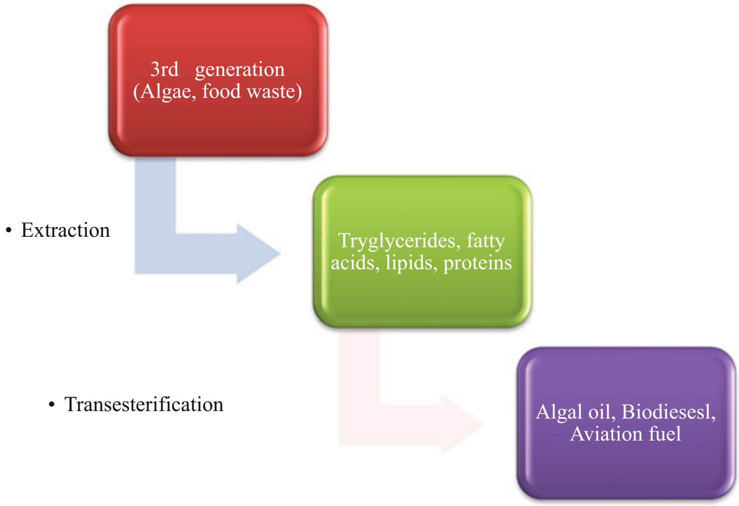
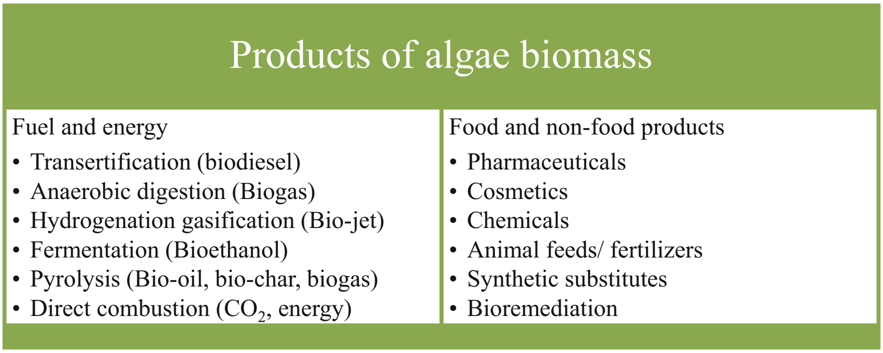


Fig. 3.6 Elementary steps for production of third-generation biofuels



Products of algae biomass

Fuel and energy	Food and non-food products
• Transertification (biodiesel) • Anaerobic digestion (Biogas) • Hydrogenation gasification (Bio-jet) • Fermentation (Bioethanol) • Pyrolysis (Bio-oil, bio-char, biogas) • Direct combustion (CO_2, energy)	• Pharmaceuticals • Cosmetics • Chemicals • Animal feeds/ fertilizers • Synthetic substitutes • Bioremediation

Fig. 3.7 Products of algal biomass

(e) Can be grown under adverse environmental conditions such as coastal seawater, saline, or brackish water

(f) Grown in wastewater (Spolaore et al. 2006, ‘Dismukes et al. 2008, Dragone et al. 2010).

On the contrary, algae cultivation has many demerits like more cost of cultivation in contrast to conventional fuel crops. Also, for the making of algal biomass, there is the obligation of more energy which constitutes nearly 20–30% of the cost of production. Various methods are used for concentrating the algal biomass which include flocculation, sedimentation, filtration, centrifugation, and floatation (Demirbas 2010a, b; Ho et al. 2011) (Fig. 3.7).

Growth rate of algae varies under different growing conditions such as temperature, nutrients, and acidity. Many products can be obtained from algal biomass which includes jet fuel, syngas, bio-oil, butanol, ethanol, and natural fertilizers (Joshi and Nookaraju 2012). Although the conversion methods of algal biofuel production (fermentation, transesterification, and hydrotreatment) are expensive and complex in comparison to fossil fuels and biofuels of other generations. However, there is a potential basis for optimism with regard to this biofuel due to its sustainability and ability to produce more products because of its diversity (EIA 2016). From all the positive features of the algal biomass, it is found that it is one of the world’s most valuable, renewable, and sustainable source of fuel which also helps in controlling environmental pollution (Suganya et al. 2016).

3.4.1 Classification of Algae

Algae is the group having eight divisions, which can be unicellular or multicellular termed as microalgae (microphytes) and macroalgae (seaweeds), respectively (Suganya et al. 2016). Roots, leaves, and stems are absent in microphytes. It can be grown upto hundreds of micrometers and is found in fresh as well as marine water

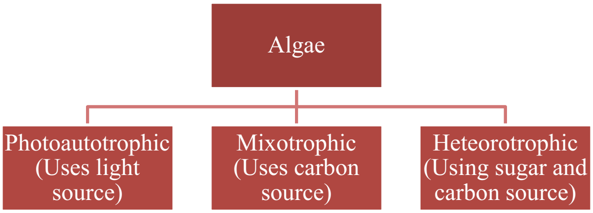


Fig. 3.8 Classification of algae under varied environmental conditions

bodies (Lee and Lee 2016). However, macroalgae has body-like structure. It is found near the sea beds and grows upto hundreds of meters (Suganya et al. 2016). Structure of macroalgae is in such a way as to store and convert the energy without development outside their cells. The easiness in the growth, as well as development of algae, has made them a sustainable source of energy in comparison to any other renewable source of energy (Kandiyoti et al. 2017). Various environmental conditions for the growth of algae is as shown in the figure (Fig. 3.8).

3.4.1.1 Technique of Algal Oil Extraction

For energy production, oil can be produced from algal biomass or these can be transformed into biofuels directly. Oil is usually extracted via various methods which include mechanical and solvent removal (Demirbas 2010a, b). Algae can be converted to biofuel through various options which include change of algal biomass to energy goods, extraction of metabolites, and processing of algal secretions (Ganguly et al. 2021). Steps tangled in the manufacture of biofuels are harvesting followed by dewatering, then extraction, and finally dispensation to energy goods and co-products (Lardon et al. 2009).

3.4.1.2 Harvesting and Drying of Algal Biomass

The cell wall of unicellular microalgae contains fatty acids and lipids that are higher plants and animals. Before mechanical and solvent extraction, harvesting and drying algal biomass is an important step. The harvesting of macroalgae is done with nets which needs lesser energy but for the harvesting of microalgae, conventional methods are used which include flocculation, centrifugation, filtration, foam fractionation (Liu et al. 2013; Prochazkova et al. 2013; Heasman et al. 2008; Csordas and Wang 2004; Rossignol et al. 1999), ultrasonic separation (Bosma et al. 2003), froth floatation, and sedimentation. Type of harvesting methods depends upon the species of algae.

For the extension of algal shelf life, drying is an important method as it prevents postharvest decay (Munir et al. 2013). For drying of microalgae, various approaches are considered to be efficient such as freeze drying (lyophilization), drum-drying, sun-drying, and spray drying (Richmond 2004; Leach et al. 1998; Williams and

Laurens 2010). Due to the presence of a higher amount of water, sun-drying is not an effective method (Mata et al. 2010). Furthermore, the effectiveness of drying method is contingent upon temperature during the extraction of lipids from algal biomass (Widjaja et al. 2009).

3.4.2 Production of Biodiesel

Biodiesel is mono alkyl esters of the long chain fatty acids, which is extracted from biomass and renewable lipid feedstocks (Demirbas 2009; Clark and Deswarte 2008,). Extraction of lipid (diatoms) has been initially done by German scientist during second World War (Cohen et al. 1995). Since the yield of oil from algal biomass is higher in comparison to oilseeds, it can be economically converted into biodiesel with the help of various techniques. Various species of microalgae are used for the manufacture of biodiesel which includes *Ankistrodesmus fusiformis*, *Ankistrodesmus falcatus, Chlamydocapsa bacillus*, and *Kirchneriella lunaris* (Nascimento et al. 2013). The content of oil from microalgae is quite high which usually exceeds 80% by weight of the dry biomass. From an acre nearly 5000–15,000 gal of biodiesel can be produced annually from algae thus reflecting its potentiality for use as biofuel (Spolaore et al. 2006; Chisti 2007) (Tables 3.4 and 3.5).

3.4.3 Production of Bioethanol

Production of bioethanol from algal biomass has been reported by many researchers. Algae are considered to be more appropriate for the manufacture of bioethanol due to the lower content of lignin and hemicellulose in algae as compared to lignocellulosic biomass (Chen et al. 2013). Numerous species of algae are used for the manufacture of bioethanol which includes *Gelidium amansii*, *Laminaria sp*., *Spirogyra sp*.,

Table 3.4 Comparison of algal biomass for the manufacture of biodiesel

Algae			
Feedstock	Biodiesel	Conditions	References
Nannochloropsis sp.	99 g/kg lipid	Oil extraction (n-hexane), transesterification with acid	Susilaningsih et al. (2009)
Spirulina platensis	60 g/kg lipid	Reaction temperature (55 °C), 60% catalyst concentration, 1:4 algae biomass to methanol ratio, 450 rpm stirring intensity	Nautiyal et al. (2014)
Nannochloropsis salina	180.78 g/kg lipid	Freeze drying, extraction with chloroform–methanol (1:1 ratio), alkali transesterification	Muthukumar et al. (2012)
Scenedesmus sp.	321.06 g/kg lipid	NaOH, temperature (70 °C)	Kim et al. (2014)

Table 3.5 Comparison of terrestrial plants for the production of biodiesel (Behera et al. 2015)

Terrestrial plants			
Feedstock	Conditions	Biodiesel	References
Soybean	189.6 g/kg lipid	Hydrotalcite (basic catalyst), methanol/oil molar ratio of 20:1, reaction time (10 h)	Martin et al. (2013)
Madhuca indica	186.2 g/kg lipid	0.30–0.35 (v/v) methanol-to-oil ratio, 1% (v/v) H_2SO_4 as acid catalyst, 0.25 (v/v) methanol, 0.7% (w/v) KOH as alkaline catalyst	Ghadge and Raheman (2005)
Azadirachta indica	170 g/kg lipid	Reaction duration (60 min), 0.7% H_2SO_4 (acid catalyst), temperature (50 °C), and methanol: oil ratio—3:1	Awolu and Layokun (2013)
Pongamia pinnata	253 g/kg lipid	Transesterification with methanol, NaOH as catalyst, temp. 60 °C	Mamilla et al. (2011)

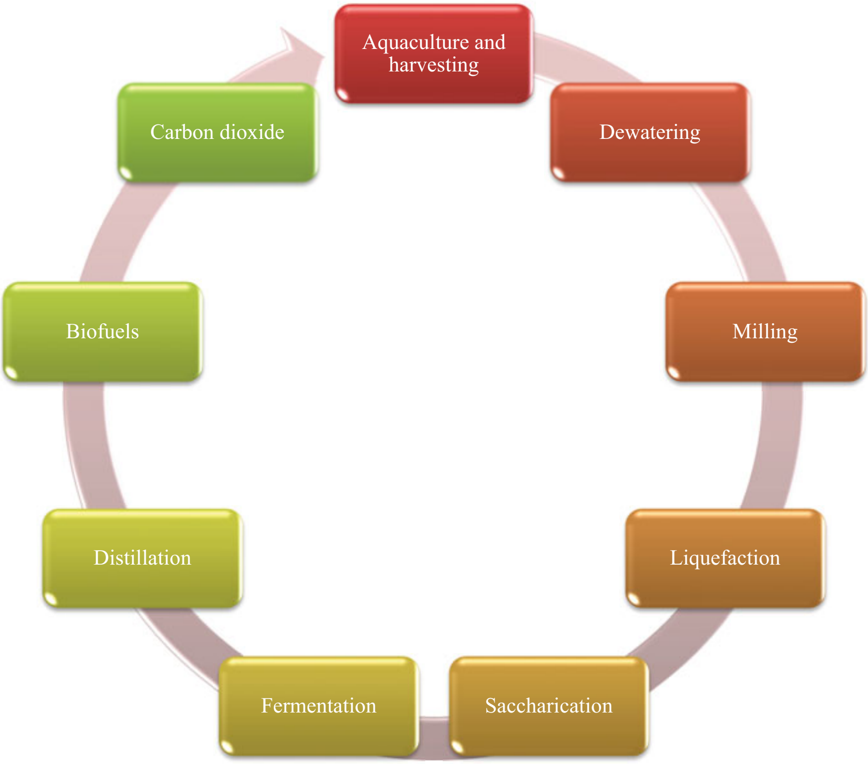


Fig. 3.9 Production of bioethanol from algal biomass through fermentation process

Sargassum sp., *Gracilaria sp.*, and *Prymnesium parvum* (Eshaq et al. 2011; Rajkumar et al. 2014) (Fig. 3.9; Tables 3.6 and 3.7).

Table 3.6 Comparative analysis of bioethanol production from algae

Algae			
Feedstock	Bioethanol	Conditions	References
Chlorococcum infusionum	260 g ethanol/kg algae	Alkaline (pretreatment), temperature (120 °C), *S. cerevisiae*	Harun et al. (2011)
Spirogyra	80 g ethanol/kg algae	Alkaline pretreatment, synthetic media growth, saccharification of biomass by *Aspergillus niger*, fermentation by *S. cerevisiae*	Eshaq et al. (2010)

Table 3.7 Comparative analysis of bioethanol production from terrestrial plants

Terrestrial plants			
Feedstock	Bioethanol	Conditions	References
Manihot esculenta	189 ± 3.1 g ethanol/kg flour	Amyloglucosidase, Enzyme termamyl 1 N HCl	Behera et al. (2014)
Rice straw	93 g ethanol/kg pretreated rice straw	Cellulase, solid-state fermentation, strain, β-glucosidase *Aspergillus niger* MTCC 7956	Sukumaran et al. (2008)
Sugarcane bagasse	165 g ethanol/kg bagasse	Acid (H_2SO_4) hydrolysis, Fermentation at 50 °C	Kumar et al. (2014)

3.4.4 Production of Biogas

As there is a presence of high polysaccharides in algal along with lower content of cellulose and zero lignin, the production of biogas from algal biomass can be done through the process of anaerobic digestion (Yen and Brune 2007; Ras et al. 2011; Zhong et al. 2012; Saqib et al. 2013).

However, for biofuel extraction from algae, there is a requirement of energy-efficient and cost-effective techniques. Use of standard harvesting techniques, design of photobioreactor, biorefinery concept, and other technologies are required which will further decrease the cost of biofuel production from algae.

3.5 Conclusion

Usage of bioenergy crops for energy production can help in employing these alternative sources of renewable energy. Commercial production of these fuels could make us sovereign for fossil transportation fuels using existing engine technologies. The most sustainable sources of energy production are bioenergy crops and biofuels. With the help of first-generation biofuels, enough biofuel cannot be produced without posing threat to biodiversity and food supply. But the use of lignocellulose as a biofuel does not contest with that of food production as these are nondigestible for humans. Also, such biofuels are cheaper than existing fossil fuels. For energy production, oil can be mined from the algal biomass or these can be converted into biofuels directly. Also, algae can convert nearly all of the feedstock energy into various kinds of biofuels. Apart from this, it is useful for the removal of carbon dioxide from the industrial chimney (algae bio-fixation), food products, animal feed, energy cogeneration after extraction of oil, and treatment of wastewater. Hence, it is one of the world's most valuable, renewable, and sustainable source of fuel which also helps in controlling environmental pollution. Thus, bioenergy crops and biofuels are considered to be sustainable sources of energy production as waste products such as forest waste and agricultural residues, manures, industrial waste, and municipal solid waste are used for producing biofuels and bioenergy.

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Chapter 4
Bioenergy from Cellulose of Woody Biomass

Shiksha Arora, Loveleen Kaur Sarao, and Ajay Singh

Abstract Bioenergy is a biodegradable, nontoxic as well as a sustainable alternative that can be used in current infrastructure as an energy source. A significant value has been added by this substitute by reduced carcinogenic emissions, increased lubricity, and several other improved characteristics such as easy handling, economical, environment friendly, and social acceptance. The use of feedstock obtained from forests and cultivated lands attract the government and researchers in designing some regulatory issues and tax relaxations and extracting the maximum yield from the woody biomass, by efficiently dealing with the lignocellulosic recalcitrance, respectively. In a world with increasing population and therefore increased energy and food challenges, local environmental and social gains from bioenergy help in generating energy by using waste obtained from several sectors and non-merchantable wood. There is still some intense research required to acknowledge the effectiveness of the pretreatments in the biorefinery to treat heterogeneous lignocellulosic substrates.

Keywords Lignocellulosic biomass (LBC) · Pretreatment · Bioenergy · Dedicated energy crops · Woody biomass · Sustainability assessment

4.1 Introduction to Bioenergy and Biomass

Worldwide the development rate of growth in human society and population size has raised a demand for food and energy considerably (Alexander et al. 2017). Present needs of energy are fulfilled by fossil fuels, mainly oil both for logistics and production of several materials in the world. Also, it has been estimated that by

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2030 (Guo et al. 2015; Jåstad et al. 2020), there will be a need for about 116 million barrels of oil/day which today is 84 million barrels of oil/day.

India, a rapidly growing and developing country also has a rise in the consumption of fossil fuel by 3% every year, generating pressure on its natural resources (Bajwa et al. 2018). The production of bio-based products can help India become socially stable and self-dependent if its stakeholders focus on the bioenergy enterprise and help the people tackle their energy needs (Ghosh 2016). Indian subcontinent is attentive to global environmental matters hence using biogas and biohydrogen as a substitute for natural gas offers a solution to meet the rising needs of energy without disturbing the environment (Bhatia et al. 2020a, b). Almost every Indian state along with the union territories utilize waste (agricultural, industrial, household, or municipal waste) to transform it into biogas. But the production system is necessarily concerned because of the topographical range from mountains, deserts, and coastal areas to plain areas. Therefore, one transformation technique cannot be operated to produce bio-products in India. The installation and design of the biorefinery system and processing system also affect the performance and the final yield of bio-based products (Bhatia et al. 2020a, b; Hiloidhari et al. 2014; Perea-Moreno et al. 2019; Rosales-Calderon and Arantes 2019).

It has been made evident in several reports and documents in the past 30 years that waste material produced can be used as feedstocks to keep its pace in producing biofuels and biochemicals (Ale et al. 2019; Ho et al. 2011; Saini et al. 2015). This waste material can be obtained from agricultural, industrial, and/or anthropogenic activities and can be used as renewable biomass resources. In this way, the management of waste can be achieved by securing a clean and green future (Ghosh 2016; Omer 2013).

Approximately 14% of the world's primary energy requirements are fulfilled by biomass (Sastry et al. 2019). Four billion m^3 of woody biomass also contributes to this 14% and constitutes about 55% of the bioenergy produced. Woody biomass is usually used as fuel wood or charcoal in the developing parts of the world (Clerici and Alimonti 2015; Guo et al. 2015; Jåstad et al. 2020; USDA Forest Service 2013). Bioenergy or biofuel systems bring into use the unmarketable as feedstock after some pretreatment(s) followed by biochemical, chemical/physical, or thermochemical processes.

Bioethanol, a substitute for petroleum oil and gasoline, as well as methanol can also be produced from lignocellulosic biomasses (LCB) (Horn et al. 2012). Generally, the use of woody biomass and forest crops is usually gaining attention for its ability to reduce and reuse waste, forest fires, value-added products, and creating a marketplace for unmarketable plants like timber (Rosales-Calderon and Arantes 2019; Wang et al. 2017). The biotransformation of LCB into biofuels require several steps to be followed such as pretreatment, fermentation, hydrolysis, and extraction of the bio-product (Kang 2014). On the other hand, the formation of biogas via anaerobic digestion (AD) from the LCB (Amin 2017) has been reported to not require any treatment (Lee et al. 2019).

Overall, the global development and utilization of bioenergy and biofuels will continue to increase, particularly in the biopower, lignocellulosic bioethanol, and

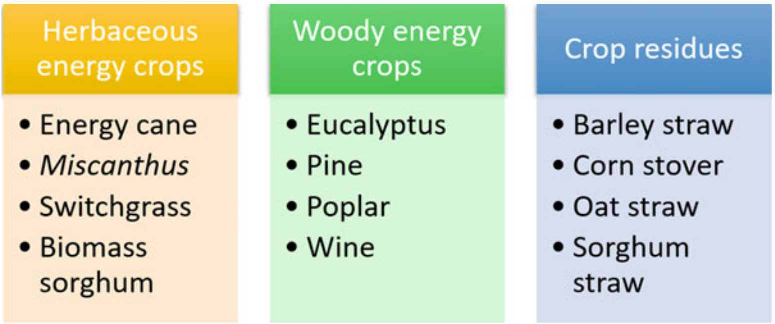

Fig. 4.1 Primary biomass sources obtained from cultivated lands

biogas sectors. It is expected that by 2050 bioenergy will provide 30% of the world's demanded energy (Perea-Moreno et al. 2019; Rosales-Calderon and Arantes 2019).

Bioenergy has been encouraged as an element of climate change and renewable energy strategies in several parts of the world. International Energy Agency (IEA) defines biomass as the biological matter derived from biogenic resources and is accessible on a sustainable basis (Lark et al. 2015). Biomass, representing the raw material required to produce bioenergy or biofuels holds high potential. Bioenergy describes any energy source based on biological matter. Biofuels is the term that is used interchangeably for bioenergy. Commonly biofuels include liquid bioenergy fuels (biodiesel and bioethanol). Unlike coal, gas, or oil, it is counted under renewable energy sources because in theory, carbon dioxide absorbed when trees and plants are burnt is balanced out by the carbon dioxide absorbed by the new ones planted to replace those harvested (Cowie et al. 2018; National Energy Education Development 2008).

All the biogenic raw matter present in the biosphere, be it animal or plant origin, also the matter obtained after their artificial or natural transformation can be used as biomass. This fact makes the concept of biofuels and bioenergy attractive because of their high availability, especially for thermal energy. The resources for biomass have gained importance because of the economic potential it holds because of their availability in abundance (Ahorsu et al. 2018; Pour 2019; World Bioenergy Association 2019). The primary resources are depicted in Fig. 4.1. Also, their by-products can be utilized as sustainable energy sources, and hence are called energy crops, specifically for generating bioenergy (Bombeck 2017). These benefits would be dispersed in rural areas where they are greatly needed and can serve as linkages for further rural economic development (Omer 2013; Perea-Moreno et al. 2019).

The objectives of any biomass energy system include (1) the optimum use and assortment of plant resources and accordingly its procedures, (2) utilization of fertilizer, land, and water, (3) Infrastructure and R & D base, and (4) minimum biomass inputs, maximum bioenergy output (Lark et al. 2015). The scientific investigation and examination of these resources as renewable energy is mainly carried out in the United States, also in China, Germany, India, and Italy. Biomass produces a consistent source of employment for activities such as collection of

Table 4.1 Numerous biomass classes and the raw material obtained from them

S. no.	Biomass Classification	Feedstock obtained
1	Agricultural crops and plant residues	Straw, corn stalks, and cobs
2	Agricultural residues of animals	Manure
3	Agricultural manufacturing residues	Nut hulls, culled products
4	Trees and their residues	Tree removals, prunings
5	Wood manufacturing residues	Sawdust, bark, culled wood
6	Municipal solid waste (MSW	Organic solid portion of waste and trash destined for landfills
7	Fast-growing plants (annuals and perennials)	Poplar and eucalyptus trees and perennial grasses including switchgrass and miscanthus

feedstocks from the farmlands and land owners (Joshi and Mehmood 2011; Tabata et al. 2021). Major categories of biomass are discussed in the following table (Table 4.1).

An extensive choice of polysaccharides constituting feedstock has been used and can be grouped under three major categories: those containing sugars (beetroot, fruits, palm juice, sugar cane, wheat, etc.), those containing starch (cereals, viz., barley, maize, rice, sorghum, wheat, etc., as well as root plants like cassava and potato), and, finally, those containing cellulose (agricultural wastes and fibers, cedar, pine, wood and wood residues, etc.) biomass (Janowiak and Webster 2010; Youngs and Somerville 2012).

All these crops/trees have been analyzed and proposed scientifically for commercial or large-scale bioenergy farming, and are known as energy crops. Following characters are a must in energy crops ideally: low energy input in their cultivation, low energy input in their processing, high yields, and high cellulose and hemicellulose content. Because biomass is basically waste obtained from agricultural produce, they are possibly sustainable when used capably as far as the nature of biomass is concerned keeping in mind the environment and ecology of the planet (Alexander et al. 2017; Pour 2019).

4.2 Effects of Biochemical Composition on the Biotransformation of Biomasses

Biomass consists of three main biochemical components: (1) cellulose, (2) hemicellulose, (3) lignin and the remaining are the inorganic matter present in minor quantities. There are evidences that recalcitrance imposed by the lignocellulosic biomass affects the hydrolysis of the biomass whereas (Sheldon 2020) several reports suggest that the degree of biomass decomposition affects the pyrolysis of

Fig. 4.2 Chemical composition of lignocellulosic biomass (LCB)

the biomass. Furthermore, the decomposition and recalcitrance are influenced by the biochemical composition of the biomass used (Lee et al. 2019). The effect of pyrolysis and level of decomposition is related to the structural stability of these main biochemical components (Tumuluru 2011). The biomass treatment by pyrolysis of celluloses and hemicelluloses results in higher oil yields as compared to the pyrolysis treatment of lignin present in the biomaterial (Guo et al. 2015). Therefore, it is apt to suggest that the biochemical composition of biological material used influences the output of bioenergy and biofuel yield. Biomass feedstock affects the efficiency of biofuel production and energy output. This possesses a major challenge for using biorefinery processes for several lignocellulosic biomasses (Bhatia et al. 2020a, b).

Lignocellulosic feedstocks (Fig. 4.2) are commonly made up of 40–50% celluloses, 25–35% hemicelluloses, and 15–20% lignin, along with several minor constituents such as minerals, soluble sugars, lipids (TGA–triglyceride acid), pectin, and protein (Chandra et al. 2007; Tabata 2018).

Lignin is principally composed of units of phenylpropane and is also a natural polymer considered to be present as the second most prominent component in the LCB (Bonawitz and Chapple 2010). The macromolecular structure of lignin is accountable for its highly energetic chemistry. This energy can be utilized to co-generate power and also as fuel in various productions together with the pulp and paper industry (Alvira et al. 2010). Lignin can also be used as a feedstock biomaterial for the production of hydrogen gas (biogas, etc.) in a biorefinery process (Lepage 2021). The monomers with aromatic phenols present in lignin have also proved to be an appropriate resource in the production of value-added biochemical compounds. These high value-added chemicals are being utilized in the making of bioadhesives and bioplastic. The manufacturing of these monomers from feedstocks creates a new marketplace for bioadhesives and bioplastics. Due to the inconsistency of the LCB in terms of their biochemical nature (Hassan 2018), the pretreatment techniques should be meticulously evaluated before the initiation of any large-scale production system (Socha et al. 2014).

4.3 Generations of Bioenergy Technology

1. First- generation (1G) bioenergy: it is highly produced from edible feedstocks: sugar crops, starch crops, or vegetable oil crops, sometimes animal fats. The biochemical composition is of celluloses and hemicelluloses and can be pretreated with common hydrolysis procedures (Kang 2014). The production of bioethanol, biodiesel, and biohydrogen have has gained interest because of their by-—products and several environmental benefits. There have been several reports and evidences that 1G pathway reduces greenhouse gases (GHGs) by 20–70% from "well-to-–wheels" (Ale et al. 2019; Ho et al. 2011).
   Advanced biofuels involve raw material acquired from other energy crops instead of edible crops, i.e., other than lipids, starch, or sugar (Ramos et al. 2016). The raw materials available for the advanced material are different in each generation but mostly they involve lignocellulose. Higher plant cell walls are composed of these macromolecules abundantly, followed by hemicellulose and cellulose. Therefore, there has been abundant development and reports of converting lignocellulose into biofuel. They are discussed in the following generations. Different pretreatments and conversion combinations are used and accordingly they have consequences on several aspects of agriculture and environment for bioenergy manufacturing (Ahorsu et al. 2018; Ale et al. 2019; Alvira et al. 2010; Hendriks and Zeeman 2009).
2. Second-generation (2G) bioenergy: Because the raw material required for 1G energy production was the edible material, 2G works on that concern by using LCB (nonedible feedstock) reducing the pressure associated with food and energy security (Luque et al. 2010; Mellor 2021). The raw material with most interest is corn stover, rice husk, wheat straw, and sugarcane bagasse, short rotation woody crops. Energy crops such as switchgrass, Miscanthus, big bluestem, Altai wildrye, alfalfa, and yellow sweet clover are grown for some purpose. Of which, perennial switchgrasses (high yield, low production cost) and miscanthus (high yielding bioenergy) are mostly used being C4 plants and having higher carbon dioxide fixation, along with other agricultural wastes. Cellulosic ethanol (biochemical processing) and synthetic diesel, aviation fuel or ethanol (thermochemical processing) are well known as biomass-to-liquids (BTLs). The presence of lignin makes the step of pretreatment necessary. The limitations associated with the cost of biomass and pretreatment techniques make bioenergy from 2G expensive than 1G (Tumuluru 2011). Researchers and industrialists are working on improving the pretreatment step so as to make 2G more efficient in the future (Ahorsu et al. 2018; Ale et al. 2019; Cowie et al. 2018; Parsell et al. 2015).
3. Third generation (3G): This generation uses algae as the raw material and it usually is based on lipid availability, and their capacity to grow in severe conditions, converting flue gases into carbon dioxide. Along with their strengths, there are some concerning geographical and technical problems. *Chlamydomonas*, *Dunaliella,* and various *Chlorella* species are some of the

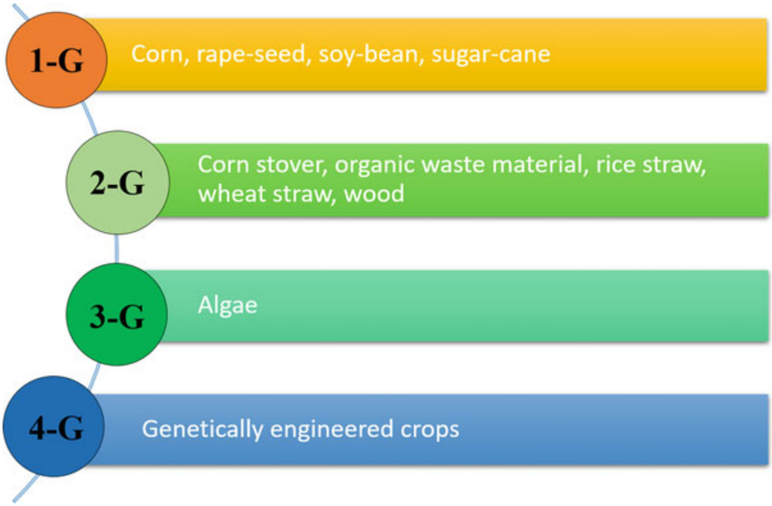

Fig. 4.3 The four generations of biotransformation techniques, along with their biomass

fast-growing algae exploited in bioenergy and biofuel production (Karpagam et al. 2021). Cost-effective 3G bioenergy is believed to obtain after overcoming the problems related to algal cultivation, their harvest, and processing by some genetic modification (Ahorsu et al. 2018; Ale et al. 2019; Meng et al. 2009).

Biofuels belonging to 1G, 2G, and 3G are based on the feedstock used, i.e., biodegradable waste or biomass by origin and all these have some pros and cons related to the biochemistry of the feedstock and the employed processing technique (Bhatia et al. 2020a, b). All the generations and their respective supply sources are represented in Fig. 4.3.

4. Fourth generation (4G): the feedstock brought in use here is cheap, readily available, and unlimited. They convert the energy stored in solar rays (solar energy) into solar-biofuels and/or electro-fuels. The systems involved are basically synthetic biological systems. Therefore, it is a perfect solution to the problems and issues related to the previous generation pathways. Also, these include the modified crops which are dedicated to bioenergy production only (Al-Ahmad 2018), so as to not interfere with the food-based cultivation (Mellor 2021). This section of genetically engineered plants is still under investigation. This generation still in its beginning phase of research and analysis, receives huge attention (Ahorsu et al. 2018; Fu et al. 2011; Parsell et al. 2015).

Even though the availability of substitutes is there as far as the use of wood for biomass power and heat are concerned, which include organic waste, agricultural residues, and dedicated energy crops, they are inclined to be yielding less energy, even with the added cost and difficulty in accumulating and transferring the raw material to the processing units (Youngs and Somerville 2012). Wood and predominantly wood pellets are at present the leading solid biomass article of trade in the world biomarkets. Consequently, it is to be anticipated to be endured as the biomass fuel of choice for a while (Jåstad et al. 2020; Lora and Glasser 2002).

Modern-day bioenergy is a broadly accepted alternative for nonrenewable fossil fuels so as to counterbalance today's dependence on them. This modern-day alternative is expected to hold a principal role in sustainable change in present energy structures, as well as its conclusive influence on maintaining a low carbon growth path along with making contributions to energy modification and safety (Khatiwada 2021). This chapter will discuss the on-farm biomass and bioenergy, recalcitrance in woody biomass, cellulosic biomass, and sustainable energy future. There have been efforts in line simultaneously to make the woody biomass in the cost competition for bioenergy or biofuels. The purpose of bioenergy is to sequester the emitted carbon and eventually reduce the emitted carbon and, in this way, have a substitute for the traditional energies and to use it in generating heat and electricity (Janowiak and Webster 2010).

4.4 Bioenergy from Woody Feedstocks

Forest crops and woody raw materials have become an important source of energy when converted into gas, liquid, or solid biofuels (Ho et al. 2011; Jåstad et al. 2020) (Fig. 4.4). These biofuels then are efficiently able to provide energy for commercial, domestic as well as industrial requirements. If the contribution of cellulosic woody biomass to bioenergy stays static, then according to DOE 2.9 quadrillion BTUs of energy is (projected) generated from wood in 2030 when the need of bioenergy rises to 9.7 quadrillion (Jåstad et al. 2020).

Wood feedstocks are well known to produce electricity, heat, as well as combined heat-power systems (CHP) in individual and co-generation plants, respectively (Amin 2017). Efficiency improvements would reduce the volume of material required. In contrast to the general notion of some current affairs to produce automotive fuels from woody biomass are novel, liquid biofuels have been documented to be produced during the first world war in the United States, also during the second world war in Germany and Switzerland (Perea-Moreno et al. 2019; White 2010).

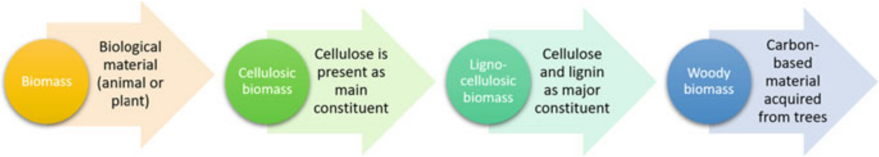

Fig. 4.4 A representational hierarchy of biomass to lignocellulosic woody biomass

4.5 Woody Biomass Energy Feedstocks

Woody biomass (USDA Forest Service 2013) can be defined as any by-product obtained after management, restoration, or hazardous fuel reduction treatments. It also includes alternatives to forest wood. Black liquor obtained easily from the paper industry is one option (Gomez et al. 2008). It has no other use and can be burnt and therefore is among the ideal feedstock for bioenergy. Forest residues are also an option, but biomass energy production depends on the rate of decay and carbon release in the forest (Galik 2021). There are several models projecting the future bioenergy production and required biomass, and the impact of biomass on climate (Zhang 2021). Many of those models have an assumption of mill and forest residues as the main feedstock (Lark et al. 2015). This also is supported by several energy companies and biomass pellet (Solomon et al. 2020; Tabata et al. 2021).

Since the past two-three decades, well-exploited energy crops are also used for biomass energy. Short rotation woody crop (SRWC) (3–14 years) technique for gum trees (*Eucalyptus)*, perennial grasses (willow, *Salix or Miscanthus*), poplar (*Populus*). To keep a balance between bioenergy supply and bioenergy source, much of the area used for bioenergy generation would be growing biomass thereby accommodating a supplementary carbon sink (Axelsson et al. 2012; Robertson et al. 2011; Schwerz et al. 2020; Werling et al. 2014).

For the large-scale biomass, silvicultural treatments similar to the agricultural ones (discing, harrowing, and plowing, trailed by hand cultivation and/or machine implanting of the desired cuttings or rootstocks) are followed, along with herbicides and fertilizers. Training and pruning also ensure the sprouting of the plants. The attained non-merchantable stems are rehabilitated into wood-chips and are transported for their conversion into biomass energy. Crops like willow are harvested after 3 years and poplar is usually ready to harvest after 8–15 years of cultivation. After the harvest, remnants are deserted to be coppiced and the next crop plantation is planned, both in case of willow and poplar. Usually, poplar trees are replanted after every harvest with the amended clones as they are cultivated as single-stem crop (Qin et al. 2012; Solomon et al. 2020).

In this way substantial bulks of biomass are obtained per year with the aim of thinning the forest, preventing wildfire also, and removing the infected and invasive forest species to regulate forest health. All this can be collected and used as biomass, but these do not have continuous supply (Neale and Wheeler 2019; Wang et al. 2020).

4.6 Pretreatment of Biomass in Biorefineries

The presence of lignocellulose in the feedstocks make their utilization tedious (Hendriks and Zeeman 2009). Consequently, there is a need for an additional step before the actual process (Bhatia et al. 2020b). This pretreatment step mainly focuses on the approachability of used chemical treatments and/or microbes to the cellulose by dissociating the cellular wall of the raw material (Tumuluru 2011). The main focus of this step is the elimination of lignin fibers thereby enhancing the efficiency of hydrolysis and further treatments (Farzad et al. 2017; Socha et al. 2014; Yang et al. 2019).

Physical pretreatment involves mechanically disrupting the lignocellulose, and it proves to be environmentally friendly. This process results in increased biomass surface area while causing a decrease in crystallinity of cellulose, maintaining the biomass without expensive impairment. Electron rays, gamma rays, and microwaves are also an option exploited to disrupt the lignocellulose structure (Ho et al. 2011; Horn et al. 2012; Yang et al. 2019).

Contrastingly, more effective methods under chemical pretreatment are also gaining attention (Tumuluru 2011). In this the biomass undergoes acid/alkaline hydrolysis, oxidizing hydrolysis, or solvent extraction (Kang 2014). Pretreatment with lime acid (woody feedstock treated with lime solutions at 180 °C), or with dilute acids (at intermediate temperatures such as 160 °C) are economical and are widely used in agri-based and/or woody biomass treatment (Chandra et al. 2007; Yang et al. 2019).

The other option available is biological pretreatment, which includes biodegradation via microorganisms. This treatment is carried out by fungal spp., of which, oxidative degradation of LCB by white rot fungi is well investigated and exploited (Fu et al. 2011; Hendriks and Zeeman 2009; Saini et al. 2015).

Every pre–treatment technique has its own advantages based on the raw material under consideration. Other pretreatments that are extensively and comprehensively studied are Enzymatic, Hydrothermal, Physiochemical, hot-water, and Hydrothermal pretreatment techniques and are used individually or in combination for better yield. To limit the production of inhibitors during the pretreatment, process conditions (temperature, pressure, pH, concentration, volume, etc.) should be precisely adjusted (Alvira et al. 2010; Grous et al. 1986; Horn et al. 2012).

4.7 Treatment Techniques of the Biomass

The technologies used for producing biomass energy are broadly categorized based on their processing technique and there are four types of treatments (Fig. 4.5).

Firstly, the technique used for approximately three decades and still commonly practiced for electricity and heat in rural, and developing parts of the world, is direct combustion (Runge 2013). The principle followed is to utilize the heat and electricity obtained from combustion (Lee et al. 2019) of the woody biomass for cooking, direct home heating, and/or industrial purposes and driving the steam power-cycle, respectively (Brauer et al. 1996; Ravaghi-Ardebili et al. 2015). The high levels of moisture contents require some combustion promotors to aid in their conversion. One such frequently used promotor is coal. Co-combustion of coal with woody biomass or biodegradable waste has been prevalent in the past for biomass energy production

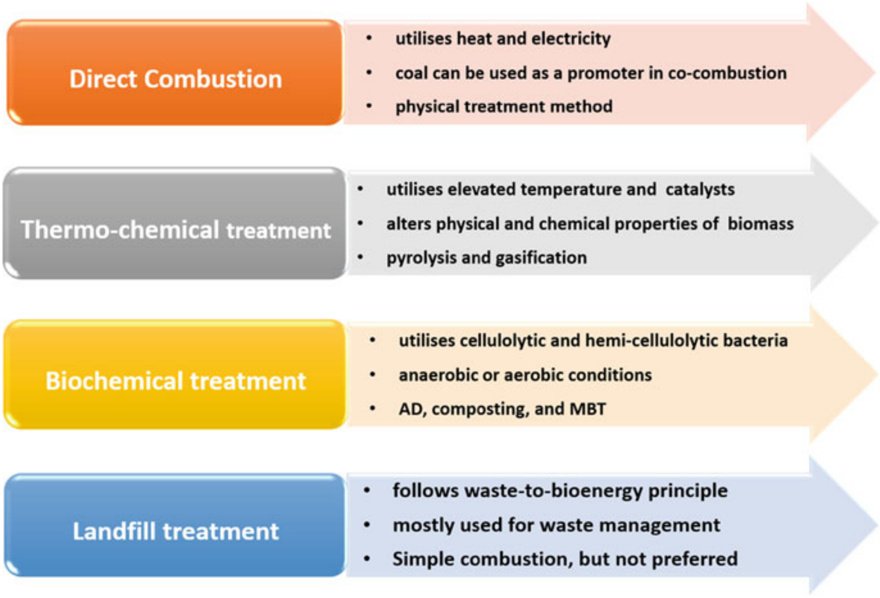

Fig. 4.5 Treatment technologies for processing the biomass into bioenergy

(Runge 2013). Emissions of CO_2, SO_2, and NO_2 cause environmental challenges and the process of co-combustion leading to flying ashes is the key bottleneck and another air pollutant from this technique to be focused during bioenergy recapture (Brauer et al. 1996; Lee et al. 2019; Tabata 2018).

Secondly, thermochemical conversion is utilized to convert biomass by persistent and higher temperatures in combination by means of catalysts supplied into the boiler unit (Chandra et al. 2007; Farzad et al. 2017). This alters the physical properties and chemical structure of the feedstock. This technology includes pyrolysis, gasification, liquefaction, and torrefaction. The basic opinion residing in the method of pyrolysis is the use of both chemical as well as thermal decompositions in amalgamation along with the benefit of catalysts active at relatively lower temperatures (Zoghlami 2019), as well as an extended vapor residence period in the conditions lacking oxygen for renovating the organic elements into the chosen liquid bio-oil, rendering charcoal and gases as by-products. Pyrolysis is a vital technique to convert the woody raw material into the desired crude-like bio-oil (Zhang 2021). After the processing by decomposition, this bio-oil can be transformed into combustion biofuels, primarily to be employed in transportation businesses and chemical industries (Ma and Hanna 1999; Ravaghi-Ardebili et al. 2015; Yang et al. 2019).

Another important thermochemical technology which renovates the raw feedstock into renewable syngas is the method of gasification. The focal component of syngas is H_2, CO, CO_2, CH_4 gases, which are expansively employed in chemical industries, transport, power production, and space heating. Gasification varies from pyrolysis in its prerequisite of relatively higher temperatures reaching between

700 and 1300 °C, with the supply of oxygen in limited amounts or even absence of oxygen in the processing conditions, so as to augment the manufacturing of syngas (Guo et al. 2015; Ravaghi-Ardebili et al. 2015).

Thirdly, the biochemical alteration employs biological as well as chemical procedures, as suggested by the name, along with the assistance from aerobic or anaerobic microbes to transform raw feedstock into biogas and bio-rest (Goswami 2020). The chief technologies operated for this purpose of biochemical renovation involve (1) anaerobic digestion, (Bhatia et al. 2020a, b; Sawatdeenarunat et al. 2016), (2) composting (Antizar-Ladislao et al. 2010; Magotra et al. 2020), and (3) mechanical–biological treatment or MBT (Cimpan and Wenzel 2013; Fei et al. 2018) .

Composting is mainly a digestion process occurring in aerobic conditions and is regarded as a prevalent green value-added technique to process and treat the raw material and biodegradable waste into renewable energy. The elementary notion of composting is to use biochemical methods along with the assistance of aerobic microorganism underneath an open-air milieu for altering biomass into eco-friendly bio-rest, which has varied applications in biofertilizer industries. Conversely, anaerobic digestion, or AD, is regarded as the most popular biochemical method for the production of sustainable and renewable energy (Amin 2017). The process of AD by biological material undergoes four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis, for which different bacteria have to work collectively for biomass transformation into gaseous fuel (Zhang 2021). All around the globe, there are thousands of AD-based bioenergy manufacturing units accepted and its ability to renovate any type of biowaste (Chu and Majumdar 2012; Gould 2015; Vasco-Correa et al. 2018). Following the biochemical decomposition technology, with the aid of anaerobic microbes growing at a persistent temperature maintained in the oxygen-free milieu, the biomass can be transmuted into not only bio-rest or fertilizer but also high-energy biogas. Biogas has its applications after filtration and upgradation in replacing conventional vehicle fuels. The biochemical composition of energy-rich biogas is mainly 60% methane, and 40% carbon dioxide (IEA 2020; Kougias and Angelidaki 2018; Vasco-Correa et al. 2018).

Based on the treatment process involved, the renovation of woody LCB as well as any biodegradable waste are all waste-to-energy (WTE) or waste-to-bioenergy procedures which target the outstanding value of these non-marketable feedstocks in the bioenergy units eventually helping the Municipal Corporation of the nation (Alexander et al. 2017; Kougias and Angelidaki 2018; Omer 2013). Other management practice for biological waste is landfill, in which the residual worth is ultimately lost. This is a cost-effective approach but also is nonsustainable in nature, despite the fact that the percentage of waste landfilled is decreasing uninterruptedly, because of the comprehensive and demanding regulations. WTE is the method of converting any biodegradable waste or non-merchantable organic matter into bio-based energy to be operated in the form of heat and power through the simple combustion technology of the raw biomaterial (Runge 2013). Nonetheless, its denotation has been widened to embrace other sources to recover bioenergy through rapid advancements in the development of treatment technology (Gelfand et al. 2013; Hendriks and Zeeman 2009; Lee et al. 2019; Socha et al. 2014).

4.8 Oil Refinery and Biorefinery

Future has its need and expectations from bio-based economies and renewable sources of energy (Dautzenberg et al. 2011). The concept of bio-based economies is regarded as the foundation stone of bio-economy which rises from thermochemical and biochemical technologies, deployed and integrated to process and convert the waste or biomass macromolecules to several useful bio-products along with their by-products (Alexander et al. 2017; Lee and Schmidt 2014; Lora and Glasser 2002).

Both, bio-based circular economy and renewable biomass to bioenergy exhibit symbiosis and regulate the recycling of carbon into efficient practices (Pinales-Márquez 2021). The economical help from the biorefinery is expected to reduce the poverty in the rural regions by fairly creating job opportunities and increasing pay for small-scale farmers (Gelfand et al. 2013; Skevas et al. 2016; Werling et al. 2014).

The EU has proposed some legislations keeping in mind the improvement and admirations for the circular bio-economy model featuring “reuse and recycle” (Sheldon 2020) and to regulate the linear traditional economy focusing on the model of “make, use, and dispose.” The idea is to break away the latter model in favor of the former circular model. Certain chemicals like citric acid (CA), ethanol, and lactic acid (LA) were not initially incorporated in the targeted potential areas of interest of the EU for bio-based products for the reason that it was considered that research work related to these chemicals had already reached an advanced stage (Pinales-Márquez 2021). Recently, it has been deduced that lactic acid obtained from cellulose and starch sources is a relatively environmentally friendly option (Bombeck 2017). Lactic acid is a monomer of poly lactic acid (PLA), which is now extensively utilized in the production of greener and sustainable energy (Axelsson et al. 2012; Farzad et al. 2017).

Despite all the efforts, LCB needs to be valorized by means of carbon emitted from the raw material to manufacture supplies of attention intended for the trade as a platform chemical. Impact on the environment is another feature supporting the sustainable progress of biorefinery systems over conventional refineries (Ahorsu et al. 2018; Dautzenberg et al. 2011; Gouveia and Oliveira 2009).

Conventional oil-based refineries depend on the rudimentary oil from which naphtha is manufactured. Naphtha is further applied as the raw organic matter in the generation of several platform compounds (viz., benzene, C4–olefins, ethylene, xylene, propylene, and toluene) (Ale et al. 2019; Bramono et al. 2011; Tabata 2018). These chemicals are in turn, utilized in obtaining other important industrial chemicals. Whereas in case of biorefineries, biomass polysaccharides are disrupted and depolymerized into their building blocks (monosaccharides such as arabinose, fructose, glucose, and xylose) and are transformed by fermentation and/or chemical

Fig. 4.6 Woody biomass sources

synthesis into innumerable bio-platform molecules (or BPM) which correspond to the conventional oil-refined platform (benzene, ethylene, etc.) molecules. The oxygen content of BPMs is higher than the petroleum platform chemicals, former can be used to treat the environment-negative oxidation reaction mechanisms into much eco-friendly reduction mechanisms (Ahorsu et al. 2018; Dautzenberg et al. 2011; Socha et al. 2014).

The final products recovered from any biorefinery system are further divided into two main collections, i.e., energy as well as material products. The former is consumed for generating electricity, energy, and heat for transportation purposes. The former is consumed for its chemical purposes and physical properties (Axelsson et al. 2012; Rosales-Calderon and Arantes 2019).

Some of the valuable energy products produced in biorefinery system are the gaseous biofuels (biogas, biohydrogen, biomethane, and syngas), the transportation biofuels (bioalcohol, biodiesel, bio-oil, and FT fuels) (Luque et al. 2010; Meng et al. 2009) and finally the solid biofuels (bio-char and lignin) (Runge 2013). The examples for value-added compounds and appreciated bio-based material formed in a biorefinery chain are (1) organic acids (lactic acid, succinic acid, itaconic acid, etc.), (2) resins and polymers (furan-based resins, starch-based plastics, phenol-based resins) as well as (3) biomaterials (cellulose, bio-fertilizers, paper, pulp, and wood panels) (Ahorsu et al. 2018; Guo et al. 2015; Kai et al. 2016). Bio-based energy groups appropriate for woody feedstock comprise of the following supply sources as depicted in Fig. 4.6.

4.9 Woody Biomass as a Basis for Bioenergy

There is a technology presently available to directly yield heat energy from woody feedstock along with some transitional biofuels intended to be kept or for their utilization in the logistics department. Bioenergy classes appropriate for woody feedstocks embrace the following (Bombeck 2017). From the following list only the first three classes are commonly utilized and have been reported as economically feasible and the remaining classes need some understanding and research work in their development (Jåstad et al. 2020; Joshi and Mehmood 2011; Perea-Moreno et al. 2019).

Bio-heat—by the direct exothermic combustion process, wood or woody biomass can be transformed into chief products of CO_2, H_2O, inorganic ash, and numerous vaporous and particulate emissions, giving off about 8000 BTUs (fuel density) of heat per pound dried wood burned (Malico et al. 2019; Thrän et al. 2015).

Bioelectricity—combining the woody combustion system with the steam boilers (Runge 2013) to produce vapors driving an electrical turbine has been a proven way to generate electrical energy (Logroño et al. 2015; Moqsud et al. 2014; Nealson 2017).

Biofuels—the derivative biofuels from numerous forms of woody feedstock have been made possible (Ramos et al. 2016). These fuels have proved to have the capacity to replace the commonly used perishable and limited fossil fuels (Hays and Ducat 2015; Kawale and Kishore 2019).

Densified wood—woody elements are crushed into specific sized particles (pellets, logs, bricks, etc.) with the aim of increasing the BTU per volume, easy transference, improved storage period, and/or augmented characters suitable for burning (Gilvari et al. 2019; Schwarzkopf 2021).

Charcoal—can be produced by processing the woody feedstock under slow pyrolysis. It can be done by heating the wooden biomass at the range of about 700–900 °F in anaerobiotic conditions for several hours. This would result in thermal degradation of woody elements to subsequently form tar, an aqueous segment, along with biochar (Goswami 2020), a solid fraction mainly composed of carbon and finally a gaseous segment. The solid char is molded into charcoal (Mander et al. 2017; Suttibak and Loengbudnark 2018).

Bio-oil—can be obtained from the aqueous segment consequent of the woody pyrolysis. Swift or quick pyrolysis resultant from instant heating rates, high temperatures, and brief resting periods are the optimal conditions to capitalize the bio-oil production and on the other hand curtails the volumes of solid fragment produced (Kawale and Kishore 2019; Oramahi et al. 2015).

Alcohol—can be developed by processing the lignocellulosic biomass under hydrolysis and fermentation arrangement. During the hydrolysis of the biomass, the wooden elements are transformed by aqueous forms of simple sugars, using acids and enzymes individually or in combination (Kang 2014). While through the fermentation step, yeast ferments the earlier obtained simple sugars into alcohol.

Bioethanol is the frequently produced alcohol and other alcohols such as biobutanol are also probable (Erdiwansyah et al. 2019; McMillan 1997).

Producer gas—An ignitable gas of CO_2, H_2, and other hydrocarbons (HOC) can be obtained by exposing the biomass to the gasification treatment. Gasification is practiced at heating temperatures of approximately 1400 °F in the presence of low or measured amounts of oxygen. (Adhikari et al. 2017). This heating changes the woody biomass into gaseous fragments (also known as the producer gas), along with some ash, char, and tar (Goswami 2020). The gaseous fraction can be often upgraded into many high-value chemicals or into syngas via catalytic conditioning (Moraïs et al. 2015; Sethuraman et al. 2011).

Biodiesel—enzymatic conversion of syngas which has been obtained from the gasification of the lignocellulosic woody feedstock to be utilized in producing renewable biodiesel (Luque et al. 2010). This synthetic biodiesel is similar to the biodiesel produced by the transesterification of triglycerides (e.g., vegetable oils and fats) or perishable diesel conventionally obtained from fossil fuels (Dash and Lingfa 2018; Hassan and Kalam 2013; Meng et al. 2009).

Drop in fuels—with the continuous work and advancements in the field of LCB and its bioenergy (Yadav et al. 2020), the next class of sustainable bio-based energy is directed towards compatible and interchangeable with fossil fuels (Taptich et al. 2018).

4.10 Swachh Bharat Mission (Gramin)

India is entirely dependent on imported coal/fossil oil to satisfy its energy needs. Any country's dependency on the imported resources of energy is critical to its economy and security as a whole. But India along with several other countries in the world is now aiming to find ways to curb its reliance on such imports (Perea-Moreno et al. 2019). In doing so, the country is on the verge of becoming a nation which is ready to develop new technologies, strategies, and frame new schemes and/or schemes to create awareness among the people about the possible substitutes. Along with Indian demand, energy substitutes have become a universal issue (Bhatia et al. 2020a, b).

All this can be potentially done by using waste material to generate biogas or bioenergy (Moqsud et al. 2014). This would help in waste management quite well and use it after processing to produce renewable energy, bioenergy. To promote this initiative Indian Central Government has ongoing policies to support this notion to become a reality one day as it has become a target to be a country that adopts greener options in the form of bioenergy, secures nationwide energy benefits and security, fights weather changes along with generating jobs by advancing these technologies (Axelsson et al. 2012; Hiloidhari et al. 2014).

In 2014, the Government of India (GoI) released this mission with the aim of making the country clean, green, and neat by removing and reusing the garbage so as to process it and transform it into valuable products and by-products. This would generate a huge number of job opportunities in the rural parts of the country focusing on bioenergy production. All these missions need certain policies to support the people involved and to make the process stable and sustainable. One such policy in India is Jaiv Indhan-Vatavaran anukool Fasal awashesh Nivaran Yojana. This policy ensures the financial and fiscal support to be provided to the entrepreneurs involved in bioenergy production using LCB from the agriculture sector and other renewable feedstocks (Khanna et al. 2013; Saravanan et al. 2018). National biofuel Policy (NBP 2018) proposed by the cabinet of India to achieve by 2030 blending of up to 20% of biofuels or bioenergy with conventional fossil-based oil/fuel (http://www.sulabhenvis.nic.in/Database/BiogasTechnology_7026.aspx). Other than bioethanol, algae-based 3G bioenergy, fuels like biogas (compressed biogas, CBG), bio-CNG, and biohydrogen are a priority (Karpagam et al. 2021; Lepage 2021). Another scheme dedicated to the setting up and commercialization of electricity and power generated from biomass is the Ministry of New and Renewable Energy (MNRE). It provides free installation, financial assistance, and maintenance warrantee of the bioenergy plant for 5 years along with proper training to the farmers in the rural areas by conducting several training workshops, and seminars to expand their knowledge and information in this field (Ministry of Drinking Water and Sanitation 2018).

These schemes and missions clearly focus on the government's focus and interest in improving India's bioenergy infrastructure and regulation to its maximum potential. The GoI has targeted to reach the goal line of providing 175 GW electricity from renewable energy capacity in the rural areas 24 h every day of every week by 2022 (Bhatia et al. 2020a, b) with the plans of a simultaneous drop in GHGs by 30–35% till 2030.

4.11 Land Management, Use, and Intensification

The acceptance and the need of bioenergy across the world has resulted in the need of increased production of biofuel-based raw material which in turn has caused huge deviations in land use. There are projections by USDA (United States Department of Energy) regarding a need of approximately 6–11 million ha from the current crop field area and pasture lands to be covered by energy crops/trees to sustainably manufacture roughly 150–380 Tg of bio-feedstock. This indicated the need for change in land use accompanied by crop management practices (Al-Ahmad 2018; Ale et al. 2019).

The consequences of alterations in land use would vary on the basis of the sort of cultivated area and its soil conditions, and management practices performed. In case of pasture land or forest area, land renovation of croplands to manufacture bioenergy by modifying the soil biochemistry and biophysical characteristics of the landscape, which can additionally cause changes in GHG emanation (Gurgel et al. 2007; Sedjo et al. 2015). Several scientific concerns and debates are active mainly on biodiversity losses, food, and land use changes, suggesting that there is a need to completely understand this interdisciplinary field of energy manufacturing along with the associated financial schemes, government policies, inter-sectoral linkages, and engagement of stakeholders in order to minimize the probable challenges during strategizing the bioenergy tactics (Khatiwada 2021).

Perennial grasslands (including miscanthus, native prairie grasses, and switchgrass) and SRWC [including willow, poplar, or hybrid poplar (*P. trichocarpa*)] are a few of the principle means of procuring bio-feedstocks. They require a relatively lower quantity of fertilizer application when equated to the food crops Also the grasses and trees sequester and accommodate carbon and enhance biodiversity (Jungers et al. 2015).

They tend to have an additional advantage in reference to bio-feedstock over the other lignocellulosic crops, that they are to garnered year-round henceforth becoming an incessant and constant source of biomass. Subsequently, they decrease the GHG discharges by approximately 80–90% than that discharged by fossil fuel (Chisti 2008; Harper et al. 2018; Joselin Herbert and Unni Krishnan 2016; Schwarzkopf 2021).

The failings associated with these potential woody feedstocks are that they are expensive and require to be transported hence making their use in the large-scale biomass to bioenergy difficult (Bombeck 2017). To cope with this, sum of farmers should be risen in recent times by encouraging them in making a positive change (Kirkland 2005; Oramahi et al. 2015; Wang et al. 2020).

4.12 Barriers to Feedstock Supply Stability

To have maintainable manufacturing of biofuels and bioenergy, processing units require a continuous and economically available supply of the raw material (Tan 2001). This would depend upon the landowner or the farmer from the urban and rural areas, respectively (Ahorsu et al. 2018). These suppliers are to be motivated and supported to help the government make their contributions in making the country independent of imported energy (Joshi and Mehmood 2011). Landowners and farmers are expected to be unsure and unfamiliar with this field as it is still a developing field in the country. Consequently, there is a need to educate and inform people about the so far emerging market and its importance (Axelsson et al. 2012; Convery et al. 2012).

A major source of woody raw material is obtained from the forest areas; therefore, there is a need to manage the forests and protect them from wildfire and other biotic and abiotic threats (Galik 2021). Forest management and sustainability work hand-in-hand with ecosystem enhancement by outdoing the disturbance-causing administrations and natural stand dynamics (Tan 2001). This can be achieved potentially by preserving the forest biodiversity. Bioenergy production is highly affected when the forest productivity decreases which further is dependent on its existing biodiversity (Gelfand et al. 2013; Robertson et al. 2011; Robertson et al. 2017; Werling et al. 2014).

Forests are providers of wood as well as LCB other than the biodegradable products, waste products, or by-products used for bioenergy development (Hassan 2018). This extraction of forest biomass would cause detrimental effects on the natural biosystem and habitat of other living organisms (Kirkland 2005). Nevertheless, the choices and conclusions on having a balanced extraction along with preserving the diversity of forests will potentially be a system-level evaluation of trade-off (Janowiak and Webster 2010). Furthermore, a feasible biorefinery is a likely answer to the logistic-bottleneck surrounding the raw material supply chain, including drying, packaging, storage, and transportation (Babin 2021; Joshi and Mehmood 2011).

Apart from the barriers associated with the supply chain of the biomass raw material, there are some associated with the processing of woody biomass material (Tan 2001). Researchers are putting their best attempts to find a way to decline the resistance against processing due to the presence of lignin macromolecules rendering the cellulose and hemicellulose microfibrils available for dissolution into the easily convertible glucan chains (Mania et al. 2020; Thompson et al. 1992). Many lignin-containing biomass have been examined already yet many still are to be inspected in finding a way to deal with the limitation of the production of bioenergy at commercial level. One efficient way is to have an extra step in processing of the biomass, i.e., pretreatment (Alvira et al. 2010; Chen and Dixon 2007; Grous et al. 1986). This step is required mainly in all lignocellulosic agriculture-based and woody biomass so as to depolymerize the macromolecule and avail the sugar molecules for transformation into biomaterials and bioenergy. Pretreatments are often used in combination, for instance, hydrolysis of the biomass is upgraded with microwaves (Janowiak and Webster 2010; Joshi and Mehmood 2011; Prasad et al. 2007).

Together, the feedstock eminence and inconsistency have a huge impression on the competence and proficiency of the applied pretreatment. Another challenge in the feedstock supply chain is its storage (Babin 2021). Water molecules in the feedstock as moisture impacts the supply cost as they rise the volume of the woody feedstocks (Ho et al. 2011). Subsequently, biomass is required in truckloads for its distribution.

To help this issue with the delivery of the feedstock, the biorefineries would gain well if they are established nearby to the outsource (landowners or farmers) so as to decrease the purchase cost (Convery et al. 2012; Joshi and Mehmood 2011; Skevas et al. 2016). Procuring the harvest residues for manufacturing bioenergy is expected to help reduce the cost of site preparation, especially in cases when harvest residues clearance is needed on the field to prepare for the next cultivation. Expenditure input on extracting and using the harvest residue is to be determined considering the expenditure related to the processing of the residue on the field. The remaining harvest residue on the fields is destined to burn or is usually managed to help prepare the field area before the next round of cultivation (Bombeck 2017; Kougias and Angelidaki 2018; Strandgard 2021). On the other hand, distant supply sources could deteriorate the feedstock quality and increase the production cost of biomaterials and bioenergy (Antizar-Ladislao et al. 2010; Ghosh 2016; Hassan and Kalam 2013; Logroño et al. 2015; Tan 2001).

4.13 Overcoming Recalcitrance Presence in Woody Feedstock

The recalcitrance of lignin along with crystallinity of cellulose microfibrils are the two chief factors obstructing the derivation of bio-products from lignocellulosic feedstock (Zoghlami 2019). To eliminate this contribution of the lignocellulosic woody feedstock, numerous biological, chemical, and physical pretreatments have been identified to maximize the fermentable sugar yield from the wooden biomass (Ho et al. 2011; Horn et al. 2012; Yang et al. 2019).

Lignin required increased energy input, which increases the cost and complexity of the biorefinery systems, which may also reduce the biomass output of carbon into final bio-products (Hendriks and Zeeman 2009; Oramahi et al. 2015). The aspects related to recalcitrance and communication are not only limited to the cellulose-lignin connections at molecular level, but also governed by a range of factors depending upon the biomass class used, cell-to-cell exchange and interaction, tissue organization (Chandra et al. 2007; Dautzenberg et al. 2011; Mania et al. 2020).

Monolignols (Bonawitz and Chapple 2010), the lignin biosynthesis substrates are to be polymerized by coupling of free radical into guaiacyl (G-subunit), *p*–hydroxyphenyl (H-subunit, also identified as 5–OH–G subunit), and syringyl (S-subunit), which form the lignin hetero-polymerase further polymerized (Vanholme et al. 2010). The genes *Arabidopsis* ferulate 5–hydroxylase (AtF5H), F5H, and caffeic acid o–methyl transferase (COMT) genes are some well recognized and studied genes responsible for monolignol biosynthesis (Fu et al. 2011; Robertson et al. 2011). These genes can be mutated or up/downregulated by using mutation agents or RNA-interference constructs, respectively, for reducing the concentration of lignin and the desired plants can be used as dedicated energy crops with reduced or no pretreatment required (Al-Ahmad 2018). Then once the lignin is removed, treatment for de-polymerization followed by deoxygenation of celluloses (hexose) and xylans (pentose) into furans can be completed. This bio-technological engineering technology of the substrate feedstock trees and the raw material is still under infancy (Jungers et al. 2015; Yang et al. 2019).

The mechanical disruption or physical pretreatment (by electron, gamma, and microwave rays) is an ecological process and focuses on increasing the surface area and decreasing the recalcitrance, preventing expensive mass loss (Hendriks and Zeeman 2009). Physiochemical or Hydrothermal pretreatment technologies such as using hot water (230–250 °C 15 min) or steam explosion (170 °C) are often used before catalytic hydrolysis (Runge 2013). Steam explosion could be of acid or ammonia fiber based on precisely adjusted conditions. The lignocellulosic feedstock is also pretreated via chemicals for solvent extraction, acid hydrolysis (diluted acids at intermediate heating temperatures of 160 °C), base hydrolysis (lime treatment at 180 °C), and oxidizing hydrolysis (Socha et al. 2014; Thompson et al. 1992). The action of fungi on the lignocellulosic feedstock is mild and eco-friendly, as far as the working conditions is concerned as compared to the conditions required for chemical or physical pretreatment. The biological pretreatment process by white rot fungi

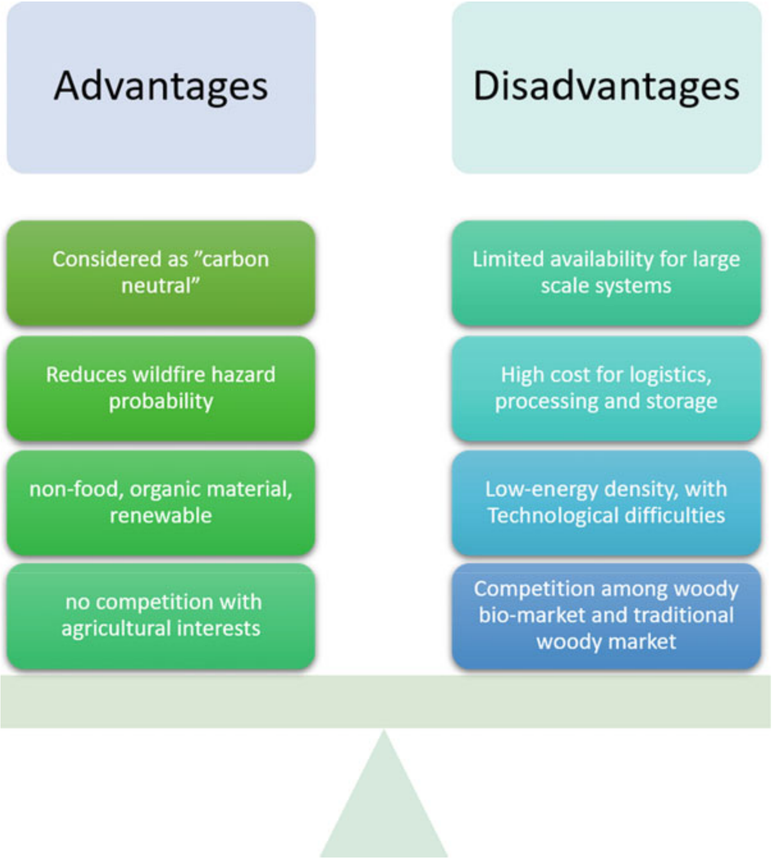

Fig. 4.7 Advantages and disadvantages of wood-based bioenergy production

centrals the oxidative-biodegradation of the constituent lignin (Goswami 2020). The biological agents are sensitive to the operative environment (pH and temperature). Also, there is some research going on for engineering these microorganisms for fermenting the lignin-cellulose-hemicellulose matrix at the commercial level (Fu et al. 2011; Lee et al. 2019; Yang et al. 2019).

Because of some lacking information and five decades of work and research, there are certain knowledge gaps and concerns (Kang 2014) which are to be addressed for better processing, despite all the positive contributions made by bioenergy to the natural habitat and environment (Xing 2020) (Fig. 4.7). The acceptance and understanding of bioenergy being a sustainable option for future demands and a low carbon energy source, itself attracts investors, government, and landowners. The awareness and knowledge of the constructive benefits of bioenergy and the formation of synergies among both food security, and energy needs an all-encompassing integrated resource valuation (Khatiwada 2021).

4.14 Future Research Needs to Fill the Research Gaps

According to the present case scenario, the success of any bioenergy initiative depends on the well-integrated system across the outsource from the fields to the final biomaterial obtained. This success can be only achieved if the key factors of the production system are comprehensively recognized as well as their impact on the climate, habitat, and management (Gurgel et al. 2007; Sedjo et al. 2015). Biodiversity preservation, clean water availability, and climate vindication are a few necessary environmental characteristics to be kept in contemplation. There are several reports over the years to gain a basic understanding that these aspirations can be achieved with some improvement in the current bioenergy systems (Gelfand et al. 2013; Robertson et al. 2011; Werling et al. 2014). To make the best of the LCB or any biomass, the below-listed points are a priority to have a guided path for better production systems:

1. To have a better knowledge about the integrated cultivation of bioenergy crop along with the agro-forest or forest growth. This system would permit a diverse harvesting system delivering resistance against several environmental stresses, providing multiple bio-network facilities (Galik 2021). The presence of biodiversity would mean a presence of possible genetic variability in desirable species. This variability can be accessed against the abiotic as well as biotic stresses which are prevalent everywhere but are extravagant in the marginal regions (Pour 2019; Solomon et al. 2020).
2. The first point completely depends on the fact that the microbiome (microbial rhizosphere) is well comprehended and recognized. The potential variation embodied in the microbiome is chiefly unidentified but this is highly necessary for the plant's nutrient uptake, disease tolerance/resistance, drought stress, etc. The best example for putting the importance of the relation between the two can be understood by the capacity of the microbial rhizosphere to fix atmospheric nitrogen for the uptake of plant (Gouveia and Oliveira 2009; Werling et al. 2014; Youngs and Somerville 2012).
3. To realize the regulatory processes of soil build-up and tenacity and utilize it for increasing the accrual of soil. Decrease in the nitrogen oxide emissions to zero or even retreating them by microbiome consumption of nitrogen oxide is expected in providing synergy in the natural climate (Adhikari et al. 2017; Ale et al. 2019; Kougias and Angelidaki 2018). These targets gain attention for better information about the relationship between soil environment and its microbiome which are highly inclined to the cropping system and ecological inconsistency at several scales with time (Jungers et al. 2015).
4. To appreciate the capacity of biodiversity levels in cellulosic plants in answering and resolving concerns about the primary biodiversity (alpha-level) levels needed to preserve a long-term production system within a low-input ecology under a chronic or intermittent stressor (Jungers et al. 2015). Also, in determining the required levels of landscape level (gamma-level) biodiversity best suited for

disease suppression, preservation of habitat and other crops (Chisti 2008; Robertson et al. 2017; Werling et al. 2014).

5. To recognize an entire field-to-product enterprise having influential synergy with the blend of ecosystem, life-cycle assessment models, and techo-economic models (Lark et al. 2015). They are supposed to be combined in providing some bearable metrics related to ecological variability and administration (Fu et al. 2011; Hays and Ducat 2015; Perea-Moreno et al. 2019). The experimental research cannot be performed in this case therefore there is a need to design models across the value-supply chain, extended to encompass information and familiarity with the environment, which is not clearly observed otherwise (Kougias and Angelidaki 2018).
6. To form the highly functional and beneficial pathway to achieve a justifiable system in a world which is principally ambitious about commercial turn–over. The main objective of the bioenergy system is to alleviate the GHG emissions into the atmosphere, for this adequate information and to the policymakers and subsidy schemers can be provided. This can persuade the landowners and farmers to grow bioenergy crops at suitable sites. A careful justification must be provided to the climate in delivering appreciated environmental services along with opportunities for the landowners and farmers (Guo et al. 2015; Joshi and Mehmood 2011; Solomon et al. 2020).

4.15 Conclusion

Renewable source of energy, biomass, and bioenergy produced from it have become all the time more significant among the local and global environment workers. Countries across the world apprehend the solutions offered by bioenergy and its bio-market against all the concerns related to traditional fuels and associated CO_2 and GHG release. This can be done by increasing the production of bioenergy at a large scale and its consumption levels equivalent to natural gas (Kougias and Angelidaki 2018).

Biomass raw material can be transformed into transport fuels and bio-based electrical energy by either of biochemical, transesterification, and thermochemical pathways in combination or individually based on the final desired product and the feedstocks used (Jungers et al. 2015). The principle of "no carbon left behind" is dependent on our understanding of the molecular basics of non-cooperation, effect of micro bundling, fibril length, and shape. Nonetheless, the conversion of non-merchantable biomass into the resultant bioenergy is considered as robust as far as conversion treatment technology, material handling, and its dispersal among the users, relative to the biofuels derived from conventional agri- or food-based raw material (Lee et al. 2019; Thrän et al. 2015).

Ongoing studies are conducted to address the concerns associated with the prevailing treatment technologies so as to expand the bio-economy and proficiency of any bioenergy manufacturing procedure operated. On one hand, researchers are doing their part for the past three decades in finding the pretreatment techniques (Kang 2014), fermentation microorganisms, and enzymes to overcome the recalcitrance in the way of commercial success by integrating the biotechnological processes with other bioprocesses (Zoghlami 2019), but the policymakers and government, on the other hand, should also be encouraging the framers and landowners from rural areas especially through supportive policy environment and an active targeted-incentive policy (Ale et al. 2019; Joshi and Mehmood 2011; Solomon et al. 2020). The targets could be awards on carbon sequestration, attained percent of renewables on the bioenergy mixture, etc. And the corresponding incentives could be in any form such as subsidy, carbon tax relaxation, and emission trading for "setting the playground" on which the bioenergy production system is established. The higher demands of biomass have a positive effect on the green, clean, and "carbon dioxide-neutral" energy production facilities, keeping in notice that the supply source should be proximal (Dash and Lingfa 2018; Qin et al. 2012).

It is clearly understood that without a subsidiary legislative environment for the manufacturing of bio-based energy, the progress made to finding a sustainable solution to climate change and increasing demands in the future for energy by day will not be understood and found up to its potential (Xing 2020). A futuristic strategical atmosphere will have to be a blend of both the desired aims as well as supporting enticements (Axelsson et al. 2012; Hassan and Kalam 2013; Saravanan et al. 2018). The desired aim could be agreed upon conquering confident amounts of renewable till a definite date, along with the interchange of renewable bioenergy permits, recompenses for investments in carbon sequestration, and of course, promotion among the communal by the administration officials. Whereas the supportive incentives could be: climate change (micro as well as macro-climate) carbon duties (carbon-levies), carbon trading, charges, allowances, aids, and elevated devaluation taxes; all directed to the "leveling the ground field" for the expected amplified usage of bio-based renewable energy (Robertson et al. 2011; Vasco-Correa et al. 2018).

The grave importance of determining the cross-cutting apprehensions of eco-technological, environment, legislative, and socio-political issues regarding the distribution of bioenergy for greener and sustainable advancements. Investment strategies are required to be considered while determining the complications and transformations also need to be addressed allied to the interdisciplinary bioenergy (Janowiak and Webster 2010; Khatiwada 2021; Lepage 2021). A plethora is associated with the understanding and examining of bioenergy in the conversion/transformation technologies, or the supply value-chains or the eco-technological scrutiny of numerous known bioenergy manufacturing pathways. Nonetheless, a slight commitment focused on how the manufacturing of bioenergy in hand with its consumption would be massively advantageous in having sustainability in development and growth (Khatiwada 2021).

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Chapter 5
Potential Technologies for Advanced Generation Biofuels from Waste Biomass

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Abstract Biofuels are quickly emerging as a way to "modernize" the use of biomass, enhance access to renewable liquid fuels and help cope with energy expenses, global warming, and security issues linked with fossil fuels. The review offers details on biofuel conversion technologies and understands the limits of "first-generation" biofuels and provides meaningful accounts on "second-generation," biofuels that abolish direct competition between food and fuel associated with most first-generation biofuels. However, these systems demand a greater level of sophistication, investments per production unit, and more extensive facilities than first-generation biofuels. The transgenic production of cellulases from plants is being undertaken to increase the efficiency and production of both enzymes and lignocellulose degradation. The convergence of developments in biological sciences, including biotechnology, carbon capture, and storage and state-of-the-art bioconversion approaches enables the idea of a "fourth-generation" biofuels and bioenergy systems to be developed. Fourth-generation biofuels are thought to help reduce greenhouse gas (GHG) emissions more efficiently than other biofuels by being more carbon-neutral or even carbon-negative.

Keywords Biomass · Biofuel generations · Bioethanol · Biogas · Biotechnological approaches

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5.1 Introduction

Fast technological advancement has raised the demand for conventional fuels worldwide as about 85% of total energy demand is quenched by these fuels (Mahapatra and Kumar 2017). However, there is a quantitative limitation of these sources and they are also likely to be exhausted in the coming years. The extensive usage of these fossil fuels over the years has devastating impacts on the environment. These limitations have necessitated the need to prioritize emerging potential technologies and processes that accelerate the transition from the use of fossil fuels to the use of renewable energy resources to solve future global energy needs, as well as to protect and/or reestablish the natural environment. (Srirangan et al. 2012). Thus, energy efficiency and renewable energy technologies are the core elements of that transition, and their synergies play an important role to solve real-world problems. Huge quantities of waste biomasses are being generated daily around the world by wastewater treatment plants, livestock farms, the food industry, agriculture, etc. The treatment and management of these sources of waste is an environmental and social challenge faced by most nations. However, in another context, these wastes can be considered as essential raw materials for major waste-to-energy (WtE) projects. High greenhouse emissions, deadly air pollution, unstable fossil-based energy prices, and strong growth of global transportation fuel demand have boosted extensive research efforts in developing bioenergy (energy derived from any fuel that is produced from biomass).

Biomass is a term used for all plant-borne organic matter, including bacteria, trees, and plants. Biomass is created through the use of green plants which, through photosynthesis, turn sunlight into plant material and include all land- and water-based vegetation. Biomass can be used as an organic matter where light energy is contained in chemical bonds. Such compounds release the accumulated chemical energy as the bonds between the adjacent C, H, and O molecules break up through fermentation, burning, or decomposition. Biomass is a significant source of energy for human beings, as it is assessed to account for 10–14% of global energy production. The chemical energy contained in plants is found in the plant materials cellulose, hemicellulose, and lignin, and their amount varies depending on the plant type. The relative amounts of cellulose/hemicelluloses/lignin are crucial aspects for assessing the adequacy of plant species as energy crops (McKendry 2002). Waste biomass is a renewable resource and therefore has been considered as an alternative feedstock to provide sustainable energy in the future. Historically, waste biomass in the form of firewood has been traditionally used to provide energy to humans through direct combustion. In industrialized countries, a wide range of feedstocks are available in abundance for biofuel production, including agricultural and forestry residues, building and industrial waste, and municipal solid waste (MSW).

Advanced technology is in the nascent stages to convert biomass into various sources of subsidiary energy, including power, gasoline (mainly methane or carbon monoxide mixtures), liquid biofuels (mainly biodiesel and alcohol), solids, and also hydrogen. The goal of biomass conversion is to offer biofuels with specified fuel characteristics that can meet the basic requirements of fuel quality. Liquid or gas biofuel can be used in a wide variety of uses, including transport and industrial processes utilizing high temperatures (Zinoviev et al. 2007).

Biofuels are rapidly becoming a global replacement for petroleum-derived transport fuels, leading to energy savings, carbon stability, and global warming issues related to liquid fossil fuels. Biofuels can potentially serve to replace conventional petroleum-derived fuels. In spark-ignition engines, alcohol fuel can replace gasoline while biodiesel, green diesel, as well as DME, are ideal for use in compression ignition engines. A variety of different hydrocarbon fuels can be produced in the Fischer-Tropsch process, of which diesel fuel is primarily used for compression ignition engines. While biofuels in the transport sector are of considerable importance, the use of these biofuels for cooking, particularly in rural areas of the developing world, can be used globally with broad relevance. The burning of such cooking fuel would produce pollutant emissions less than those from solid fuel cooking. About three billion people in developing countries are burning solid fuels and are seriously harmed by indoor air pollution (International Energy Agency 2006). Biofuels could thus play a critical role to improve people's health. The scale of biofuel production needed for cooking purposes is however much smaller than that necessary for fuel transport. One estimation is that about 4 or 5 exajoules of safe cooking fuel a year are enough to satisfy three billion people's basic cooking needs. It amounts to about 1% of the world's commercial energy consumption (Goldemberg et al. 2004). The use of biomass residues and waste as primary resource for biofuels is a promising proposal to reduce environmental issues concerning waste disposal, by converting the wastes that would otherwise have been left to decompose into useful biofuels. Considering the world's energy demand crisis, waste management and disposal, global warming, and fossil fuel depletion, this chapter has been focused on the research and systematic review works that can offer advanced solutions or orientations to simultaneously reduce waste biomass and create a sustainable energy source as this can be a step in contributing/fulfilling the current knowledge gap between energy, the environment, and climate change.

5.2 Waste Valorization: A Concept

Different potential conversion technologies can provide a promising solution for the dual purpose of waste management and renewable energy production. Waste valorization has been shown as a process of converting waste biomass into useful products like biofuels, chemicals, etc. It relies on the assumption that even after the intended use, the waste biomass still contains untapped polymeric substances that can be converted to either energy or other chemical forms. Such products make waste a valuable resource that should not be left unharnessed. So, the concept is currently being applied to both wastes, i.e., synthetic as well as biowaste, with promising success, and it is the basis of the current waste-to-energy (WtE) approaches. Moreover, due to the fast depletion of natural/primary resources,

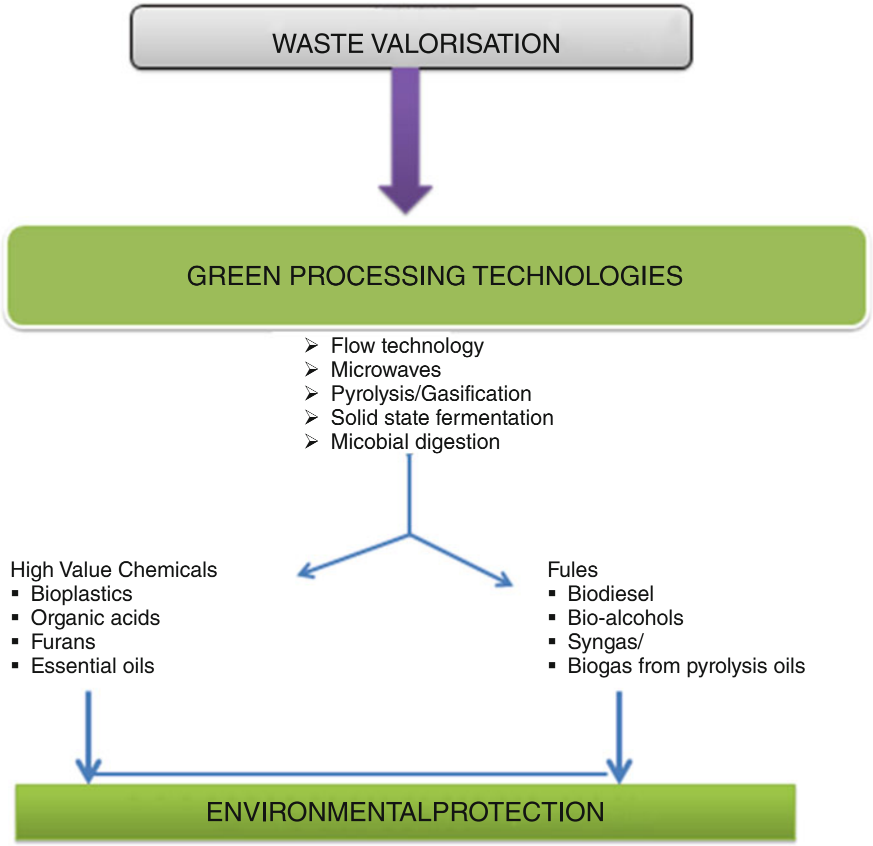

Fig. 5.1 Waste biomass valorization is essentially a concept of recycling waste into more usable industrial chemicals

waste valorization is not a luxury for academic exploration but rather a much-needed technology for cost-effective and sustainable waste management options and generation of renewable energy as well as production of high-value chemicals such as bioethanol and materials such as nano-bioplastics (Fig. 5.1). Apart from renewable energy and high-value chemicals, waste valorization offers additional advantages including amelioration of waste mal-odors and environmental pollution, and reduction of the volume of waste, resulting in the recovery of more space for other uses. In a typical process, high-value chemicals are produced from waste residues through any of the four downstream processing, i.e., using inorganic and organic chemicals, a combination of chemicals and enzymes, biotechnological approach using genetically engineered organisms, and green processing technologies whereby only water is used as a reagent in waste volarization (Arancon et al. 2013).

Waste-to-Energy (WtE), defined as the process of recovering energy in the form of either electricity and/or heat from waste, Bosmans et al. (2013) apply the waste

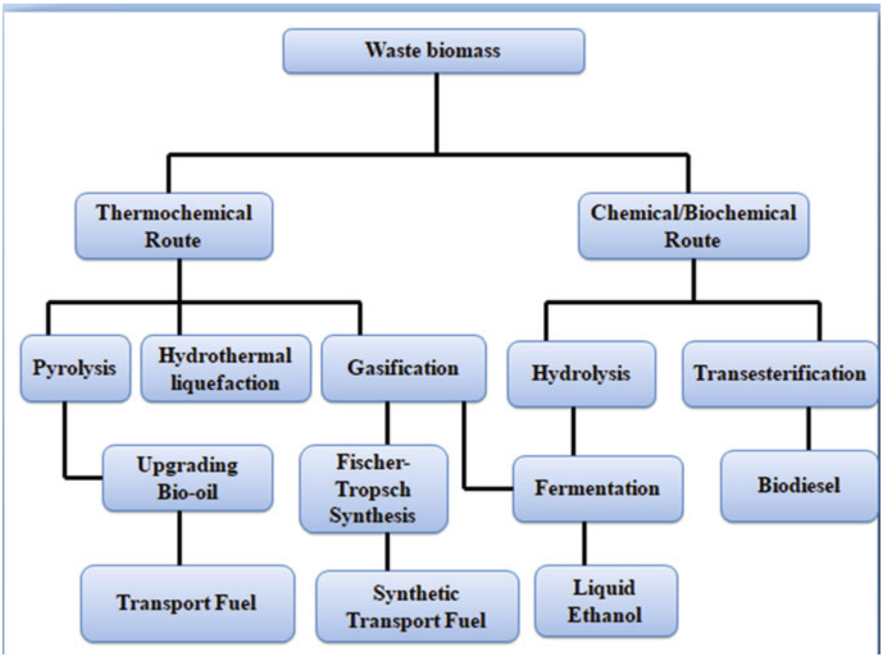

Fig. 5.2 Different waste-to-energy conversion technologies

valorization concept to generate renewable energy such as heat and biofuels (biogas, syngas, and bioethanol). Waste-to-Energy technologies are categorized into two major groups namely; (a) thermochemical processes comprising combustion, pyrolysis, and gasification; and (b) biological processes comprising anaerobic digestion and bioethanol fermentation (Fig. 5.2 and Table 5.1). These WtE technologies provide cheap sources of energy that is crucial for industrial processes such as drying, packaging, and preservation of industrial products.

Valorization research has evolved through the years, with many techniques and developments achieved in recent decades (Table 5.1). Waste biomass including wheat, orange peel residues, lignocellulosic feedstocks, etc., are currently explored as sources of chemicals and biofuels. Pfaltzgraff et al. (2013) noted that the valorization of food wastes into fine chemicals is more advantageous and less energy and time-consuming as compared to its possibilities for biofuel production. Because of this, related waste processing technologies, particularly related to biofuel production have also been proposed to address energy efficiency and profitability from a range of different lignocellulosic feedstocks. Toledano et al. (2013) reported a lignin deconstruction approach using a novel Ni-based heterogeneous catalyst under microwave irradiation. Different hydrogen donating solvents were explored for lignin depolymerization, finding formic acid as the most effective hydrogen donating reagent due to the efficient generation of hydrogen for hydrogenolysis reactions (from its decomposition into CO, CO_2, and H_2) and its inherent acidic character that

Table 5.1 Different methods for conversion of waste biomass into bioenergy

S. no.	Method	Type of bioenergy	Type of feedstock	Composition/Yield/Efficiency/Energy recovery	Operating condition	References
1.	Gasification	Fuel gas	Pine woodchips	Syngas composition: H_2 gas: 26–42% CO gas: 25–37% CO_2 gas: 16–19% CH_4 gas: 8–11%	Dual circulating fluidized-bed gasifier Temperature: 700–900 °C Steam to fuel ratio: 0.3 $kg \cdot kg^{-1}$	Ngo et al. (2011)
		Bioelectricity	MSW and hazardous waste	Plant efficiency: 41.10% Power:81 W	Co-gasification using plasma gasifier Composition of MSW: 90%wt Oxygen volume: 95%	Mazzoni et al. (2017)
		Fuel gas	Paddy straw	Efficiency: 33.78% CO gas: 2.01% H_2 gas: 5.48% CH_4 gas:0.51%	Temperature: 600–800 °C Oxygen ratio: 33% Airflow: 0.6 $Nm^3 \cdot h^{-1}$ Feed rate: 1.12 $kg \cdot h^{-1}$ Equivalence ratio: 0.2	Liu et al. (2018)
2.	Liquefaction	Biocrude oil	Microalgae	Yield: 60.0%	Temperature: 350 °C Reaction time: 15 min	López Barreiro et al. (2015)
		Biocrude oil	*Jatropha curcas* cake	Energy recovery: 41.48–54.78%	Temperature: 250 °C Catalyst: ChCl–KOH DESs Reaction time: 40 min	Alhassan et al. (2016)
		Bio-oil	Domestic sewage in high-rate ponds	Yield: 44.4%	Temperature: 300 °C Operation time: 15 min Biomass/water ratio: 1/10 ($kg \cdot kg^{-1}$)	Couto et al. (2018)

		Crude biodiesel	Wet and dry microalgae (*Nannochloropsis* sp.)	Biodiesel yield Wet microalgae: 14.18% Dry microalgae: 12.48%	Fermentation and ethanol assisted liquefaction Temperature: 265 °C Ethanol: 15% (v/v) Ethanol to algae ratio: 2:1	Rahman et al. (2019)
3.	Pyrolysis	Bio-oil	Sugarcane residues sugarcane leaves and tops	Yield: Sugarcane leaves: 52.5 wt% Sugarcane tops: 59.0 wt%	Fast pyrolysis **Temperature**: Sugarcane leaves (429 °C) and sugarcane tops (403 °C) Nitrogen gas flow rate: 7 L·min^{-1} Biomass feed rate: 300 g·h^{-1}	Pattiya and Suttibak (2017)
		Biochar, Bio-oil, and gas	Greenhouse vegetable wastes and coal	Biochar yield: 40.22, 54.65, 45.93%	Fast pyrolysis Temperature: 500 °C Catalyst: calcite, dolomite, and zeolite Nitrogen gas flow: 1450 mL·min^{-1}	Merdun and Sezgin (2018)
		Syngas (H_2 and CO)	Spent coffee grounds loaded with cobalt	Yield concentration H_2: 1.6 mol% CO: 4.7 mol%	Catalyst: Co-biochar Generation of H_2: CO_2 as atmospheric pressure Reaction time: 110 min Generation of CO: Temperature 700 °C	Cho et al. (2018)
		Bio-oil	beech wood	Yield: 86.10%	Hydrotreatment Temperature: 250 °C Catalyst: $NiCu/Al_2O_3$	Boscagli et al. (2018)
4.	Anaerobic digestion	Methane	Biomass from coculture of microalgae and bacteria	325 mL CH_4/g volatile solids	CaO pretreatment Temperature: 72 °C Reaction time: 24 h Anaerobic incubation temperature: 35 °C	Solé-Bundó et al. (2017)
		Methane	Sewage sludge	181 mL CH_4/g volatile solids	Thermal pretreatment Temperature: 95 °C Reaction time: 10 h Anaerobic incubation temperature: 35 °C	Passos et al. (2015)

(continued)

Table 5.1 (continued)

S. no.	Method	Type of bioenergy	Type of feedstock	Composition/Yield/ Efficiency/Energy recovery	Operating condition	References
5.	Alcoholic fermentation	Bioethanol	Microalgae biomass (*Chlamydomonas mexicana*)	0.22 g ethanol·L^{-1} h^{-1}	Simultaneous enzyme hydrolysis of biomass and fermentation with immobilized yeast Anaerobic incubation Temperature: 30 °C RPM: 120	El-Dalatony et al. (2016)
		Bioethanol	Biomass of two microalgae strains	0.18 kg·kg^{-1} biomass	Combined sonication, heat, and enzyme pretreatment of biomass Anaerobic incubation Temperature: 37 °C pH 5.5 Hydraulic retention time: 2.5 days	Hwang et al. (2016)
		Mixture of acetone, butanol, and ethanol	Microalgae biomass (*Chlorella vulgaris*)	0.32 g·L^{-1} h^{-1}	Lipid extraction of biomass: ionic liquid, acid hydrolysis (2% H_2SO_4), and detoxification (resin L-493) of biomass residue, then fed to yeast under anaerobic condition	Gao et al. (2016)
6.	Photobiological hydrogen production	Hydrogen	Microalgae biomass (*Chlorella* sp.)	11.65 mL·L^{-1}	Medium: modified TAP Glycerol concentration: 16 g·L^{-1} Anaerobic condition pH: 6.8 Light intensity: 48 μmol·m^{-2} s^{-1} Temperature: 30 °C Reaction time: 24 h	Sengmee et al. (2017)
		Hydrogen	Microalgae biomass (*Chlamydomonas reinhardtii* CC124)	0.60 mL·L^{-1} h^{-1}	Medium: sulfur-free TAP 40 mg·L– 1 nanoparticle Anaerobic condition Reaction time:72 h	Giannelli and Torzillo (2012)

7.	Transesterification (Acid/Base Enzyme Catalyst)	Biodiesel	Crude oil of *Pongamia pinnata, Jatropha curcas, Calophyllum innophylum*	90%	Esterification: Temperature: 60 °C Reaction time: 3 h Transesterification: mixture of oil with methanol Temperature: 60 °C Reaction time: 2 h	Yunus Khan et al. (2018)
		Biodiesel	Refined sunflower oil	Yield: 94%	Optimized conditions: Methanol-to-oil molar ratio: 9:1 Catalyst: 0.3 wt% Temperature: 67 °C Reaction time: 3 h	Bet-Moushoul et al. (2016)
8.	Supercritical fluid	Biodiesel	FAME	100%	Optimized conditions: Methanol-to-oil molar ratio: 40:1 Pressure: 200 bar Temperature: 350 °C Reaction time: 10 min	Farobie and Matsumura (2015)
		Lipid	Corn	99%	Optimized conditions: Temperature: 60 °C Pressure: 300 bar CO_2 flow: 3 ml/min 10 min static extraction 150 min dynamic extraction	Toribio et al. (2011)
9.	MFC	Bioelectricity	MSW	Power density: 1817.88 $mW{\cdot}m^{-2}$	Two chamber MSW MFCs with alkali hydrolysis pretreatment	Chiu et al. (2016)
		Bioelectricity	Fermentable household waste	Power density: 29.6 $mW{\cdot}m^{-2}$	Dual-chamber MFCs	Chatzikonstantinou et al. (2018)

induces acidolytic cleavage of C-C bonds in lignin at the same time. The heterogeneous acidic support also acted as a Lewis acid, coordinating with lignin thereby promoting acidic protonation, and eventually dealkylation and deacylation reactions. Lignin deconstruction to simple aromatics including syringaldehyde, mesitol, and related compounds could serve as the basis for a new generation of renewable gasoline.

Biological treatment technologies including anaerobic digestion and composting have been reported extensively in past years. Under anaerobic digestion, biogas is generated as the main product. Takata et al. (2012) reported the production of 223 m^3 biogas from 1 ton of food waste. However, Bernstad and la Cour Jansen (2012) reported that the yield of biogas production may vary depending on the composition of waste and the existence of detergent. Numerous studies show that the lack of enough nutrients limits the ability of enzymes to digest waste (Zhang et al. 2005). This can divert waste from landfill, and thus prevent the emission of GHG to the environment. Also, the solid residues can be used as compost, which can reduce the amount of used chemical fertilizers. Economically, anaerobic digestion can generate electricity on-site and may reduce energy cost. Also, it can be adopted in sewage treatment facilities thereby eliminating transportation costs. Another way to valorize waste is by incineration for energy recovery. However, burning food waste is an energy-intensive process and may remove important functional groups from the treated feedstocks.

Frederick et al. (1996) experimented gasification and pyrolysis of primary sludge generated from a recycled fiber paper mill for producing a biofuel gas for energy and reusing the residual ash residue as an admixture mineral for Portland concrete. The authors performed the gasification experiments in a batch furnace over a temperature range of 500–900 °C, using air as the gasifying medium with an equivalence ratio of 0.58. Higher temperatures above 900 °C were reported to be effective in the calcination of kaolinite and $MgCO_3$ compounds, and thus the overall yields of ash inorganic residues after gasification were reduced to approximately 45% of the total dry sludge feed input. The ash was later tested for its properties as a concrete admixture mineral and was found to be slightly outside the required specification. The authors carried out a material and energy balance of the total gasification system. The thermal efficiency of the process, which was defined as the heating value of the product gas plus the energy available from steam generation divided by the total energy input, was 69.8% (at a reference temperature of 25 °C). It was stated that there was enough residual heat from the product gas cooling to provide heat energy for both drying the sludge and preheating the air used for gasification. The product gas contained 17.1% hydrogen and 5.4% carbon monoxide, by volume; the remaining composition of the gas was not stated. The gas produced had a gross heating value of 2.64 MJ/Nm^3 (dry basis), and the authors discussed that using oxygen-enriched air for the gasification reaction would help quite considerably to increase this value as it reduces the N_2 present. However, using a gasifying agent with high oxygen purity would in turn incur higher operating costs of the gasification process.

Mendez et al. (2009) experimented the pyrolysis behavior of a range of paper mill waste materials using SEM, FTIR, DRX, and TGA techniques. In general, paper mill sludges from recycled paper showed high $CaCO_3$ and clay contents, as well as lower values of organic matter, and this was more profound in wastes obtained from the deinking process ($CaCO_3$ content of 44–46.9 wt%). This is due to the removal of inorganic fillers from recycled paper. FTIR and DRX of the primary sludge and reject wastes, which were derived from a paper mill producing paper from virgin wood, revealed an elevated content of cellulose fibers when compared with recycled paper sludge. TGA at 900 °C with a heating rate of 10 °C/min using nitrogen was implemented on the samples. TGA indicated that the degradation of cellulose, as well as the presence of ash, lowered the starting temperature for weight loss. For the recycled paper sludge samples, weight loss continued at temperatures higher than 500 °C due to kaolinite dehydration and carbonates decomposition.

5.3 Biofuels Types and Generations

Biorefineries produce vast ranges of biofuels. Biofuels are commonly referred to as the "fuel of the future," the idea was first conceptualized and developed by Rudolph Diesel in the late nineteenth century. Since its inception, biofuels have been used primarily in the automotive industry due to their potential to replace gasoline and diesel. However, advancements in the field have shown that aside from its utility as a sustainable transport fuel, biofuel can also be used for manufacturing, cosmetic, pharmaceutical, heating, and agricultural processes. Nevertheless, there have been ongoing debates concerning the use of agrofuels over fossil fuels despite the former's obvious market potential and environmental benefits. The skeptics cited issues regarding the economic and environmental impacts of producing biofuel, raising questions over its feasibility and sustainability. In spite of this, continued research and development have been invested into the enhancement of biofuels, negating most of the abovementioned concerns. Additionally, governments, industry players, and civil society have started several initiatives to develop criteria for the sustainable production of biofuels (Olaganathan et al. 2014). Through the combined efforts of meticulous administration, as well as the constant endeavor of improving biofuels, the merits of pursuing a future powered by biofuel will far outweigh any consequences eventually. Biofuels can be classified according to the type of technology and the feedstocks of biomass they transform to fuel. The major biofuels from the first, second, and third generations have been closely studied with their respective feedstocks and potential production technologies (Fig. 5.3).

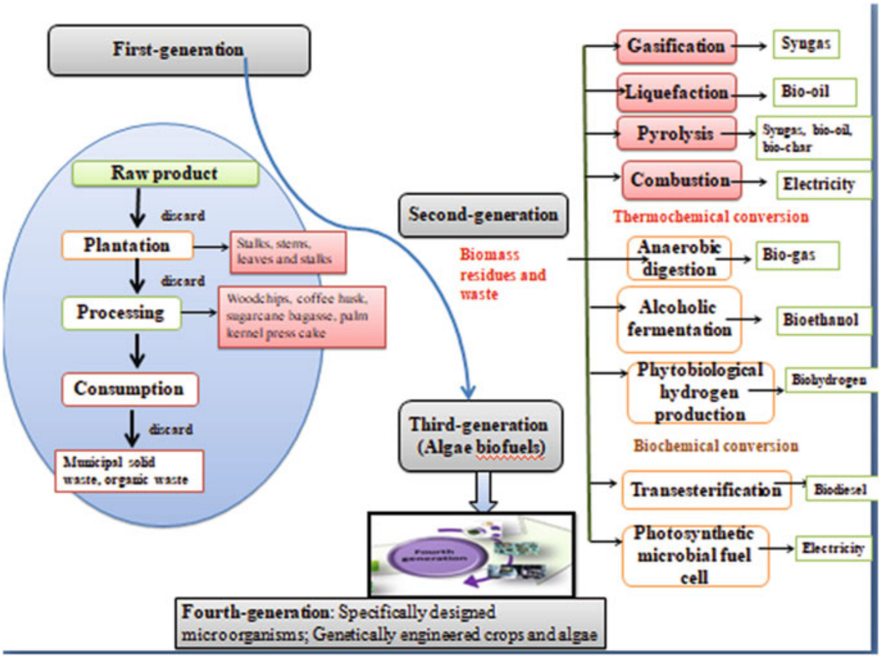

Fig. 5.3 Development of biofuel generation with highlights on the second-generation biofuels produced by biomass residues and waste and their conversion pathways to produce a wide variety of bioenergy

5.3.1 *First-Generation Biofuels*

First-generation biofuels produced from edible biomass, such as starch (from potato, wheat, barley, and corn) or sugars (from sugarcane and sugar beet), initially showed a promising capability in minimizing fossil fuels combustion and lowering atmospheric levels of CO_2 which is consumed by crops as they grow (Rodionova et al. 2017). However, concerns arose about using edible crops as feedstocks and the impacts on croplands, biodiversity, and food supply. First-generation biofuels, which are produced commercially today at around 50 billion liters per year, include biodiesel (bio-esters), bioethanol, as well as biogas. Unlike the other two types of biofuels, biogas, which is derived from anaerobic processing of manure and other biomass sources, has limited utilizing the transportation sector. The fuels are evaluated either by their abilities to be blended with petroleum-based fuel for use in internal combustion engines or by their utility in alternative vehicle technology such as natural gas vehicles or flexible fuel vehicles (Alalwan et al. 2019). Several points must be considered in the evaluation of edible biomass to produce biofuel. These are (a) the biomass chemical composition, (b) energy balance, (c) availability of croplands and the contribution to biodiversity and cropland value losses, (d) competition with food needs, (e) cultivation practices, (f) emission of pollutant gases, (g) impact of mineral absorption on water resources and soil, (h) use of pesticides, (i) cost of the biomass and its transport and storage, (j) soil erosion, (k) economic evaluation considering both the coproducts and feedstocks, (l) creation or maintenance of employment, and (m) resource availability such as water (Alalwan et al. 2019).

5.3.1.1 Bioethanol

The processing of bioethanol involves fermenting sugars obtained from starch and sugar sources (e.g., cereals such as corn or maize and sugar cane). This may be used exclusively in specially equipped cars or mixed with diesel, as long as fuel quality is complied with. Brazil is the largest producer of ethanol worldwide with an annual average of 18 billion liters (36% of global output) (UNICA 2020). Sugarcane is the main feedstock and ethanol is extracted from both molasses and cane juice and approximately 50% of the sugarcane harvest from Brazil is used for the production of ethanol from the juice. To make use of the massive supply of ethanol, the production and sales of Fuel Flexible Vehicles (FFVs) that can work on petrol, ethanol, or some mixture of those fuels have increased drastically (Anonymous 2006). The USA is the largest producer, producing 15,800 million gallons of ethanol. In North America, starch-containing crops are enzymatically hydrolyzed to obtain the sugars either by the dry grind (67%) or the wet mill (33%) process. Dry mills tend to be smaller (capacity) in scale and are primarily used only for ethanol processing. Modern wet milling facilities generate 1 gallon of ethanol, which consumes 35,150 Btu of thermal power and 2134 kWh of fuel. The thermal energy production decreases to 32,150 Btu/gal if molecular sieves are used (Shapouri et al. 1995). Various valuable products are produced by the wet mill ethanol process, such as nutraceuticals, pharmaceuticals, and organic acids. The dry grinding process is primarily developed for ethanol and animal feed processing. These countries are expanding the production of biofuels of the first generation that in Brazil is expected to double by 2013 (Macedo 2007). Ethanol is wholly made from sugar cane molasses in India. About 60% of cane is used for sugar production, 30% for jaggery, and the seed balance. India is in close fourth position after the USA, Brazil, and China in terms of global ethanol production. India's ethanol production for 2019 is 530 million gallons (http://www.ethanolindia.net) (Anonymous 2020a). India's National Biofuel Strategy 2018 set an ethanol mixing target of 10% by 2022 and 20% by 2030. India however is struggling to meet 5% of petrol blending. Thatis because the production of Indian sugar cane is only adequate to fulfill domestic sugar demand. The scope for most biofuels of first-generation is constrained for petroleum substitution or carbon emissions mitigation efficiencies. The substantial quantity of fossil fuel used to generate this ethanol, on an energy basis, greatly counterbalances the carbon emissions reductions from photosynthetic uptake of carbon by crop plants. Besides, the use of agricultural land was incompatible with the hierarchy of first "food' then "feed" and finally "fuel" (Bharadwaj et al. 2007).

Bioethanol production from corn can be classified into wet and dry mill processes. The wet mill ethanol process has usually a higher production capacity than the dry process and produces some valuable coproducts such as nutraceuticals, pharmaceuticals, organic acids, and solvent (De Corato et al. 2018). In addition to ethanol, the dry milling process produces distillers' dried grains and soluble (DDGS) which is an excellent livestock feed because it contains protein, fats, and carbohydrates. On the other hand, in addition to ethanol the wet milling process produces corn oil, and two types of animal feed which are corn gluten meal (CGM) and corn gluten feed (CGF) (Alalwan et al. 2019).

5.3.1.2 Biodiesel

The other popular first-generation biofuel is biodiesel made from oilseed crops. The vegetable oil-based fatty acid ester (FAME), i.e., biodiesel, is becoming increasingly important as an environmental fuel alternative for diesel fuel. Biodiesel (FAME) is made from vegetable oils and animal fats in the presence of a homogeneous and heterogeneous catalyst, by chemical reaction with methanol or ethanol (Meher et al. 2006; Kulkarni et al. 2006). Along with liquid acid or liquid base catalyst, a homogeneous catalyst entails a transesterification reaction. Heterogeneous catalyst requires the use of strong catalysts, which concurrently catalyze the transesterification of triglycerides and esterification of free fatty acids in the oil to methyl esters. The catalyst is restored after the reaction. The biodiesel produced in this way can be used purely in specially designed vehicles or can be combined with automotive diesel up to 5% in any given proportion. The USA and Brazil are leaders in biodiesel production, totaling around 6.5 billion liters in 2019 and 5.9 billion liters, respectively (https://www.statista.com/) (Anonymous 2020b). In the USA biodiesel production is primarily carried out using soybeans. Palm oil is used for biodiesel production in Southeast Asia (Malaysia, Indonesia, and Thailand). Jatropha biodiesel is being used in India as part of the wasteland reclamation strategy (Government of India Planning Commission 2005).

Biodiesel fuel depends mainly on oil crops and 75% of its production cost is due to the feedstock production cost. More than 350 oil-bearing crops, both edible and nonedible, have been suggested as a promising feedstock for biodiesel manufacturing (Alalwan et al. 2019). The most common food crop sources are rapeseed, soybean, palm, sunflower, peanut, safflower, corn, rice bran, coconut, olive, castor, milkweed seed, and linseed. *Jatropha curcas, Pongamia glabra, Madhuca indica, Salvadora oleoides*, cottonseed oil, Tobacco, Calophyllum Eruca Sativa Gars, *inophyllum*, terebinth, rubber seed, desert date, Jojoba, neem oil, leather pre-fleshings, apricot seed, *Pistacia chinensis* Bunge Seed, sal (Shorea robusta) and fish oil, Moringa oleifera and croton megalocarpus are common nonedible oil sources.

5.3.1.3 Biogas

Biogas originates in anaerobic (without air) environments during the process of biodegradation of organic materials. Natural biogas production constitutes an integral part of the biogeochemical cycle. The anaerobic digestion cycle is conducted in several steps containing various bacteria. Firstly, the carbohydrates, proteins, and fats present in biomass feedstock are converted to fatty acids, alcohol, CO_2, H_2, NH_3, and S^{2-} by hydrolytic and fermentative bacteria. This stage is called “hydrolysis” or “liquefaction.” Next, the hydrolysis products are digested into acetic acid, H_2, and CO_2 by acetogenic (acid-forming) bacteria. The last element in the chain of microorganisms is the methanogenic (methane forming) bacteria that degrade organic compounds and introduce the decomposed products back into the atmosphere. Biogas, a source of renewable energy, is generated in this phase of the bio-geothermal carbon cycle (Balat and Balat 2009). Anaerobic digestion takes place in an airtight chamber, known as the digester. The digester must retain a minimum temperature of 18 °C to encourage bacterial activity. At elevated temperatures up to 65 °C, the processing time will be reduced and the tank volume needed will be lowered by 25–40%. In the normal temperature range (mesophilic bacteria) however more anaerobic bacteria thrive than do the ones with a high-temperature range (thermophilic bacteria). High-temperature digesters do appear to be disturbed by variations in temperature, so close supervision is required for productive activity (Hamzah et al. 2019). The biogas generated in a digester (also referred to as “digester gas”) is a gas blend of over 90% of the sum of methane and carbon dioxide. Biogas characteristically contains little amounts of hydrogen, hydrogen sulfide, nitrogen, methyl mercaptan, and oxygen. The energy intensity of the digester gas depends on the methane level. The amount of methane varies from roughly 55–80%. Typical digester gas produces about 600 Btu of energy per cubic foot at a 65% methane level.

Anaerobic digestion in landfills constitutes a possible cause of methane production from solid waste (Schirmer et al. 2014). Municipal drainage is made of biomass solids from agricultural sources, and many wastewater processing plants use anaerobic digestion to minimize their volumes. Anaerobic digestion stagnates sludge and kills infectious agents. Digestion by sludge produces 60–70% methane biogas with a power level of approximately 600 Btu per cubic foot. The underground degradation of cellulose present in urban and commercial solid waste produces biogas. The digestion in the landfills is an unregulated biomass decay process. The productivity of the plant depends on the waste type, amount of moisture, temperature, and other factors. Biogas, generally referred to as “landfill gas (LFG),” is usually 50% coal, 45% CO_2, and another 5% gas. The energy content of landfill gas is 400–550 Btu per cubic foot. Landfill gas is equivalent to natural gas as it involves the separation of volatile organic compounds and CO_2 to have economic benefits. Effective separation technology is needed to extract toxic and other pollutants from the LFG, to use them as a natural gas replacement. The pollutants constitute toxic vinyl chloride and hydrogen sulfide. The typical application of landfill gas to energy includes electricity generation by the internal combustion engine, generator, micro-turbine, direct usage of heaters, dryers, furnaces, greenhouses, and ventilation. The high cost associated with methane purification and processing has resulted in a growing interest in generating liquid fuels from anaerobic digestion instead of gaseous fuel (Lee et al. 2007). Methanol generation as liquid fuel has numerous benefits. In the first instance, this technique will be used for commercial use of low sulfur and low ash fuels. Besides, liquid fuel can be handled, stored, and shipped even more efficiently than gaseous products.

5.3.2 Second-Generation Biofuels

A wider variety of feedstocks, primarily covering nonfood crops, can be used to produce second-generation biofuels, for example, cellulose-rich plant biomass or agricultural residues, nonfood crop feedstocks, forestry wastes, wastepaper, municipal waste, and various industrial wastes. The second-generation biofuels, share the characteristic of lignocellulose biomass, allowing the deployment of cheaper, nonedible feedstocks thus reducing competition between food and fuel. The net energy return from second-generation ethanol is much higher than ethanol derived from corn (Lynd et al. 2006). The net carbon (emitted–consumed) from combusting second-generation biofuels is neutral or even negative. Lignocellulosic biomass can produce approximately 442 billion liters of ethanol per year. The cost-effectiveness of this generation of biofuels still needs development because there are several technical barriers that need to be overcome. The use of waste plant biomass has attracted researchers for a wide variety of uses such as feedstock to generate heat and electricity by direct burning or as a raw material for wastewater treatments. However, utilizing it as an inexpensive source of biofuel is very attractive (Alalwan et al. 2019). A wide variety of abandoned materials can be used as biofuel feedstock such as agriculture waste, poplar trees, willow and eucalyptus, miscanthus, switchgrass, reed canary grass, and wood and they mostly consist of plant cell walls whose primary components is polysaccharides (75%) (Alalwan et al. 2019). These polysaccharides have a high sugar content which is preferred for biofuel production. Second-generation biofuels can be categorized as thermochemical or biochemical, in terms of processes used to turn them into biofuels. Biochemical processing can be employed for second-generation ethanol or butanol production. In contrast, thermochemical processing can be used with all other fuels, including methanol, Fischer-trópsch fluids (FTL), and Dimethyl ether (DME).

5.3.2.1 Second-Generation Biochemical Biofuels

Although the fuel characteristics of ethanol or butanol of the second generation are similar to those of the equivalents of first-generation, biochemically produced second-generation are sometimes referred to as “cellulosic ethanol” because the starting feedstock is lignocellulose. The integral steps for the production of second-generation biofuel include pretreatment, saccharification, fermentation, and distillation. The technologies for low-cost processing of biomass into fuels are being designed. Such technologies include cost-effective thermochemical pretreatment, highly efficient cellulases and hemicellulases, and competent fermentative microorganisms.

Cellulose, hemicellulose, and lignin are separated by a pretreatment process so that complex cellulose- and hemicellulose-based molecules can be split up into their basic constituent sugars by enzyme-catalyzed hydrolyses. Cellulose is a crystalline framework of repeated glucose monomers. Its crystallinity renders the disassociation to single sugars difficult, however when unbundled, the sugar molecules are easily fermented with established fermentative microorganisms into ethanol. Hemicellulose consists of 5-carbon sugar polymers and is broken into its component sugars, for example, xylose and pentose, fairly simply. Lignin is a recalcitrant structure comprised of phenols, which cannot be fermented. Most research has been undertaken in recent years to improve cellulose digestibility before exposure to microbial conversion. The chemical treatments include sodium hydroxide, peracetic acid, acid hydrolysis using sulphuric acid and formic acid, and organic solvent ethylenediamine and n-propylamine (Martínez et al. 2005; Weil et al. 1994). Besides, steam or acid/alkali-steam pretreatment was also found to be appropriate.

The hydrolysis involves synergism between three enzymatic components, viz., endoglucanases, exoglucanases, and β-glycosidases. It is produced by several bacteria and fungi. Many filamentous fungi are excellent cellulase producers and, in particular, several researchers have studied the soft rot fungus *Trichoderma resei* in depth. However, its industrial use is constrained by the high processing costs as well as low enzyme activity. For industrial uses, cellulases require high absorption, catalytic efficiency, thermal stability, and low product inhibition. Cellulolytic enzymes are costly and have a prolonged rate of hydrolysis. To be used for fuel alcohol production, it is imperative to build an eco-friendly, efficient enzyme system unaffected by end-product and substrate inhibitions. The demand for these enzymes would quickly increase if a few properties of these enzymes are enhanced, and these are made available for use at a reasonable rate.

For cellulosic ethanol production, a variety of concepts have been suggested. One strategy is the use of separate hydrolysis and fermentation (SHF). The other concepts include a system called SSF (Simultaneous saccharification fermentation) which combines hydrolysis and fermentation in the same reactor, or consolidated bioprocessing which also incorporates enzyme production with the saccharification and fermentation steps (Zhang and Lynd 2005).

Although the technology for the production of cellulose ethanol has been developed, it still requires considerable research, development, and demonstration efforts in competitive (without subsidies) production of lignocellulosic biomass. There is a need to develop biomass feedstocks with low lignin and high cellulose content, effective enzymes to expedite hydrolysis, and the production of high-temperature resistant, ethanol-tolerant microorganisms that can ferment multiple sugar forms (i.e., 6 and 5 carbon) (Houghton et al. 2006). Genetic engineering is particularly important for the improvement of biomass feedstock (Stricklen 2006). It can be made substantially easier to genetically alter industrially relevant microorganisms, especially for cellulose hydrolysis or pentose fermentation (Jeffries 2006). However, fermentation of lignocelluloses with yeasts results in diluted alcohol which further requires distillation thereby decreasing the overall efficiency of the process (Balat 2006; Chynoweth et al. 2001).

5.3.2.2 Second-Generation Thermochemical Biofuels

Thermochemical processing defines the conversion of waste biomass into a range of products, by thermal decay and chemical reformation, and essentially involves heating biomass in the presence of different concentrations of oxygen. The clear advantage of thermochemical processing is that it can essentially convert all the organic components of the biomass compared with biochemical processing which focuses mostly on the polysaccharides. Thermochemical biomass processing requires much higher temperatures and pressure than methods used in biochemical systems. The defining features of thermochemical biofuels are the versatility of feed products, adaptability to the thermochemical process, and the variety of fuels generated. The thermochemical production of biofuels involves combustion, gasification, or pyrolysis of biomass.

Biofuels Based on the Gasification Process

Gasification is the thermochemical conversion of carbonaceous feedstock to gaseous products through a partial oxidation process at elevated temperatures. In biomass gasification, the lignocellulosic structure of biomass is thermally cracked into carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2) as the main constituents of syngas and minor amounts of methane (CH_4) and a variety of trace gases. The composition of syngas depends on some parameters such as feedstock properties (ash, moisture, particle size), gasifying agent (air, steam, pure oxygen, or a combination of them), type of gasifier (fixed bed, moving bed, fluidized-bed, entrained flow), and operation condition (temperature, gasifying agent to fuel ratio, etc.) (Alauddin et al. 2010).

The gasification includes the reactions of biomass with air, oxygen, or steam generating a gaseous combination of CO, CO_2, H_2, CH_4, and N_2, either known as producer gas or syngas, based on the relative quantities of the gas components (Rowlands et al. 2008). The low heating value of producer gas (4–10 MJ per liter) is primarily used as a stationary power-generating fuel. In contrast, syngas is used mostly for the processing of a range of fuels as well as chemical intermediates.

Syngas Production

Syngas plays an important role as an intermediate in the production of several industrial products, such as Fischer-Tropsch liquids, methanol, and ammonia.

Currently, syngas is produced from fossil fuels, mainly coal, natural gas, and naphtha. Syngas from renewable resources, such as biomass, exhibits a promising prospective. This is because biomass is a CO_2-neutral resource and is distributed extensively around the world. Several biomass to methanol demonstration projects have been developed recently, such as the Hynol project in the United States, the BioMeet and Bio-Fuels projects in Sweden, and the BGMSS project in Japan (Lv et al. 2007). There are three different routes of syngas from biomass, viz., syngas from biomass-derived oil, syngas from biomass-derived char, and syngas from reforming of biomass gasification gas (Lv et al. 2007). Two thermochemical methods are possible for the production of syngas (H_2 and CO) from biomass, first is by using high temperatures or a catalyst at somewhat lower temperatures (Rensfelt 2005). The first path takes typically upto 1300 °C and typically involves an entrained flow gasifier. The second step makes use of a fluidized-bed gasifier and a downstream catalytic reformer both operating at around 900 °C. Three system principles are described as appropriate for the development of syngas as follows:

CFB Gasifier Plus Tar Cracker

To obtain a nitrogen-free gas, an oxygen-blown CFB gasifier is used. Tars, BTX, and the hydrocarbons are cracked and converted into chiefly H_2 and CO in a downstream tar cracker functioned at 1300 °C (Boerrigter et al. 2004). The syngas is treated/cleaned with the same methods used for the processing of fossil syngas: dust filters, wet scrubbing for NH_3 and HCl, ZnO filters H_2S, and active carbon filters. The gas is compressed at the FT synthesis pressure (25–60 bar) after the conditioning (H_2/CO modification and CO_2 removal).

Entrained Flow Gasification

Through the process of CFB and tar cracker, biomass is gasified and then burned in the tars and hydrocarbons at a high temperature. The high temperature can alternatively be set directly in the gasifier, especially the entrained flow (EF) gasifier. The cleaning and conditioning of the downstream gasifier is identical to the previous principle, but no additional compression is required. The chips for biomass (~5 cm) used to feed a gasifier of CFB have to be pulverized either immediately or after a moderate thermal treatment, viz., torrefaction (Van der Drift et al. 2004).

CFB Gasifier, OLGA, Plus Reformer

In the third step, another strategy is adopted to eliminate tar and to process hydrocarbons. Using the OLGA tar removal process, the tar and BTX are collected after gasification and returned to the gasifier. Hydrocarbons that are not removed with OLGA are therefore transformed into a catalytic reformer after the wet cleaning step. The conditioning and compression are comparable to the first concept.

Syngas Cleaning and Conditioning

Until FTS, gas purification is a big operation. Trace contaminants such as NH_3, H_2S, HCl, dust, and alkalis in ash are found in any raw syngas. To combine a biomass gasifier and a catalytic reactor, gas cleaning is a vital step. FTS catalysts must be completely protected from contaminations, namely tar, hydrogen sulfide, carbonyl sulfide, ammonia, hydrogen cyanide, alkali, and dust particles (Tijmensen et al. 2002). The gas cleaning systems include a pump, Rectisol unit, and downstream gas polishing for the elimination of traces. Since the H_2/CO ratio requires typical modification, the gas conditioning often involves a water-gas shift reactor (Van der Drift and Boerrigter 2005). The Rectisol unit ensures that most impurities are eliminated, and CO_2 is segregated.

Biofuels from Bio-syngas

To synthesize an array of chemicals, including Fischer-Tropsch oil, methanol, dimethyl ether (DME), mixed alcoholics (MA), and pure H_2, cleaned and conditioned biological syngas may be used. Also, all the syngas that traverses the catalyst is converted to liquid biofuels for most of the plant designs. The unconverted syngas is used to provide energy for any or all power required to operate the plant and to supply the electricity to the grid in some situations.

Fischer-Tropsch Liquids

German scientists Franz Fisher and Hans Tropsch founded the FTS in 1923. FTS works primarily at synthesizing CO- and H2 gas mixture from long-chain hydrocarbons (Anderson 1984; Schulz 1999), described in the reaction as follows:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O(n = 1, 2, 3, \ldots)$$

In the presence of a cobalt (Co) based catalyst, one mole of CO reacts with two moles of H_2 resulting in hydrocarbon chain elongation. The CH_2- serves as a building block for hydrocarbon extension. The liquid selectivity of the process is a crucial aspect of the efficiency of the FTS (Tijmensen et al. 2002). For hydrocarbon synthesis, a ratio of H_2/CO must be at least 2. If water-gas shift operation includes using iron (Fe) catalysts, the water formed in the reaction can react with CO to form additional H_2. The H_2/CO usage ratio can be as weak as 1.7 owing to the commonly occurring WGS reaction in iron catalytic systems (Steynberg and Dry Mark 2004). Depending upon the operation, standard operating conditions for the FTS are 475–625 K and 15–40 bar pressures. The type and volume of liquid material produced depend on the reaction temperature, pressure, residence time, the reactor type, as well as the catalyst used. For liquid-phase FT synthesis, catalysts and reactors have been thoroughly investigated (Davis 2002). Iron catalysts have more excellent sulfur resistance, are low-priced, and contain abundant olefin and alcohol products. However, the Fe catalysts' lifespan is short and typically limited to

8 weeks in commercial installations. The benefits of cobalt catalysts are a faster turnaround and longer life. In general, hydrogenation cocatalysts are more stable, and thus contain fewer unsaturated hydrocarbons and alcohols than iron catalysts. The Fischer-Tropsch reaction results in a great variety of products, namely, light hydrocarbons (C1 and C2), LPG (C3-C4), naphtha (C5–C11), diesel (C12–C20), and wax (>C20) fractions. The maximum number of liquid fuels derived from the adequately cleaned and conditioned syngas is roughly 70% (total syngas-to-fuel energy efficiency), and about 25% of the energy is released as heat. The remaining 5% (i.e., unconverted syngas, C1–C4 products) of energy in the FTS gas can be used to produce electricity. The FTS process can be successfully used to produce liquid hydrocarbon fuels from syngas. The sizeable hydrocarbons can be hydro-cracked primarily into high-quality diesel. The products from FTS are primarily aliphatic straight-chain hydrocarbons (CxHy) (Demirbas 2008). Synthetic FT diesel is a high-quality ultra-clean fuel as it does not contain sulfur and aromatic products. According to Dry (2001), FT diesel has a high cetane number of about 75, while the market requirement is 45–50 (Dry Mark 2001). Because of this high number of cetanes, FT diesel could be blended with lower quality conventional diesel, which would not otherwise be used as an automotive fuel. Fischer-Tropsch diesel fuel can deliver benefits in terms of both PM and NOx emissions (May 2003). Raw FT naphtha has a minimal number of octans and needs significant modification to manufacture appropriate standard gasoline. Many applications for naphtha, including feed for steam cracking to produce ethylene and propylene and solvent manufacturing, are available. At ambient conditions, the heavier compounds produced by the FT synthesis form solid wax. This wax is of the highest quality and can be sold or cracked for more FT diesel output. FT liquids can also generate high-quality lube oils and jet fuel.

The high prices of crude oil and environmental conditions force the global potential for FTL production to grow. In addition to the Shell Gas to Liquids (GTL) plants in Malaysia (14,500 barrels a day (bpd), and the PetroSA plant in South Africa (23,000 bpd) that started in 1993, there is a further extension of commercial GTL facilities close to start-up or advanced planning stages. The demand for FT fuels from gasified coal is also increasing. Coal fuel production of FT fuel was initially marketed at the Sasol I, II, and III factories, developed between 1956 and 1982 in the south of Africa (175,000 bpd total capacity). Chinese first commercial carbon-FT project is scheduled in Mongolia in 2007 and early 2008, to generate 20,000 bpd. The US Department of Energy is funding a 5000 bpd FT liquid CTL pilot project in Pennsylvania and numerous plans are being made for larger coal to fluid plant elsewhere in the USA. A process route called Carbo-V® has been developed by the German Choren industries, where clean syngas is produced from biomass and converted to liquid fuels via the Fischer-Tropsch process. In 1998, a 1 MW pilot plant (the α factory) was started in Freiberg, Germany. The industrial plant, set up in 2003 produced 13,000 tons of synthetic automotive fuels annually (Mattias 2005; Kavlov and Peteves 2005).

Biomethanol

Fischer-Tropsch's resourcefulness is that syngas can generate not only hydrocarbons but also oxygenated compounds. The straight-chain alcohols are formed in the presence of iron catalysts in Synthol reactions at 400–430 °C and 14 MPa pressure (Davis 2005). However, since 1960, industrial production from natural gas has been dominated by an imperial chemical industry that has created a lower temperature and pressure process, in which CO, CO_2, and H_2 derived from steam reforming are reacted by a $Cu/ZnO/Al_2O_3$ mixed catalyst at 250 °C and 5–10 MPa (Agrell et al. 2002). Recent advances have been made to merge methane syngas production and ZnO's reduction into metallic zinc. The syngas, with an H_2/CO ratio of 2:1, is optimal for the production of methanol (Su et al. 2019). An alternative path is also necessary for the renewable route for methanol through biomass gasification. Methanol however is inferior to ethanol with an energy content of only 75% (wt or vol) and about 50% less than that of standard gasoline. Methanol blends with traditional gasoline can be handled up to 20% without any alteration of the engine. However, the corrosive influence of methanol on some surfaces limits its scope (Biomethanol. http://www.refuel.eu/biofuels/biomethanol/) (Anonymous 2020c). Table 5.2 enlists the major biomethanation companies in India along with their products, technology, and cost analysis.

A program initiated in 2000 between the Ministry of Agriculture, Forestry, Japanese Fisheries, and Mitsubishi Heavy Industries, in Nagasaki, built the first pilot plant to study and assess the development of biomethanol. For the development of methanol, different feedstocks including wood, rice husk, rice straw, and rice bran were explored. The pilot plant has been built with a capacity of 240 kg per day with 9–13% methanol yield. The experimental analyses found that the cost of production of biomass gasification methanol was around twice that of traditional fuel on an equivalent energy base (Hamelinck and Faaij 2002). In South Africa, the large-scale processing of methanol by biomass gasification was projected to produce refined methanol at the cost of up to \$0.38 per liter (\$1.66 per Gallon) (Amiguna et al. 2010). However, because of the direct methanol cell technology, this approach was later discouraged. A micro-DM suitable for the powering of MP3 players was created in Japan, and a US patent was granted in March 2007, to cover aspects of DMFC design (Izenson 2007).

Dimethyl Ether

Dimethyl ether can be generated utilizing thermochemical means with biomass-derived syngas. As a clean-burning alternative to diesel fuel, dimethyl ether (DME, CH_3OCH_3) has been suggested and a deep interest has been raised for the diesel replacement in Japan and elsewhere in Asia. It is completely inert, non-carcinogenic, virtually non-toxic, and does not develop peroxides by sustained air exposure (Hansen et al. 1995). This is a suitable replacement for liquefied petroleum gas (LPG, a propane and butane mixture), owing to its physical characteristics. Unless the DME mixer standard is limited to 15–25% by volume, DME and LPG mixtures

Table 5.2 Major biomethanation companies in India (their products, technology, and cost analysis)

Company and headquarter	Operations	Waste treats	Plant type and waste input	Technology	Applications	Operational states	References
Quantum Green Energy Pvt. Ltd. Bengaluru	Design, supply, and installation of biogas plants	Food and kitchen waste	Portable Biogas Plant (40–60 kg/day) Rs.1.5Lac/Unit Industrial Biogas Plant (50–1000 kg/day) Rs. 2.5–25Lac/unit	Anaerobic digester Plug and play	Cooking, heating electricity, boiler Bio-CNG bottling, piped biogas biofertilizer	Tamilnadu, Karnataka, Andhra Pradesh, Telangana, etc.	Quantum Green Pvt. Ltd (2020)
Green Brick Eco Solution Pvt. Ltd. New Delhi	Design and supply of various instruments and devices required in biogas plants	MSW, garbage, and kitchen waste	Portable Biogas Plant, for kitchen, plant 50–500 kg Rs. 3.0 Lac/unit	Delhi UASB technology and activated sludge process are followed in installations	Biogas generation, biogas purification and bottling, biogas to power, and biogas monitoring systems	New Delhi, UP, NCR Region, Haryana, Rajasthan, MP, etc.	Green Brick Eco Solutions Pvt. Ltd (2020)
B-Sustain Energy projects Pvt. Ltd. Chennai	Design, manufacturer, supply, and installation of biogas plants	Distillery waste, leather industry waste, wastewater treatment plant sludge	Semi-Automatic Household Biogas Digester, 700 Ltr Rs. 18,000/unit	UASB technologies for biogas generation	Cooking, heating electricity	Tamilnadu, Karnataka, AP, Telangana, etc.	B-Sustain Energy Projects Pvt. Ltd (2020)
VNS Enviro Biotechq Pvt. Ltd. Chennai	Manufacturer, supply, and installation of biogas plants	MSW, kitchen waste, wastewater sludge, poultry waste	Automatic Industrial Biogas Plants, 100–500 kg Rs. 3.0–10 Lac/unit	Adopted modified UASB technology	Cooking, heating, electricity, and transportation fuel	Tamilnadu, Madhya Pradesh, Karnataka, Andhra Pradesh, etc.	Indian Mart InterMESH Ltd. (2020)
BijSon Innovations Private Limited Jaipur	Manufacturer, dealer, supplier, and distributor of	Kitchen, hospitals, educational institutes waste and commercial	BijSon Automatic Biogas Plant, usage: home 1–150 kg	Anaerobic digestion using Hyperactive Microbial consortia for	Cooking, heating electricity, boiler Bio-CNG bottling electricity	Punjab, UP, MP, Haryana, Himachal, Jammu and Kashmir,	BijSon Innovation Pvt. Ltd (2020)

(continued)

Table 5.2 (continued)

Company and headquarter	Operations	Waste treats	Plant type and waste input	Technology	Applications	Operational states	References
	small and larger scale biogas plants	establishments, etc.	Rs. 50,000–5 Lac/unit	specific locations and regions		Gujarat, Chandigarh, Rajasthan, Uttrakhand, etc	
Emerald Enterprises Kerala	Design, manufacturer, and supplier of domestic biogas plants	Kitchen, hospital, educational institutes waste, etc., MSW	2 Cubic Meter FRP Portable Biogas Plant 20 kg/day Rs. 38,000/unit	Anaerobic digestion and fermentation	Cooking, heating electricity, boiler	Kerala, Goa, Pondicherry, Karnataka, Diu Daman, etc.	Emerald Enterprises Kerala (2020)
Envirorise Technologies Llp Bengaluru	Manufacturer, supplier, distributor, and importer of customized biogas plants	MSW, kitchen waste, wastewater sludge, poultry waste, and other industrial wastes	Automatic Biogas Plant, 100–500 kg Rs. 2.0–23 Lac/unit	Advanced USAB technology with improved biogas production	Cooking, heating electricity, boiler Bio-CNG bottling vehicular fuel, piped biogas	Tamilnadu, Odessa, MP, Karnataka, Andhra Pradesh, Telangana, Bihar, West Bengal, etc.	Envirorise Technologies Llp Bengaluru (2020)
Britt Envirotech, Pvt. Ltd. Tamilnadu	Manufacturer, exporter, supplier, distributor, wholesaler, trader, retailer, and importer of premium quality biogas plants	Domestic kitchen waste and MSW	Domestic Biogas Plant, 1–5 kg/day Rs. 25,000/unit Industrial Biogas Plant, 15–50 kg/day Rs. 1.2 Lac/unit	Upflow Anaerobic Sludge Blanket Technology	Cooking, heating electricity	Tamilnadu, Karnataka, Kerala, Goa, Maharashtra, Madhya Pradesh, Odessa, etc.	Britt Envirotech, Pvt. Ltd (2020)
Synod Biosciences Pvt. Ltd. Bengaluru	Waste collection at source, to segregation and processing, including setting up of biogas plants for	Animal waste, MSW, domestic and kitchen waste	Portable Biogas Plant, 1–5 kg/day Rs. 23,500/unit Commercial Portable Biogas Plant, 10–50 kg/day	Anaerobic digestion technology	Cooking, heating electricity, boiler	Bengaluru Karnataka, Tamil Nadu, Maharashtra. Kerala, etc.	Synod Biosciences Pvt. Ltd (2020)

	homes and community establishments		Rs. 1.5 Lac/unit Community Biogas Plant, 125–1000 kg/day Rs. 2.5–30 Lac/unit				
Perfect biogas and Management Pvt. Ltd. New Delhi	Construction of biogas digesters/tanks attached with biogas filtration system and finally manufacturing of biogas generator	Kitchen waste, dairy industry waste, poultry waste	Biogas Digesters Fixed Dome, Floating Dome, Overhead Digesters, etc., 20–1000 m^3 in Rs. 2.5–20 Lac/unit	Anaerobic digestion technology	Heat and electricity generation	New Delhi, Haryana, Rajasthan, UP, etc.	Perfect biogas and Management Pvt. Ltd (2020)

can be used for LPG-designed combustion machines, without any system modifications (Griffith 2002; Marchiona 2002). However, DME is an environmentally friendly gas that has to be pressurized to be used in updated diesel engines. Air products has also developed a liquid-phase synthesis that is oligomerizing DME to produce clean-burning oxygenated liquid fuel, which can be used as neat or blended diesel fuel in nonmodified engines but is still in its early technological and testing stages.

SNG (Substitute Natural Gas)

SNG (substitute natural gas) is highly pure methane (CH_4) obtained from the methanation of synthesis gas. SNG is exchangeable with natural gas and can be delivered in prevailing pipes for heating, power generation, or other industrial uses such as the manufacture of hydrogen. Approximately 170 million scf/day of SNG is generated by the Dakota Gasification company from North Dakota Lignite. SNG production can be carried out from coal with an efficiency of 60% (HHV basis) (Gray et al. 2004).

Hydrogen Production

Hydrogen is a resultant product of gasification of coal feed and the extract ash with intact residual carbon. The production facility involves both the clean-up of syngas, water-gas transitions, and the purification of hydrogen to generate highly pure hydrogen which is supplied to liquefaction reactors. For the gasification of oxygen, an air separation plant is also mandated. Another approach to hydrogen production is fast pyrolysis and the transformation of carbohydrate fractions to bio-oil. A two-step process shift reaction for hydrogen production involves bio-oil production via pyrolysis and its subsequent catalytic steam reformation at 750–850 °C over a nickel-based catalyst. Additionally, natural gas may also be used for the production of hydrogen utilizing steam methane reforming or partial oxidation (Demirbas 2008). The price and supply of natural gas in a given location dictate the best choice for hydrogen production.

Fischer-Tropsch Liquids from Biogas

Biogas is the product of decaying biological material, where oxygen is not available and is generated in public landfills. Methane is the principal ingredient of biogas, which can be converted into biomethane and renewed to syngas. Biogas can be prepared using food waste, sludge, manure, etc. It is virtually similar to natural gas, and GTL technology can be used in the processing of biogas FT liquids (Mortensen 2019).

Bio-Oil or Pyrolysis Oil

Pyrolysis is the thermochemical degradation of organic material in the absence of oxygen at high temperatures. Pyrolysis typically takes place under pressure and at working temperatures greater than 430 °C (800 °F). Biomass pyrolysis generates a range of yields of char, bio-oil, and pyrolysis gas, depending upon different parameters such as temperature ranges, particle size, and retention time (Demirbas 2000). Pyrolysis varies in that it does not require reactions of oxygen, water, or any other high-term reagent from other conditions, such as combustion and hydrolysis (Fig. 5.4).

The pyrolysis cycle can be categorized into three types, based on operating conditions: (a) Conventional pyrolysis, (b) Fast pyrolysis, and (c) Flash pyrolysis. Conventional pyrolysis occurs under a slow heating rate (0.1–1 K/s), residence time (45–550 s), and utilizes huge wood pieces. Pre-pyrolysis is the first step of biomass decomposition that takes place between 550 and 950 K. In this step, specific internal rearrangements such as the elimination of oxygen, the dislocation of bonds, the formation of free radicals, carbonyl, carboxy, and hydroperoxide groups occur (Shafizadeh 1982). The second step of solid decomposition is central to pyrolysis. It continues at a high rate, leading to pyrolysis products being produced. In the third level, the char breaks down very slowly and makes stable residues rich in carbon (Fig. 5.5).

Fast pyrolysis takes place in a range of 850–1250 K at a quick-heating rate (10–200 K/s), a short definite residence time (0.5–10 s), and a fine particle size (<

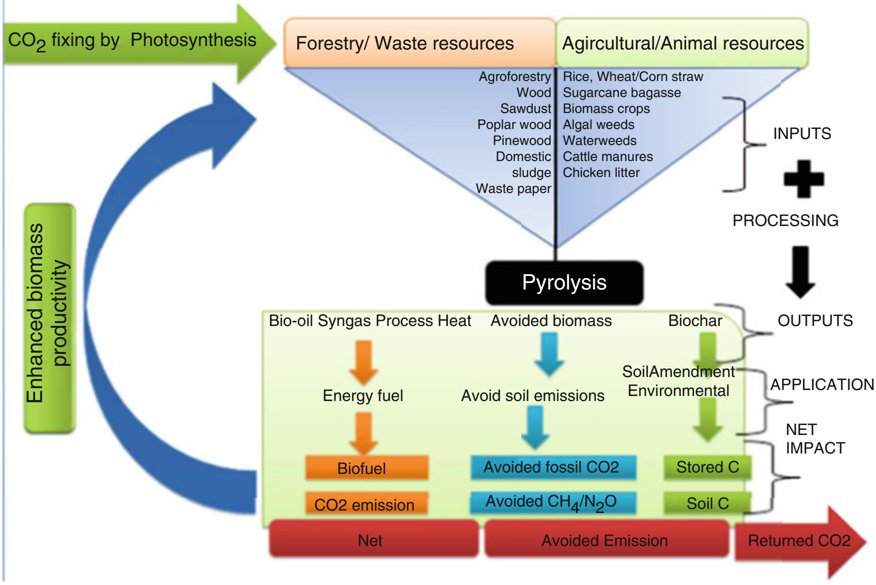

Fig. 5.4 Mechanism of pyrolysis for conversion of waste feedstock to biofuel

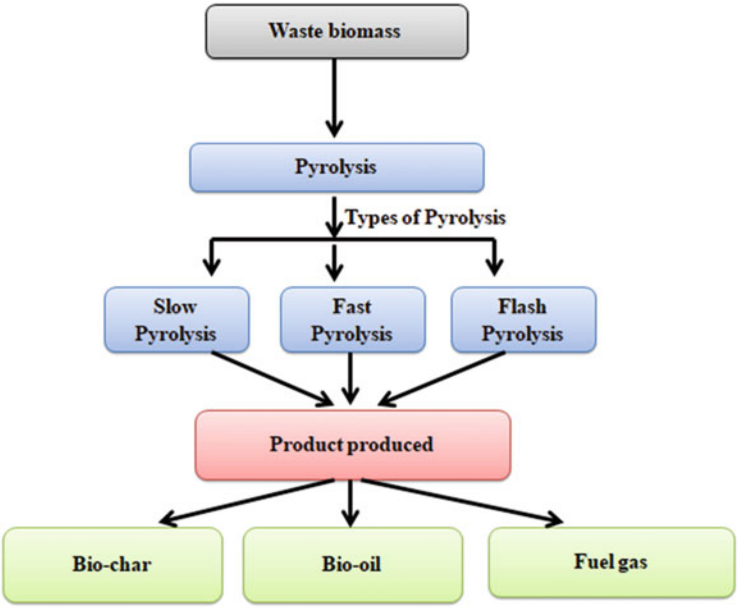

Fig. 5.5 Different types of pyrolysis processes

1 mm), resulting in the biomass decomposition to produce vapors, aerosol, and some charcoal-like char. A dark brown, mobile liquid with a heating capacity that amounts to half that of standard fuel oil is produced after cooling and condensation of vapors and aerosol. Depending upon feedstock, fast pyrolysis gives rise to 60–75% of bio-oil, 15–25% solid char, and 10–20% non-condensed gases (Shafizadeh 1982). Flash pyrolysis varies considerably from conventional pyrolysis, gradually performed on large wood pieces. It occurs in the temperature range of 1050–1300 K, short residence time (<0.5 s), fast heating rate (>1000 K/s), and very fine particle (<0.2 mm). Bio-oils are usually provided by biomass pyrolysis through the flash pyrolysis (Demirbas 2000). For the production of bioslurry, the extracted oil may be mixed with the char. Bioslurry can quickly be fed into the gasifier for effective conversion to syngas (gasifier condition: 26 bars; 927–1227 K). For the flash pyrolysis cycle, the transformation of biomass to petroleum can be up to 70% efficient. For engines and generators, the so-called biocrude can be used. This is also taken into account as feedstock for refineries (Demirbas 2000; Mohan et al. 2006).

Liquid Fuel from Liquefaction

Liquefaction means the low-temperature breaking of biomass molecules due to high pressures yielding liquid distilled fuel. The downside of this method is to deal with comparably low yields, comprehensive equipment needs to have the necessary pressure ranges (50–200 bar), and low temperatures of about 200–400 °C (Zhang et al. 2019). Additionally, the feeding systems and reactors are more complicated and expensive than the pyrolysis process. As a result, there is diminished interest in liquefaction and is perceived to be the least mature conversion process.

In the field of thermochemical conversion of biomass, lignocellulosic materials can be converted directly to a liquid similar to heavy fuel oils by reacting them with synthesis gas in the presence of a suitable catalyst. Aqueous liquefaction of lignocellulosic involves desegregation of the wood ultrastructure, followed by partial depolymerization of the constitutive compounds. In the alkali liquefaction, deoxygenating occurs through decarboxylation from ester formed by hydroxyl group and formate ion derived from carbonate. Alkali salts such as sodium carbonate and potassium carbonate can act as a catalyst for the hydrolysis of macromolecules such as cellulose and hemicellulose into smaller fragments. The heavy oil obtained from the liquefaction process is a viscous tarry lump, which sometimes caused troubles in handling. For this reason, some organic solvents (e.g., propanol, butanol, acetone, methyl ethyl ketone, ethyl acetate) need to be added to the reaction system. All these solvents, except ethyl acetate, may be reproduced from wood during liquefaction. This suggests that the solvent can be recovered for reuse. The oil yield is reported to be higher with catalytic aqueous liquefaction than with non-catalytic aqueous liquefaction. The average oil yield is around 31% in the non-catalytic process and 63% in the catalytic process (Naik et al. 2010). In the liquefaction process, the amount of solid residue increased in proportion to the lignin content. Lignin is a macromolecule, which consists of alkylphenols and has a complex three-dimensional structure. It is generally accepted that free phenoxy radicals are formed by thermal decomposition of lignin above 525 K and that the radicals have a random tendency to form solid residue through condensation and polymerization. Bio-oil obtained from air-dried wood by high-pressure liquefaction (HPL) results in a complex mixture of volatile organic acids, alcohols, aldehydes, ethers, esters, ketones, and nonvolatile components. These oils could be upgraded catalytically to yield an organic distillate product which is rich in hydrocarbons and useful chemicals. Compared to bio-oil obtained from the fast pyrolysis method, their yield from HPL process is much lower and highly viscous (NAik et al. 2010).

5.3.3 Third-Generation Biofuels

The modern approach to third-generation biofuels includes the use of microbial enzymes to accomplish the current chemical pretreatment procedures for cellulosic or starchy raw materials (Carere et al. 2008). The degradation of lignocellulosic biomass is achieved using a microbial enzyme attack near to room temperature. Therefore, microbial enzymes may serve to make the biofuel industry cleaner and greener.

Microalgae have great potential to achieve high lipid content due to their high photosynthetic ability. Specifically, the lipid production capacity per unit dry is between 15 and 300 times that of conventional crops (Alalwan et al. 2019). Anaerobic digestion of organic biomass, which is known as methanogenesis, is used to produce biogas fuel. The main requirements for this process are cellulosic and hemicellulosic sources. Thus, microalgae are a promising source of third-generation biofuels.

5.3.3.1 Bioethanol Via Consolidated Bioprocessing of Cellulosic Biomass

A recent techno-economic study of the corn stover process based on dilute sulphuric acid and SSF, reveals that the costs of the pretreatment and processing or procurement of cellulase enzymes tend to be the primary barriers to be removed (Himmel et al. 2007; Foust et al. 2009). Consolidated bioprocessing that couples simultaneous saccharification of lignocellulose and fermentation into a one-step arbitrated either by a single microorganism or microbial consortium, not only reduces the costs of conversion of lignocelluloses to ethanol, i.e., pretreatment elimination, increased cellulose hydrolysis yield but also improves enzyme activity to reduce its consumption and improves both yield and specificity (Lynd et al. 2002). CBP therefore has the potential to reduce total production costs by twofold costs as well as improve efficiency. Simulations by Lynd et al. (2005) showed that CBP could generate ethanol at the cost of approximately ca. 1 US cents/L in contrast with 5US cents/L in SSCF setup (Lynd et al. 2002, 2005; van Zyl et al. 2007).

CBP allows producing low-cost bioethanol, but currently, no organism can transform lignocellulosic biomass into ethanol at high rates. To develop such organisms, two approaches are put in place. The native cellulolytic strategy attempts to enhance natural cellulolytic microorganisms to produce high yields and tolerance for inhibitory substances. A naturally non-cellulolytic organism with high tolerance and yields is engineered to grow on cellulose through a recombinant cellulolytic strategy.

5.3.3.2 Native Cellulolytic Strategy

Most of the thermophilic anaerobes that can produce ethanol are used in the native cellulolytic strategy. The thermophilic aerobes have many advantages which is why these are considered suitable for the industrial conversion of lignocellulosic biomass into ethanol. First, there exist organisms such as *Clostridium thermocellum* that can achieve direct conversion of lignocellulosic biomass to ethanol. Second, being anaerobic, these can grow in the absence of oxygen; thus, there is no need to have aeration in fermenters, cutting down the overall cost of industrial fermentation. Third, the optimum growth temperature of *C. thermocellum* is about 60 °C, which enables the elimination and recycling of ethanol by evaporation and distillation, makes costly cooling systems redundant, and aborts contamination issues. Fourth, anaerobes generally have a low cell yield, so large quantities of the substrate are converted to the final product (Demain et al. 2005).

Despite these organisms' advantages, one of the main disadvantages is that achieved ethanol yields remain relatively low compared to good producers of ethanol such as *S. cerevisiae*. This is because not only ethanol but also other components, including lactate and acetate, are produced during the fermentation of glucose. There are two ways in which genetic modification can reduce the development of these undesirable byproducts. Either the pathways genes that produce the byproducts can be knocked out or genes from the ethanol-producing pathway can be over-expressed. Knock-out is more feasible because it is irreversible and is usually easier for poorly developed genetic setup to manage. The Masoma corporation (Lebanon, Hampshire) intensively investigated *Thermoanaerobacterium saccharolyticum* for consolidated bioprocessing using gene deletion to eliminate wastage of organic acid and hydrogen formation (Shaw et al. 2009). The comparatively poor tolerance of these organisms to ethanol is also a concern. Inhibition of glycolytic enzymes, disruption of cell membranes, reduced pyridine nucleotide path, and alcohol dehydrogenase inhibition are the pathways proposed for ethanol inhibition (Lynd et al. 2002; Demain et al. 2005).

C. thermocellum is best suited for CBP with the native cellulolytic strategy because it can directly convert cellulose into ethanol and is one of the most widely studied cellulolytic anaerobes. However, *C. thermocellum* cannot convert pentose sugars. Therefore, a coculturing of *C. thermocellum* with a thermophilic anaerobe capable of producing ethanol from pentoses is of considerable importance. The *C. thermocellum* and *Clostridium saccharolyticum* coculture studies had already been carried out in 1980. Several attempts with *Clostridium thermohydrosulfuricum*, *Thermoanaerobacter ethanolicus,* and *Thermoanaerobium brockii* as co-organisms at that time have also been reported, but no newer studies surfaced afterward (Demain et al. 2005). The only nonbacterial wild-type microbe actively perceived for CBP is *Fusarium oxysporum*. As early as 1980, the microorganism able to ferment xylose and hexose sugars to ethanol were recognized, and several cellulose-degrading enzyme strains were identified thereafter. Hemicelluloses can be used with poor conversion efficiency in acid hydroxylate (0.22 g of ethanol per gm of sugar consumed). With 60% of the theoretical yield based on total glucose and xylose, the brewers spent grains can be converted directly into ethanol. Comprehensive metabolic engineering will probably be needed for *Fusarium oxysporum* for an effective ethanologenic, and thorough study of biochemical networks will start disclosing possible intervention sites (Xiros and Christakopoulos 2009; Panagiotou et al. 2005).

5.3.3.3 Recombinant Cellulolytic Strategy

For the recombinant cellulolytic strategy, non-cellulolytic organisms, namely *S. cerevisiae*, *Z. mobilis,* and enteric bacteria, such as *Escherichia coli* are used. They have also been shown to be ideal for industrial processes, as they are robust and stable. Naturally, *S. cerevisiae* cannot ferment pentoses and efforts have been underway for more than three decades to improve upon this. A further concern is that cellobiose and other cellodextrins make a significant proportion of the final products of hydrolysis and are often not degradable by *S. cerevisiae*. Katahira et al. (2006) developed a strain that can ferment xylose and cellobiose by inserting the β-glucosidase from *Aspergillus aculeatus* gene in the genome of the yeast. However, even the xylose and cellobiose utilizing organisms prefer glucose as a substrate. The mechanism called glucose repression results in gene repression, which regulates the metabolism of alternate carbon sources when glucose is above a specific concentration. The glucose suppression system will be deregulated to reach high ethanol levels through the use of all available hexoses and pentoses (van Zyl et al. 2007). The expression of a functioning cellulose network is probably the most challenging task inside the cellulolytic recombination strategy. The expression of single cellulolytic enzymes has already been achieved (van Zyl et al. 2007). However, the organism needs specific cellulases to process all the various sugars for its growth on lignocelluloses. Fujita et al. (2004) designed an *S. cerevisiae* strain that expresses an endoglucanase II and a cellobiohydrolase II from *Trichoderma reesei* and a β-glucosidase 1 from *A. aculeatus,* that could be grown on phosphoric acid swollen cellulose (PASC). They achieved 3 g/L ethanol within a 40 h period. The problem with CBP was that their strain was not grown from the beginning on the substrate, but was previously grown on aerobic SDC media. Den Haan et al. (2007) reported a strain that contained endoglucanase from *T. reesei* and a β-glucosidase of *Saccharomycopsis fibuligera*, could grow on PASC and resulted in 1 g/L ethanol. Compared to the 26 g/L produced by *C. thermocellum* this yield is still very small and well below a concentration which should be of economic value. Provided that a high yield of ethanol is one of the main objectives of CBP, byproduct production can also play a part in the fermentation process with *S. cerevisiae.* For example, upto 4% of the glucose used in fermentation is utilized for the production of glycerol. Eliminating the production of glycerol could increase the yield of ethanol by more than 10%. The production of glycerol is an attempt to reoxidize surplus NADH in cells, and, hence, maintain the redox balance, especially in anaerobic conditions, it also has essential functions in stress reactions, for example, response to heat shock reactions. Various successful efforts have been made to minimize the production of glycerol, but these are all under laboratory conditions. Whether cells with diminished glycerol production will better perform under extreme industrial conditions however is uncertain (Den Haan et al. 2007). Byproducts developed mainly during pretreatment can inhibit the growth of *S. cerevisiae.* Weak acids, furan derivatives, phenol compounds, and inorganic salts are inhibitory substances. Many successful efforts have been made to improve metabolic engineering resistance to some of these compounds. Profound research is going on inorganic salt tolerance. However, given that the composition of the inhibitors varies with the pretreatment method, the feedstock used, and the process conditions, these improvements are somewhat restricted in their application to the industrial process. With rational genetic engineering strategies, the multiple tolerances that are needed are tough to achieve because each tolerance needs its genetic modifications, and bringing them together in one organism is difficult. Ethanol tolerance of *S. cerevisiae* is also subject to optimization. Some yeast strains tend to demonstrate inhibition of growth at 5% concentrations, and higher concentrations of ethanol inhibit more sensitive strains. Research has been focused on Sake yeasts because of its high tolerance to ethanol (Nevoigt 2008).

5.3.3.4 Consolidated Process Based on Transgenic Plants with Expressed CWD-Enzymes

A consolidated process based on cell wall degrading enzymes (CWD) expressed by the plant has been developed which enables combined pretreatment, simultaneous saccharification and fermentation and removes any detoxification, washing, and separating phases (Zhang et al. 2011). CWD-expressed plants achieved substantially higher and faster hydrolysis of biomass than the control plants with a moderate pretreatment (Zhang et al. 2011). The increased hydrolysis can reduce the load of the exogenous enzymes while retaining a comparable hydrolysis efficiency. The low-cost sugar production from transgenic crops for the biofuels, biochemicals, and biomaterials synthesis was demonstrated *in planta* expression of CWD-enzymes. Rapid initial hydrolysis can reduce hydrolysis times, provide an advantage to a simultaneous saccharification and fermentation process, and reduce the equipment and operation requirements. CWD-enzymes in maize and other plants are being established using *Agrobacterium*-mediated transformation technologies (Ishida et al. 1996; Gray et al. 2004).

5.3.4 Bioproduction of Hydrogen

With depleting fossil fuels, bio-hydrogen is increasingly considered as a potential renewable and top energy source for its clean combustion and its high specific energy, i.e., 123 MJ/kg or ~3 times higher than petro-based fuels (~46 MJ/kg). The enhanced demand for hydrogen has been significantly influenced by its use in the desulfurization of transportation fuel, and by the growth of the transportation sector (Baeyens et al. 2020). Co-currently the quality of crudes is diminishing, leading to a decrease in hydrogen generation from crude processing. This has caused refineries to reevaluate the hydrogen availability. Though hydrogen is proposed as an alternative to fossil fuels, this application is however depending on the availability of technologies to enable sustainable production of hydrogen, most of which are still under development. Bio-hydrogen could soon be entering the fuel market, provided the cost of the pre-cited steps decreases considerably. Under this circumstance, worldwide ongoing research on hydrogen generation and storage is intensive.

Large industrial-scale hydrogen production from biomass or carbohydrates, i.e., hydrogen by fermentation, is undoubtedly desirable and favored; however, still at the level of laboratory or pilot scale. Since hydrogen yields are reported to be low, it is important to select feedstock that is cheap, rather than using carbohydrate-rich raw materials such as starch, corn, or sugars of high commercial value and contributing to the human food requirements. Waste biomass streams, with lower but accessible concentrations of carbohydrates, and offered at a limited or at zero cost (since needing to be treated prior to discharge) are economically the selected feedstock for bio-hydrogen production. It is therefore important to compare the different feedstock towards their real hydrogen production potential. Hydrogen production by fermentation generally refers to three main categories, i.e., firstly by dark-fermentation, where no light is involved; secondly by photo fermentation with light as the source of energy; and thirdly by combining photo- and dark-fermentation.

Chen et al. (2008) combined dark and photo fermentation for overall hydrogen yield and COD reduction. The dark-fermentation effluent mainly comprised acetate and butyrate, and Rhodopseudomonas palustris WP3–5 was used as inoculum in photo fermentation. The total hydrogen yield could be enhanced from 3.80 mol H_2/mol sucrose to 10.02 mol H_2/mol sucrose, and a high COD removal of 72.0% could be obtained. They further found that acetate was the most favorable carbon later source for Rhodopseudomonas palustris WP3–5 in photo fermentation, whereas inhibition occurred when butyrate was used as the carbon source.

5.3.5 Biodiesel from Microalgae

Microalgae biofuels are recognized as a feasible renewable energy option, without significant limitations accompanying conventional biofuels (Nigam and Singh 2011; Chisti 2007). Microalgae on an area basis can produce 15–300 times more oil than the typical crops for biodiesel production. Also, due to their short harvest cycles (≈1–10 days, depending on the process), continuous harvesting with exceptionally higher yields can be achieved in comparison with traditional crops (Schenk et al. 2008). The use of microalgae for the production of biofuels provides the following benefits relative to higher plants: (1) Microalgae synthesize and build up significant amounts of neutral lipids (20–25% dry biomass) with a high rate of growth; (2) Microalgae can be grown all year round, so oil yields per area of microalgae crops could greatly outweigh the yield of best oil crops; (3) Microalgae require less water than terrestrial crops and thus reduce the freshwater burden; (4) Application of herbicides or pesticides is not needed for cultivation; (5) Microalgae sequesters CO_2 from fossil fuel-fired power plants and other sources thereby reducing significant greenhouse gas pollution emissions. (1 kg of dry algal biomass utilizes about 1.83 kg of CO_2); (6) Helps in bioremediation of wastewater sources by removing NH^{4+}, NO^{3-}, PO_4^{3-}; (7) Along with their capacity to thrive under harsher conditions and their decreased nutrient demands, microalgae can be grown in unarable soil in the salt/brackish/coastal waters and do not compete with traditional agriculture for their resources (Dragone et al. 2011) (Fig. 5.6).

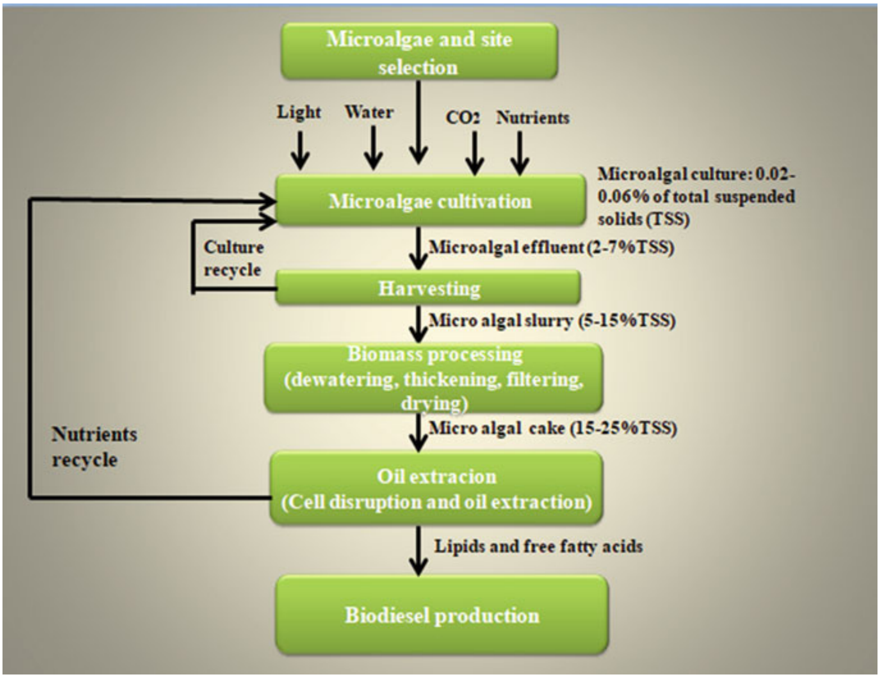

Fig. 5.6 Pictorial representation of biodiesel production from microalgae

Microalgae can be grown inside open-cultural systems such as ponds or lakes as well as in closed-culture systems called photobioreactors (PBRs). Open-culture structures are typically less costly to install and maintain, more durable, and efficient than PBRs. However, open systems are energy-intensive when it comes to nutrient distribution due to problems with mass transfer, and their depth is limited to 15 cm to provide enough light for the microalgae to grow. Moreover, ponds are susceptible to variations in the environment, and controls on temperature, evaporation, and light intensity are not viable. These open systems need more land than PBRs and are more likely to be contaminated by both the bacteria and microalgae present in the area of the culture installations (Manzanera 2011). PBRs are more versatile and intensive land-usage systems designed to meet the specific physical-chemical requirements of the chosen algae allowing the cultivation of species unfitted to open ponds. Nutrient homogenization, light distribution, pH, temperature, CO_2, and O_2 control can easily be regulated in them. Closed systems therefore provide more stable and suitable conditions for production, allowing for higher cell densities and minimize contamination. However, PBRs have a variety of technical issues, which make them non-competitive in race-way pond applications. These problems include overheating, biofouling, accumulating oxygen, problems with scaling up and high building, operation, and maintenance costs (Chen et al. 2011). The cost of development of Biomass PBRs is one order greater than in open systems. PBRs will be profitable if biomass added value is high. Otherwise, the best alternative is open ponds. The estimation of open and closed systems efficiency is complex and relies upon a variety of considerations, such as algal species and the method of measurement of productivity.

For microalgae, three criteria are widely used to determine productivity. The first is the volumetric productivity, i.e., productivity per reactor volume unit (g/L·day), area productivity (AP), defined as productivity per unit of surface occupied by the reactor (g/m^2·day) is the second parameter. The third is illuminated surface productivity (ISP), namely the productivity per unit of reactor illuminated surface area (g/m^2·day). However, aside from efficiency, the preference for closed or open systems relies on other factors (Richmond 2010).

PBRs can either be operated in batch or continuous mode. When used in continuous mode, there are many advantages. First of all, continuous culture offers a superior batch control function. Secondly, the growth levels can be controlled and sustained for long periods in a stable state. Dilution rate regulation can modulate the accumulation of biomass.

Moreover, because of the steadiness of continuous reactors, the outcomes are more consistent and reproducible, and the system has higher output efficiency (Molina-Grima et al. 2000). However, some constraints make the continuous process, in some instances, unsuitable. The difficulty of controlling the production of some no-growth related products is one of these limitations. For example, the method also needs fed-batch culturing and a continuous influx of nutrients that may result in a washout.

The viscosity and heterogeneity of the culture medium can make filamentous organisms challenging to grow in continuous PBRs. Another concern is that a faster-growing contaminant will cause the displacement of the original strain. The contamination risk and loss of bioreactor reliability are made more pertinent when long incubation periods are necessary, so the potential initial investment is in the procurement of high-quality equipment (Mata et al. 2010). Microalgae production experience dramatic changes both in operational (temperature, wind, microbial contaminations, etc.) and commercial terms (improvements in downstream processing, development of non-algal biofuels, etc.). In light of all the criteria listed above, it can be identified that any biodiesel project based on microalgae is unique. These projects thus have to be formulated by thinking in terms of versatility, adaptability, and also multipurpose installation (Richmond 2010).

5.3.5.1 Micro Diesel Using Whole-Cell Catalysts

The energy costs of industrial ethanol and biodiesel processing can be minimized by pure or immobilized enzymes derived from microorganisms. It is difficult to purify cellulases used for the treatment of lignocelluloses such as wood debris and waste paper like the lipases used in the transesterification of lipids yielding biodiesel. Consequently, their costs are far too high for commercially feasible use (Shieh et al. 2003; Ranganathan et al. 2008). The inactivation and inhibition of reactants and substrates is another limiting factor for the use of these enzymes. Such drawbacks underlie intensive attempts to make the reusability of enzymes feasible through protein engineering (Ebrahimpour et al. 2008).

The research interest is also targeted at the immobilization of enzymes in variable supports or the use of GMOs also known as whole-cell catalysts, which contain the required enzymes, preventing their exposure to substrates and functioning as micro-refineries (Kalscheuer et al. 2006). Microbial production of biodiesel involves the creation of genetically modified microorganisms that can transesterify and generate ethanol with lipids and, where possible, optimize the whole process by itself. The production guidelines for the biodiesel industry were developed by Steinbüchel and associates in 2006, using the *Escherichia coli* strain. Their methodology consisted of heterologous expression in *E. coli* the genes from *Zymomonas mobilis, adhB*; encoding for alcohol dehydrogenase, *pdc*; encoding for pyruvate decarboxylase, and *atfA;* for *Acinetobacter baylyi* nonspecific acyl transferase ADP1. The resulting strain was able to ferment aerobic ethanol from sugars as well as to enzymatically transesterify the alcohol with fatty acids from lipid metabolism, resulting in the FAEE known as microdiesel (Kalscheuer et al. 2006). The biodiesel-producing *E. coli* on a pilot plant scale has been used by Elbahol and Steinbüchel, with glycerol and sodium oleates as the carbon and fatty acid sources, respectively, to promising outcomes (Elbahloul and Steinbüchel 2010). But these experiments suggest that the commercial implementation of their results is still a long way off and that the process needs to be changed to make engineered strains adapt to diverse lipid and lignocellulosic sources. Such alterations will allow the usage of forest and agricultural wastes, making the biodiesel production process as adaptable as chemical transesterification.

5.3.5.2 Biodiesel from Oily Biomass

Microalgae are not the only option to produce biofuels from oily biomass. Many prokaryotes and eukaryotes can build up large concentrations of lipids. However, because of variations in the form of storage lipids, all species are not appropriate for biodiesel production. As stated by Waltermann and Steinbüchel (2010), many prokaryotes synthesize polymeric compounds, such as poly(3-hydroxybutyrate) (pHB) or other polyhydroxyalkanoates (PHA), while only a few are found to have an accumulation of triacylglycerols (TAGs) and wax esters (WE) in the form of intracellular lipid bodies. The eukaryotes, predominantly consist of storage TAGs, with the absence of PHAs, and WE accumulation has exclusively been reported in jojoba (*Simmondsia chinensis*). The lipids are both energy and carbon storage compounds that assure the metabolism viability during starvation. Similar to PHAs, TAGs, and WE, synthesis is encouraged by cellular stress and nitrogen scarcity along with the abundance of a carbon supply, during unbalanced growth (Kalscheuer et al. 2004). The prokaryotes reported to have an accumulation of TAGs are nocardioforms such as *Dietzia* sp., *Gordonia* sp., *Mycobacterium sp*., *Nocardia* sp., *Rhodococcus sp*., and *Streptomycetes*. Members of the gram-negative genus *Acinetobacter* also showed TAGs storage (Waltermann and Steinbüchel 2010).

Among eukaryotes, except for algae, yeasts of the genera *Candida* (Amaretti et al. 2010), *Saccharomyces* (Kalscheuer et al. 2004; Waltermann and Steinbüchel 2010), and *Rhodotorula* (Cheirsilp et al. 2011) are the strong biodiesel producing candidates. Steinbüchel and collaborators have worked with *Saccharomyces cerevisiae* H1246 (a mutant strain unable to accumulate TAGs) on the heterologous expression of the nonspecific acyltransferase WS/DGAT of *Acinetobacter calcoaceticus* ADP1 (Kalscheuer et al. 2004). TAGs, as well as fatty acid ethyl esters and fatty isoamyl esters, were reestablished in the yeast. This study confirms that *Acinetobacter calcoaceticus* transferase has tremendous potential for the synthesis of a wide variety of lipids in prokaryotic and eukaryotic hosts for biotechnological applications. Likewise, the engineered strain developed with *Escherichia coli* TOP 10 (Invitrogen) could directly produce fatty acid ethyl esters (biodiesel) from oleic acid and glucose (Kalscheuer et al. 2006). Cheirsilp et al. (2011) studied a coculture of oleaginous yeast *Rhodotorula glutinis* and microalga *Chlorella vulgaris* in industrial wastes. The effluents used include seafood processing wastewater and sugar cane molasses. They found a synergism in the mixed culture. In the presence of *C.vulgaris* which served as an oxygen source for the yeast, *R.glutinis* grew faster and accumulated more lipids, while microalgae obtained excess CO_2 from yeast. The optimal conditions for lipid production were microalgae to yeast ratio of 1:1, initial pH of 5.0, molasses concentration at 1%, 200 rpm shaking, and light intensity at 5.0 flux under 16:8 h light and dark cycles.

5.3.6 Fourth-Generation Biofuels

Biofuels of fourth-generation are just a step further from third-generation biofuels. The keywords are “Carbon capture and storage” both at the feedstock or manufacturing technology level. Biomass crops are viewed in fourth-generation systems as efficient machines for carbon capture that removes CO_2 from the atmosphere and seal it in their branches, trunks, and leaves. The rich carbon biomass is then converted by second-generation technologies into fuel and gases. The feedstock is not only optimized to maximize production performance but is also expected to produce more carbon dioxide as the crop grows. The processing techniques are often coupled (mostly thermal) with “carbon capture and storage” technologies, which funnel the carbon dioxide produced in geological deposits (such as geological storage, in depleted petroleum fields), or by mineral storage (as carbonates). Fourth-generation biofuels can therefore efficiently reduce greenhouse gas emission by being more carbon-neutral or even carbon-negative compared to the other generation biofuels (Fig. 5.7). Fourth-generation biofuels optimize the concept of “Bioenergy with Carbon Storage (BECS).”

The Taiwan National Science Council, staff members of the US Department of Agriculture and North Carolina State University’s Taiwan Forestry Research Institute (TFRI) worked out a gene modification experiment that not only developed eucalyptuses with greater than average CO_2 absorption capacity but also produced

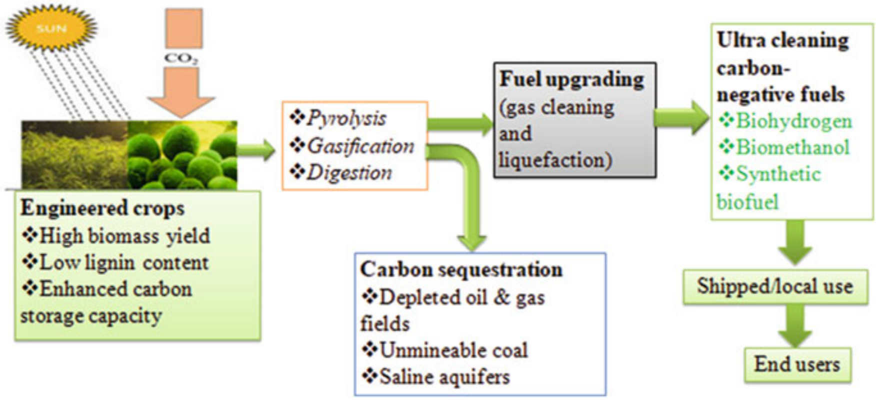

Fig. 5.7 Fourth-generation biofuel sources and production

less lignin and more celluloses. TFRI researcher Chen Zenn-zong, Taiwan Forestry Research Institute stated that cellulose, hemicelluloses, and lignin are all made from carbon elements (https://www.iatp.org/news/gene-modified-eucalyptus-ingests-more-co2-taiwan).

Nonetheless, in industrial methods for the processing of pulp and bioethanol processing, only cellulose can be used. Lignin is the "glue" that holds cellulose together. Cutting the lignin barrier is an essential obstacle to cellulosic ethanol production. Increasing the demand for genetically modified eucalyptus for the relevant industries has been changing the cellulose-lignin relationship to improve the tree absorptiveness of CO_2 to reduce greenhouse gases. More CO_2 is absorbed if more trees are planted for growth. These are also gradually being used to produce next-generation biofuels with their high biomass yields. These include cellulosic ethanol and fuels derived by processes involving pyrolyzes (bio-oil) and biomass to liquids that produce synthetic biofuels (gasification and synthesis through the Fischer-Tropsch process). Eucalyptus is an important crop for solid biofuels (wood biomass), which can also be ignited with coal or used in biomass plants (Cavalett et al. 2018). Estimated evidence indicates that eucalyptus planting has enormous potential in the tropics. A European project analyzing green steel production based on the use of tropical biomass revealed that 46 m ha in Central Africa were available. These broad fields may be cultivated with eucalyptus without a significant adverse effect on the climate (Biopact 2007).

5.3.7 *Future Perspective*

There is already a substantial market for biofuels in developed countries primarily fuelled by regulatory mandates for biofuels to be blended into petroleum fuels. Driven by highly stringent regulatory requirements, continued high oil prices, and energy security issues, this market will be rising dramatically in the years ahead. Export prospects in biofuels or feedstocks for biofuels will increase over the years. The drawbacks of biofuels of the first generation are food versus fuel conflict, economic nonviability, and the elimination of greenhouse gas emissions. Greater farming efficiency would tend to reduce food and fuel disparities to some degree, and it would also be useful to focus on the production of biofuel feedstock in countries less suitable for food crop production. Lignocellulosic Biomass, relative to the feedstock of primary biofuels, is typically (a) not edible and thus not directly comparable with food production; (b) can be grown exclusively for energy purposes thereby making it possible to obtain a higher yield per unit area; and (c) contains more of the superior plant resource thereby increasing the efficiency of land use. These fundamental properties of lignocellulosic materials translate into significant environmental and energy gains for second-generation biofuels, compared with other biofuels of the first generation. Worldwide, there are various attempts to commercialize biofuels of the second generation. The research and development advancements, accompanied by experiments on a commercial scale, are required to demonstrate the feasibility of unsubsidized cellulosic ethanol. Even with supportive policies and facilities, time is needed before second-generation biofuels will be able to make an impact in any developing country, because of the research, production, and demonstration criteria required to enter the stage of commercial deployment. In terms of years, it is likely a minimum of 5–10, though less than 10–20, to create a commercial second-generation biofuel industry.

A technology investment program must be in effect in one country for effective implementation and transition of innovations. Regional research programs should fulfill this purpose for smaller countries. An innovation system refers to people engaged in a wide variety of practices and organizations including (a) academic universities and institutions that produce fundamental information and assimilate expertise from the global community; (b) businesses capable of establishing joint ventures with international firms and incorporating innovation and development into emerging technologies; (c) government departments that will identify and promote the science and development change requirements needed; and (d) the public policy framework focused on development.

The early (pre-commercial) phases of production of technology will ideally continue with participation in technological creation (Gray et al. 2004) and in several other major developing countries, these programs are in operation, including India and China (Mortensen 2019). Although biofuel technologies of the first generation are reasonably well known but still face economic challenges. Competitive second-generation industries would be encouraged by the establishment of regulatory criteria for the use of biofuels, particularly in large countries or regional clusters in smaller countries. Specific support for research, production, and demonstration grants or discounts on biofuel costs should also be taken into consideration.

5.4 Conclusion

Biofuels remain a key solution to mankind energy crisis, and there is an ongoing search to find stability between sustainability and expenditure. A multitude of issues pertaining to first-generation biofuels such as competition with food crops have been addressed by its second-generation successor. Subsequently, several companies around the globe have utilized them in their day-to-day operations so as to reduce costs and reduce their ecological footprints. However, there is the sticking matter of plant-based fuels being space- and time-consuming. Furthermore, demand for these biofuels may exceed our ability to produce them. As such, further research and development have been invested third- and fourth-generation biofuels due to the belief that the best biofuels will cut out the middleman entirely and bypass crop plants. Instead, they will rely on algae and a few microorganisms that have the capacity to directly and efficiently turn sunlight into energy through photosynthesis. These next-generation biofuels have greater production and environmental benefits as opposed to their predecessors. Microalgae for instance only require a small amount of arable land, and its high photosynthetic rate gives it the ability to accumulate a considerable amount of lipid. Fourth-generation biofuel on the other hand probes the limits of nature by experimenting with microbes. While results have been promising from an environmental perspective, both generations have yet to be proven on a large-scale basis. The biggest challenge is finding a way to make these biofuels commercially viable while keeping them environmentally friendly. Nevertheless, should these issues be conquered, the entire energy landscape will be altered for the better. Moreover, it could even affect worldwide trade as a nearly identical version of petrol or diesel can be manufactured domestically rather than being imported from the Middle East. For now, experts continue to invest time and money towards finding a way to make these next-generation biofuels commercially viable; whoever manages to do so will make more than profits, they will be making history.

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Chapter 6
Biological Pretreatment Strategies for Second-Generation Lignocellulosic Biomass to Enhance Ethanol Production

Manmeet Kaur, Mandeep Kaur Gill, Shivani Sharma, G. S. Kocher, and H. S. Sodhi

Abstract The tremendous population explosion in the last 25 years has resulted in overall rising by approximately 200% in the total energy consumption. In order to meet the energy needs, alternative non-conventional sources have been explored globally in addition to standard fossil fuel as a modest start. Due to its availability in essence and far less impacts on the environment than coal and oil sources, bio-fuel reformation is an indispensable fuel of choice for the production of lignocellulosic materials. Lignocellulose, however, is an obstinate component and is hard to break into desirable products as the building block of plants. There are several limitations on common "physico-chemical" methods used for the pretreatment of the substratum. Conversely, the use of microbial ability to hydrolyze biomass is an amusing field of investigation. Lignocellulosic biomass treatment is an innovative strategy to biological for delignification. This method is very "monetary," "high efficiency," "ecologically friendly," and "non-toxic material formation," such as "furfural" and "hydroxymethyl furfural". There has been revealed a biological approach using direct microorganisms and the use of microbe extracted enzymes. Fungi such as "soft-rot fungi," "brown-rot fungi," and "white-rot fungi" are included in microbial treatment. The plant polysaccharides are mainly degraded with minimum lignin degradation, with both "brown-rot" and "soft-rot fungi" while both the lignin and polysaccharide components are thoroughly mineralized. Due to the complexity of the substrate, it is necessary for several oxidative and hydrolytic enzymes to synergistically hydrolyze components of the biopolymer such as bioethanol or other energy substances. This chapter contains easy information on latest events in effectual microbial degradation methodologies to effectively choose the most significant substances of lignocelluloses for bioethanol.

Keywords Lignocelluloses · Pretreatment · Lignin · White-rot fungi · Paddy straw · Wheat straw · Oxidative and hydrolytic enzymes · Second-generation ethanol

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6.1 Introduction

The rapid urbanization was enormous during the last century. The enormous population growth ranged from 2.7 billion in 1955 to 7.6 billion in 2018. The reserves and utilization have been significantly burdened. The result was a substantial increase in worldwide energy consumption. The rise in energy supply (including both renewables and non-renewables) is valued at nearly 200% between 1990 and 2016 (GESY (Global Energy Statistical Yearbook) 2017). Oil remains the main fuel source in the entire globe, representing 32.9% of total of the world's energy use; while coal supplies about 40% of the world's electricity (WER 2016). The main energy source is petroleum and oil; however, it is quickly depleting all over the world (Tong et al. 2012). Traditional non-renewable energy resources are restricted. Renewable sources, however, have a great future to sustain our constantly challenging culture. Biomass was the primary source of energy until the early nineteenth century. 18% of the consumed total energy comes from renewable sources, with a major share of bioenergy (14%) and 10% of global energy supplies. Production of ethanol is expanding, with an area of around 134.5 and 39 billion liters expected to rise by 2024 (REN21 2006). The increase in fuel needs due to urbanization, development of energy-driven technology, transport has serious consequences that are quickly erasing the non-renewable energy source associated with oil reserves.

It is assessed that by 2025, the energy ultimatum of several developed and developing countries will increase approximately 50%. Bioenergy is a significant alternative for non-petroleum, renewable energy, by using a sustainable and cost-efficiency approach. Like bioethanol, biofuels are mainly plant-borne from controlled lignocellulose biomass conversion (Aulitto et al. 2019).

Appropriate use of these cellulosic products can help to demote the devoir of lignocellulose waste by limiting greenhouse gas and producing clean energy. Bioethanol, a green product that emanates fewer carbon monoxide, is generated mainly from sugar, starch, or cellulose (around 12–15%) (Zainab and Fakhra 2014). The use of sugarcane and maize, highly demanding food materials, which initiated affecting the world's alimentary demand over production, was the first biofuel generation (1Gen biofuel). It has derived experts' attention towards second generation (2Gen biofuel) including organic waste and cellulosic biomass. In almost all countries, cellulosic biomass such as "farm residues" and "industrial waste" acts as "ample" and "affordable" source. However, the cultivation of "cash plant," "cotton," "corn," "honge," "mixed paper waste," and other substrates takes place for the power generation of second-generation biofuels. Third and fourth-generation biofuel production depends on the 'formulation of vegetable-oil' and 'bio-diesel' from various sources such as "oilseed algae" (Byadgi and Kalburgi 2016).

Among the most plenteous subsystem in nature is lignocellulosic substrates, made of "cellulose," "hemicellulose" and "lignin." It represents an enormously large number of sustainable energy resources on the planet with numerous uses (Kumar and Sharma 2017). This plant product includes a significant substantial part of the prevalent food sources. By using plant biomass as an origin of bioethanol, judicious use of assets that do not affect food supplies and ecological degradation is needed (Isikgor and Becer 2015). Rendering to the renewable standard rules, the Energy Independence and Security Act 2007 sets an epoch of renewable fuel volumes up to “36 billion gallons” in 2022. The estimated cellulosic material resource amounts to “16 billion at 36 billion” (JoVE Science Education Database 2017).

Over, 1.75 billion cellulosic materials out of “18.15 billion gallons” of substitute power were proposed for 2014. Throughout the subsequent “Environmental Protection Agency (EPA)” proposal, however, it was diminished to 17 million gallons due to technical constraints. The advancement of the transformation of celluloses to ethanol is a rigorous field of investigation (Kahn et al. 2019). The productive use of lignocellulosic materials involves many complications. Lignocellulosic ingredients have a rebellious property in a rigid manner, which precludes their split into beneficial by-products. To enhance the demolition of the cell wall of the raw material, it is vital to comprehend the pretreatment and property method. Various methods, including “physical,” “chemical,” and “biological” are available for the preparation of lignocellulosic materials (Saravanakumar and Kathiresan 2014).

In this field, eco-friendly and economic methods are indeed demanding. After pretreatment downstream processing involves “operating cost,” “costs of capital,” “ecological factors.” “costs of biomass,” “waste generation,” etc. There is indeed a massive trade between pretreatment processes where biological processes have many advantages as they are economically economical, environmentally friendly, and energy efficient. While several reviews have outlined the conventional processes of pretreatment, a comprehensive biological pretreatment analysis along with pros and cons of the process is permissible. Therefore, this chapter deals with the notable advancement and future perspectives for lignocellulosic biomass pretreatment processes emphasizing the biological processes, enzyme hydrolysis of different lignocellulosic feedstocks to produce bioethanol (Kumar and Sharma 2017).

6.2 Ethanol: Biofuel History

Ethanol is a fuel used during modern human history, which is technically sophisticated. Bioethanol was also used as an invention of ignition engines. Ethanol was among the most popular lighting agents in the 1850s, producing about “90 million gallons” of ethanol. The taxation of ethanol in order to aid civil war finance has raised the perspective of ethanol. Kerosene got cheaper and in the 1860s ethanol was quickly substituted as the first light.

Ethanol production had touched ten million gallons till 1914. But petroleum emerged as a fuel in 1919 and ethanol was used again, with fuel diminishing. By the early 1940s, during the World War II, ethanol was reversed when used for fuel and synthetic rubber. The United States produced approximately “600 million gallons” of ethanol yearly during this period (Morris 1993). The supply for ethanol decreased and declined for another two decades at the culmination of the Second

World War, mainly in view of cheap oil imports (Campbell and Laherrere 1998). Before 1970s, the scarcity of "gasoline" has accelerated concern about rising crude oil prices and escalating political precariousness that has taken ethanol into the world again.

6.3 Generation of Biofuels

A propitious part as a discretion source of energy is the controlled bioconversion of lignocellulosic biomass producing hydrogen, methane, or ethanol. Bioethanol is one of the intermediates produced by fermentation of the different sugars for anaerobic degradation (Ahring and Westermann 2007). In 1897, Nikolas Otto used ethanol in the internal combustion engine for the very first time as motor fuel (Saini et al. 2015). At the end of the twentieth century, countries such as Brazil and the United States started to make biofuels from biomass such as sugarcane and maize (Marin et al. 2016). Researchers continue to work towards improving the productivity of biofuels, which can be classified into four different generations.

6.3.1 First-Generation Biofuel (1 Gen)

Bioethanol production is known as "first-generation biofuels" from feedstock like sugarcane, starch, grain, molasses, animal fats, and vegetable oil. 1 Gen biofuels are mainly produced from sugarcane, maize, or molasses, according to the use of feedstock. Approx. 21 million m^3 of sugarcane and maize grains produces approx. 60 million m^3 of ethanol from plants worldwide (Lennartsson et al. 2014). Sugar extraction from these sugar cultivations involves mechanical pretreatment such as "crushing and grinding," "enzyme hydrolysis," and "ethanol fermentation." The distillation and dehydration processes separate ethanol from the product.

In ethanol production, two main processes exist for starch, "dry grinding" or "wet grinding." The process of dry grinding includes crushing all maize together with "high-protein animal feed" (known as "soluble grain dry distillers") in order to produce ethanol. On the other hand, in the wet process, the soaking of maize is carried out and then germ, starch, and fibers are separated (Devarapalli and Atiyeh 2015).

However, since biomass was straightway competitive with food supply the usage of raw ingredients in the "biofuels" production has been reprehended substantially (Nigam and Singh 2011). In order that the proposal meets the claim for energy sources, which would have substantial mutilation to biodiversity, etc., large agricultural land mass would meet the requirement of raw materials (Saini et al. 2015). However, IEA 2008 is concerned about the potentially disadvantages of bioethanol of first generation, such as:

- **Corrival between fuel and food:** It's also that developing bioenergy options, especially bioethanol based on food, may have an adverse impact on food requirements. Furthermore, rising food prices have such a pessimistic effect on the developing world, which has relatively low disposable incomes. This alarm caused the search for additional biofuels.
- **Deforestation:** Ergo, prolonged biofuel production can lead to huge habitat destruction from persistent vegetative cover to production of food.
- **Multiple feedstock versatility:** Innovations and plant designs are preferable to commercial viability, which can flexibly process with a numerous distinct feedstock. Storage of crops can increase biofuel costs if the plant operates around the year on many food crops used for biofuels and the costs of production of biofuels can be accelerated by storing raw substances.

6.3.2 Second-Generation Biofuel (2 Gen)

Second-generation biofuel is derived mainly from cheaper, naturally occurring organic wastes which does not impede with the provision of sustenance. Different forms of lignocellulosic feedstock include "herbal and wood energy crops," "forest residues," and "agricultural residues" such as "sugarcane bagasse," "rice straw." "banana waste," and "rice husk"). Cellulosic ethanol is a gene for biofuels (Byadgi and Kalburgi 2016).

The "Fischer-Tropsch process (FT)," a catalytic process, produces a synthesis of liquid fuel transport and other valuable chemicals (based on cobalt and iron catalyst). In the existence of a transition metal catalyst, this synthetic process results in hydrogenation of carbon monoxide gas (Choudhury and Moholkar 2013). Howbeit, the consumption of resources is a daunting challenge which required to be addressed for the production of an "affordable," and "sustainable biomass energy" source through the substratum quality, pretreatment, and fermentation processes.

Net carbon emissions are expected to be "reduced," "energy efficacy increased," and "energy dependency reduced" and limits of first-generation biofuels potentially overcome (Antizar-Ladislao and Turrion-Gomez 2008). Financial implications of cellulosic ethanol transition include "renewable nature," "lasting acceptable," "miniature emissions of net coal," "high energy efficacy," and "little energy dependence" (IEA 2008). Nonetheless, many steps must be taken to enhance second-generation biofuel processes, reduce costs, and improve switchover reliability and performance.

6.3.3 Third-Generation Biofuel (3 Gen)

Algal biofuels have a number of benefits over 2Gen biofuels, such as non-interfering with agro-food, "easy growth," "high lipid content," "low cost," and "high-power renewables," which can be used for third-generation biofuels. A range and potential sources of biomass fuel production have been found and studied, including *Chaetoceros calcitrans*, *Nannochloropsis sp.*, *Chlorella species*, *Scenedesmus*, and *Botryococcus braunii* (Dutta et al. 2014). However, the algae's lipid content may vary depending on the species and conditions of stress. There seem to be a number of other technological restrictions preventing the development of this 3Gen biofuel technology (Aro 2016).

6.3.4 Fourth-Generation Biofuel (4 Gen)

Biofuel (4Gen) fourth generation is an emerging biofuel field that benefits from biofuel generation compared to previous generations. Biomass feedstocks that absorb CO_2 are turned into fuel in this technology. It is derived from an amalgamation of imitation biology and knowledge, including the design, construction, and re-design of existing natural biological systems for useful applications (Aro 2016). Sustainable energy production and carbon sequestering is the basic aim of this development. Few algal (*Schizochytrium*, *Chlorella*, *Scenedesmus*, etc.) and microbial *Bacillus anthracis*, *Bacillus subtilis*, and *Acinetobacter*) are testified as impending biological contenders for 4 Gen biofuels (Dutta et al. 2014) (Table 6.1).

6.4 Current Status of Bioethanol

6.4.1 Worldwide Production Status of Bioethanol

The global bioethanol production has risen significantly even before the energy crisis of 1970. (Campbell and Laherrere 1998). The revenue increased to more than 65 billion liters in 2008, with less than one billion liters expected in 1975 reaching 100 billion liters in 2015 (Licht 2005). The IEA (2008) forecasts a 1% rise in global crude prices annually.

America's share of global bioethanol products is "50%," and Brazil accounts for "39%" of the production capacity (Gnansounou 2010). Brazil is among the most up-to-date countries in the production of ethanol, and closely all Brazilian automobiles use wholesome "ethanol" or "petrol" and ethanol permutations (75:25) (Mussatto et al. 2010). Brazil's great proportion of ethanol incorporated to petrol is indeed an effort by government to limit oil supplies (Prasad et al. 2007). This has subsidized to a vivid upsurge in the ethanol production in Brazil between 555 million liters (1985/1976) and 16 trillion liters of sugarcane (2005/2006) (Orellana and Bonalume 2006).

Like Brazil, America has become an immense investor in ethanol exploration, increasing its bioethanol production from "6.16 billion liters" to "39.3 trillion liters" in 2000, which is "10.4 trillion gallons" to "39.3 billion gallons" in 2009 (Petrova and Ivanova 2010). Nowadays, maize accounts for over "95%" of ethanol production in the United States. It was, notwithstanding, predicted that at the end of 2012 it

Table 6.1 Detailed analysis of biofuel production (Aro 2016)

Biofuel generation	Feedstock source	Examples of biofuels	Processing method	Advantages	Disadvantages
First generation	Edible oil seeds, food crops	Bioethanol, biodiesel, biobutanol	Fermentation of sugars, esterification, and transesterification of oils	Economical fuel production technology	Low yield
Second generation	Lignocellulosic wastes feedstock material, forest residues	Biodiesel, bioethanol	Physical, chemical, and biological pretreatment of raw material and fermentation	Substrates not competing with food stuff	Highly efficient
Third generation	Algae	Biobutanol, methane, biohydrogen, bioethanol	Algae cultivation, harvesting, oil extraction	Easily cultivated	Processing consumes more energy
Fourth generation	Algae and microbes	Bioethanol, biohydrogen, biobutanol	Metabolic engineering of algae	Higher yield and lipid content	Mostly genetically modified organisms, highly new area of research

would produce around “1.53 billion liters” of cellulosic ethanol (Solomon et al. 2007). The greater proportion of ethanol is mass-produced in Europe from “wheat” and “sugar beet” (Prieur-Vernat and His 2006). The biofuel approach of the European Union seeks to reduce oil dependency and the unfavorable effect on global. The OECD share of the economy oil demand is predicted to decrease from 57 to 43% (IEA 2008). China has capitalized a lot in the ethanol production, importing around 52% of the total oil in 2008, because it is the biggest manufacturing sector (Fang et al. 2010). Biofuel ethanol production started with four grain plants manufacturing approximately “1.75 billion liters” of ethanol as a biomass feedstock in China in 2002. The government of China restricted grain-based ethanol projects. Numerous non-food crop production ethanol technologies such as cassava and sweet are developing (Li and Chan-Halbrendt 2009).

There are also other countries such as Korea and Japan. For energy security and sustainability, a native and reasonable power basis has developed an extraordinary precedence. In 2003, Japan began production of biofuels, with an annual total bioethanol volume of around “30,000 liters” by 2007 (Matsumoto et al. 2009). In order to execute 3% (E3) and 5% (E5) ethanol blending nationwide, Korea consumes around “10 milliards of liters” of gasoline per year and 3 to 5 million liters of ethanol is needed (Kim et al. 2010). The government in Korea therefore announced that it intends to increase biofuel supplies from 0.2 billion liters (2008) to 5 billion liters between now and 2030.

6.4.2 Credentials of Bioethanol Production in India

In 2003, the forecasting team of the Indian administration, which identified “bioethanol” as the main biofuel, produced a comprehensive biofuel development report. The ethanol blend was suggested for 10%; in India by 2011–2012 and the oil blend was mandated for 5% in 11 states and three territories of the territorial union of India. Popularity was “0.64 billion liters” for ethanol in 2006, while petrol doped/blended at 5%. Strong price is estimated to be “2.2 billion liters” for 10% blending in 2017 (Sukumaran et al. 2010). According to an estimated figure in 2006, the true ethanol production was only “0.39 billion liters,” and this was insufficient in oil demand uncertainty the over-all gasoline had to be incapacitated at “5%.” Ethanol is primarily produced from sugarcane molasses in India, but its substratum must be food supply competitive and must thus supply the necessary amounts of ethanol. Consequently, the country prerequisites to change bioethanol technologies which practice biomass feedstuffs permitted from feed or food. The utmost apposite bioethanol technology for the nation is mass-produced using “rice straw.” “wheat straw,” “rice husk,” “bagasse,” and “sugarcane” (Sukumaran et al. 2010). The cumulative bioethanol production from the organic matter is estimated at worldwide 491 gigaliters (GL) per year, according to Kim and Dale (2004).

India alone produces “25%” of total world ethanol production, i.e., 123 GL/year, if all available lignocellulosic residues are used for the production of ethanol.

Therefore, a geographical distribution assessment and precise biomass available information in various parts of the country are a prerequisite for considering a bioethanol production plant. In perspective of this, 500 district studies in 23 countries for the evaluation of lignocellulosic accessibility data were sponsored during the ninth plan. Furthermore, it has been co-funded with the "Biomass Resource Atlas of India" project by "Bangalore" and the "Regional Remote Sensing Service Center (RRSSC)," which purposes to highlight the accessible biomass from district research and certain other outlets of authorized cultivar-knowledge.

6.5 Plant Lignocelluloses: Constituents

The plant cell walls make up about "90%" of its dry cellulose biomass; "hemicellulose" and "lignin" (Saini et al. 2015). The foremost part of the plant cell is cellulose. The polysaccharide in a linear line, high molecular weight of thousands of β (1–4) is made of cellular with the chemical formula $C_6H_{10}O_5)_n$, which has a linked D-glucose unit (Prasad et al. 2018). Hemicellulose and cellulose hydrolysis protection for plantations in order to maintain its rigid structure is provided by lignin, which is also the second richest natural organic polymer. Lignin is a polymer that combines the largest ether and carbon bonds that polymerize the monomers of 4-hydroxyphenylpropanoids, which form laccases and peroxidases in plants (de Gonzalo et al. 2016). Macromolecular fiber provides mechanical resistance to plant body fibers, reduces water permeation by the plant body's cell wall, but also helps to protect plants against extracellular enzymes being incorporated into the natural surroundings. The hemicellulose contains "glycosides" associated with β-1 backbone; "xylose," "glucomannan," and "beta-glucans." Therefore, hemicellulose intricacies and pretreatment type are necessary in different enzymes (Alvarez et al. 2016). "Cellulose," "lignin," and "hemicellulose" make a significant contribution to strengthening the cell wall.

Lignocellulosic biomass is predominant in woody and non-woody components of the plant waste. Wood biomass in its physical and chemical compounds has a greater amount of lignin than agricultural biomass, making its microbial digestion very recalcitrant. The configuration of ligno-cellulose depends heavily on the category and resources. Typically, 10–25% lignocellulose, 40–5% cellulose, and 5–30% hemicellulose are present as a composition. Enzymatic or chemical hydrolyte methods are the best way to break down cellulose polymers. The glucose and xylose are released, respectively, and after hydrolysis of "cellulose" and "hemicellulose" might be castoff for "ethanol fermentation" (Anwar et al. 2014). Lignocellulosic biomass is predominant in woody and non-woody components of the plant waste. Wood biomass in its physical and chemical compounds has a greater amount of lignin than agricultural biomass, making its microbial digestion very recalcitrant. Wood biomass is physically designed to be resistant to lignin-containing biomass and therefore extremely recalcitrant for microbial destruction. The notable features of wood biomass also deviate in structure (hardwood and softwood). Hardwoods are generally thicker than softwoods. The hardwoods have a greater xylan and less mannan than the softwoods, with minor cellulose, hemicellulose, and lignin composition differences (Alvarez et al. 2016). For the entire assimilation and usage of plant sources, an assemblage of operative "oxidative" and "hydrolytic" enzymes is indispensable.

(a) **Cellulose:** The cellulose $(C_6H_{10}O_5)_n$ consists of insoluble, crystalline, enzyme-resistant microfibrils, which form the larger part of the linear polysaccharide chain and the major components of plant cell. This linear polysaccharide D-glucose molecule is interlinked to β-1,4 glucose units by "hydrogen bonding" and "van der Waals interactions" (Chatterjee et al. 2015). This highly complex polysaccharide is highly strong and, because of its cellulose alternative repeated unit, forms cellobiose in a transverse 180 °C mesh. Cellulose may be arranged according to structural shapes ("crystalline") and distorted ("amorphous") regions (Horn et al. 2012). Certain irregularity molecules, such as "surface micropores" and "large corpuscles" also exist in crystal cellulose, which makes it heterogeneous and partial in the aqueous medium. Plant fibers, such as "hemp," "jute," "flax," "cotton," "wheat straw," "rice," "wood," and other terrestrial biomass are a major source of cellulose (Chatterjee et al. 2015). Heterogeneous molecules can influence the movement of cellulose. Cellulose enzymes are mediated by cellulases belonging to the "glycosylic hydrolase enzyme family." There are three types of cellulase groups, namely "endo-β-1,4-glucanase" (containing the cellulose molecule's non-crystalline section), "exo-β-1,4-cellobiohydrolase" (containing the cellular crystalline section), and "β-glucosidase" (cleave of the molecule of cellulose) (Willis et al. 2010).

(b) **Hemicellulose:** The heterogeneous biopolymers are the main and secondary cell walls of hemicelluloses. Hemicelluloses are biosynthesized in Golgi apparatus through the glycosylate pathway, then transduced to the cell wall by the plasma membrane.

Diverse configuration of the hemicellulose contents is available for various plant species. "Glucomannan," "galactomannan," "galactoglucomannans," "glucuronoarabinoxylans," and "xyloglucan" are the mixed links of glycoside and have different angiospermatic and gymnospermatic lines (Sorieul et al. 2016). Hemicellulose compound complexity and pretreatment type are therefore required for substratum degradation by various hemicellulolytic enzymes (Alvarez et al. 2016). As the main hemicellulose component of softwood species, (Galacto) glucomannans are bound by "linear chain of ß-(1,4)"-related units D-glucopyranose and D-mannopyranose (Shimizu 2001). Cellulose fibers, structural proteins, neutrals (XG), and some negative pectorins in the primary wall of the type I contain celluloses, whereas primary cell type II is found only in monocots with the presence of cellulose and mixed connective glucans (Sorieul et al. 2016).

(c) **Lignin:** Lignin is a "non-carbohydrate"'; "alkyl-aromantic heteropolymer" that is abundantly available in plant cell walls (contributing about 30% to

Table 6.2 Configuration of various lignocellulosic surplus

S. no.	Lignocellulosic substantial	Lignin (%)	Cellulose (%)	Hemicellulose (%)	References
1	Sugarcane bagasse	~20	42	25	Kim and Day (2011)
2	Sweet "sorghum"	~21	45	27	Kim and Day (2011)
3	"Corn" cob	~15	45	35	Howard et al. (2003)
4	"Rice" straw	~18	32.1	24	Howard et al. (2003)
5	"Wheat" straw	~20	33–40	25	Prasad et al. (2007)
6	"Corn" stover	~18	38	33	Byadgi and Kalburgi (2016)

lignocellulosic materials, mainly guaiacyl and syringyl monoaromatic phenylpropanoid unit) (Gall et al. 2018). It consists of three monolignols: coniferyl, p-coumaryl, and sinapyl alcohol which differ in the measure of their methoxylation (hydroxycinnamyl aromatic alcohol monomers) (Cragg et al. 2015). Lignin oligomers have the oxidation of phenylpropanoid subunits: "guaiacyl (G),"; "p-hydroxyphenol (H)," and "syringyl (S)" both of which vary in individual plants, to those monolignols (coniferyl alcohol, p-coumaryl alcohol, and sinapyl alcohol) (Fisher and Fong 2014). Lignin is a foreseeable source of natural aromatic substances such as guaiacyl, syringyl, and tricin, which are associated with a binding of β-ether and require the active use of β-etherase enzymes in lignin polymers to easily obtain important components (Table 6.2).

6.6 Lignocellulosic Agriculture Residues

6.6.1 Paddy Straw

The monocotyledon Paddy belonging to the *Oryza* genus comprises two species grown, namely *Oryza sativa* or *Oryza glaberrima* from Asia and Africa (Khush 1997), both of which are better produced and grown in 112 nations, and only in western Africa. Paddy is the third most important food of approximately "50%" of the nation populace in footings of crop production (Slayton and Timmer 2008). Paddy is grown in India in 43 million ha and produces approximately "96 million tons" of paddy straw (Sari and Budiyono 2014).

Punjab tends to produce 17 million tonnes, from which approximately 15 million tons are resolved out of the area through incineration, each year in an agrarian State of India (Anonymous 2014). For the aforementioned purposes, growers use straw burning:

1. brief period of post-paddy cultivation for wheat sowing
2. decrease in the number of crops and livestock that are fed by straw

3. live stocks are fed with abundant fodder
4. involving enormous costs of equipment purchasing, cuts, ploughing, and transportation
5. limited labor allocation for straw handling
6. consequences of crop damage from infectious diseases caused by straw in the soil
7. High-SiO_2 content in straw, preventing deterioration of the straw

In addition to organic particles, which include polycyclic aromatic hydrocarbons, n-alkane (Gadde et al. 2009) and different dioxins, uncontrolled straw burning releases various types of pollutant into the environment, such as CO_2 and trace amounts of SO_2 (Korenaga et al. 2001). These pollutants have reportedly caused serious illnesses in humans, including cancer. In addition, open field CO_2 emissions pretense a somber peril to the milieu as they make a noteworthy influence on global warming. The huge amount of heat produced by the combustion of straw directly affects the soil properties, decreasing humidity and flora (Anonymous 2013).

6.6.2 Wheat Straw

Wheat is one of the foremost garners in the biosphere. The “internodes,” “the nodes,” “the leaves,” “the stripes,” and comprise wheat straw. Compositional analyzes for wheat straw demonstrate the presence of “cellulose (~40%),” “hemicellulose (~25%),” and “lignin (~20%).” (Rodriguez-Gomez et al. 2012). The use of wheat straw sources has shown a massive investment trend. However, wheat straw in a form of CO_2 emissions is the ideal option for sustainable development in the social structure (Tian et al. 2018). Worldwide production in 2009 was estimated to be about 690 ktons and worldwide, 730 million tons in 2014. Every year, large amounts of wheat straw are produced as a waste of wheat, and after rice straw, the most abundant biomass in the world. After grain harvesting, the by-product is wheat straw, with bright prospects for bioethanol fuel worldwide. However, the usual elimination of wheat straw is discarded or burned in the field, leading to significant environmental and economic waste problems. Wheat straw is the primary source of renewables. Wheat straw is cheap and rich in lignocellulosic biomass, so it is capable of producing bioenergy (Zheng et al. 2018). It ought to be eminent that the prevalent, ~400 million tons, of that amount remain unused and may become an accessible organic matter for ethanol production, bearing in mind other implementations for wheat straw such as soil-plowing or tillage, burning, bedding, and ruminant drilling (Tishler et al. 2015).

6.7 Biological Pretreatment Methods

Various researchers have studied biological pretreatment carefully, given that the method is very “inexpensive,” “less energy-consuming,” and “refulgent.” This method is used to amend “lignin” and vitiate biomass hemicellulosic content of microorganisms or enzymes as a catalyst. Several white-rot and brown-rot fungi have been studied in order to prevent biomass, such as *Pleurotus ostreatus*, *Phanerochaete chrysosporium*, *Postia placenta*, *Ceriporiopsis subvermispora*, *Gloeophyllum trabeum*, and *Trametes versicolor* have been studied (Canam et al. 2011).

An evaluation of biological pretreatment and its uses are shown in Fig. 6.1. In fact, the following inherent benefits also contributed immensely with the biological pretreatment technique by white-rot fungi-

1. safe and reliable methods
2. energy-efficient and cost-effective consumption
3. preferential deterioration
4. in certain instances, biomass treated could be used immediately for enzyme conversion or fermentation
5. significantly raise a number of forage and agricultural wastes cellulose digestibility. (Keller et al. 2003). The whole pretreatment has many special characteristics, so researchers have looked for biological pathways to achieve the desired objective. Many scientific papers for testing and assessing biological pretreatment beyond the existing level have already been reportable. Organosolvent such as “ethanol,” “glycol ethylene,” “methanol,” “n-butylamine,” and “butanol” are also used in the biological process of improving the internal area lignin protective

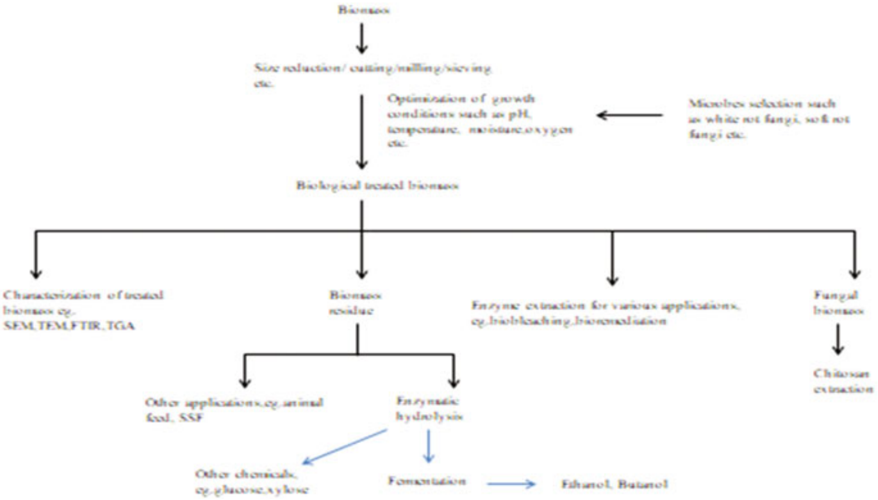


Fig. 6.1 Overview of biological treatment and its applications

layer, eliminating hemicellulose and disturbing the crystalline nature of cellulose (Monrroy et al. 2010).

Nevertheless, the “biological pretreatment” is an imperceptible progression despite all of these advantages, and also certain significant components (hemicellulose and cellulose) of biomass are consumed by another microorganism or certain foreign invaders. Compared to chemical and physical therapy methods, low saccharification rates (35–40%) are found (Ma et al. 2010). Many researchers have taken advantage of various microorganisms and this zero-pollution approach is very important since it aids to heighten “fermentation” and “enzyme saccharification” deprived of significant investment of capital.

6.7.1 Lignocellulose Depolymerization

(a) **Cellulose degradation:** The enzymes are produced from either “non-complex systems” or “cellulosome complexes.” Cellulase from distinctive microbials can be obtained (Janusz et al. 2017). The “endoglucanase,” “exo-1,4-β-exoglucanase,” “β-glucosidase,” and “cellobiose” belongs to “glycoside hydrolase” groups of three different enzyme classes. The cellulase enzymes or enzymes that distort cell walls consist of catalytic modules and CBMs, which are linked to other accessory domains. Anaerobic bacteria have a superior multienzyme complex, known as “cellulosomes” that can be permitted or permanent on the cell surface in cellulose degradation (Chatterjee et al. 2015). Precise fungal strains have a complex multienzyme associated with cell walls and have a set of “cellulolytic enzymes” (Dashtban et al. 2009).
Goyal et al. (2011) have established a least conglomerate comprehending a dissimilar population of the “endoglucanase,” “exoglucanase,” or “β-glucosidase” gene signifying an efficient mini-cellulose machinery using an unambiguous interface between various pairs of cohesion-dockerins. In *Neocallimastix patriciarum* J-11, Wang et al. (2014) identified electrophoretically a complex of cellulosome multienzymes, with 12 proteins, 8 components having zymography analysis of β-glucanase activity. Haitjema et al. (2017) and his squad used the high standard genome of *Neocallimastix californiae, Anaeromyces robustus,* and *Piromyces finishes* with uncatalyzed dockerin domains with long-reading single-molecule technology to assemble anaerobic fungi (NCDDs).

(b) **Hemicellulose Degradation:** “L-arabinitol” is a hemicellulose hydrolysate by-product, which can successfully reduce D-xylose to xylitol biocatalytically. L-arabinitol may be reduced to L-arabinitol by xylose reductase. Adequate showing of enzymes at the microbial cell surface is prerequisite for hydrolysis of “cellulose” and “hemicelluloses” to effectively interact with the extracellular polysaccharide plant cell wall. Long et al. (2018) showed that the xylan containing plant biomass was being treated with a high temperature two-stage hydrolysis treatment. Over the first stage, xylan were removed at high temperature (85 °C), following the removal of thermostatic xylanase (Xyn10a) from *Thermotoga thermarum* DSM 5069. High accessibility of the cellulose is thus achieved with high temperature xylanase treatment that helps to further reduce the viscosity of slurry biomass (Long et al. 2018). *Hypocrea jecorina*, β-glycosidic enzyme where β-glycosidic hydrolysis between two adjacent molecules, in dimers and glucose oligomers, is the final step of the cellulosic biomass degradation. Gudmundsson et al. (2016) has replaced β-glucosidase from *H. jecorina* (HjCel3A) in enzyme mixtures, which has led to greater efficiency in the saccharification of the lignocellulose materials, with β-glucosidase Cel3A of the thermophile fungus *Rasamsonia emersonii* (ReCel3A).

Trichoderma reesei PB-3 could be found to be a potential strain for the extraction of biomass and for the production of ethanol for fed-batch fermentation (Li et al. 2018). Furthermore, *Aspergillus nidulans* and *Fusarium oxysporum* fungal cellulolytic cocktails that have a controlled expression of *Aspergillus fumigatus* xylosidase lead to a very high hemicellulose yield and a less accumulation of xylobiosis, compared with *Myceliophthora thermophila* cellulolytic cocktails on steam maize stove (no acid impregnation) (Martín Perez et al. 2017). However, the factors that cause adverse effects on sugar derivation during hydrolysis of lignocellulosic biomass include “microbial biocatalysts,” “lignin-derived phenols,” “carboxylic acids,” “furan derivates,” and some “lignocellulose by-products” (Kim et al. 2018).

(c) **Lignin Degradation:** The steps towards lignin biodegradation are both depolymerization and cleavage of the aromatic ring. Lignin deconstruction in three phases: beOe4 oxidation in links to “arylglycerol compounds,” “aromatic rings cleavage,” and “beOe4 oxidation” in cleaved aromatic rings. The restrictions of breaking down lignin and restriction on recovery for generating high aromatic products were fully described by Bugg and Rahmanpour (2015). The researchers indicate difficulty in “bond cleavage,” “their physical features,” “structure heterogeneity,” “variations in the lignin molecule,” and “depolymerization” against the “repolymerization” production of mixtures of compounds related to biological processes (Bugg and Rahmanpour 2015). Lignin biodegradation by microbial enzymes is a process that contains aromatic components from ligninolytic peroxidase enzymes or laccase enzymes (Ausec et al. 2011). The process of “enzymatic combustion” of microbial interference of the lignin biodegradation is reviewed by Kirk and Farrell (1987). The intensity of a lignin-rich tiny proportion (in wheat straw) was reported to be essential for the biodegradation and production of a short-chain fatty acids in ligninolytic mitotic fungus *Aspergillus fumigatus* from aromatic compounds (Baltierra-Trejo et al. 2015). *Botryosphaeria dieback* (family Botryosphaeriaceae) fungi have been reportedly enzymatic to deteriorate the lignin and to overcome chemical, physical, and seedling damage (grapevine studied) with aggressive effects (Stempien et al. 2017). Houtman et al. (2018) have revealed in a study on *Phanerochaete chrysosporium* that its lignin peroxidase is not a ligninolytic oxidant, but that veratryl alcohol cation radical. Through symbiosis, modified secreted proteins may increase lignin degradation in prevalent white-rot *Pleurotus ostreatus* (oyster) (Feldman et al. 2017).

6.7.2 White-Rot Fungi

The basidiomycete wood-rotting fungi are typically categorized into white-red and brown-red fungi. Numerous white-rot fungi entail biodegradation of lignin, including *Echinodontium taxodii*, *C. subvermispora*, *Phlebia suberialis*, and *P. chrysosporium* (Isroi et al. 2011). Mostly in hard woods, like birch and aspen, white-red fungi grow well. But at the other hand, on soft-woods such as “spruce” and “pine” and certain species like *P. radiata*, *Phellinus pini*, and *Heterobasidion annosum* grow well. However, the viability of biologic pretreatment is still at an early stage owing to the tremendously elongated time intervals and the confront of particularly decreasing lignin (Shaw et al. 2008). Fungal growth in lignocellulosic biomass leads to dry matter loss. The decline and judicious degradation of lignin depends heavily on the strain of degradation. For example, wheat straw decomposes very slowly or badly from *Flammulina velutipes*, *Fomes marginatus*, and *Laetiporus sulphureus*. Therefore, “white-rot fungi” are not passable for biological delignification.

While this removal of lignin alone from lignocellulose is extremely difficult, certain unique fungal species, such as *Hapalopilus rutilans*, *P.ostreatus*, *Stropharia rugosoannulata*, *Pleurotus eryngii*, *Lentinula edodes*, and *C. subvermispora* are highly related to lignin; and they are able to consume lignin more rapidly than non-linear biomass content. Such strains consequently provide an excellent delignment and can be productively used in lignocellulose biological pretreatment (Tuyen et al. 2012).

White-rot fungi are found in the wild more frequently than in the nature of gymnosperm. In particular, the lignin units of syringyl (S) are more selectively degraded, while the degradation-resistant units of guaiacyl (G). The microscopy of the transmitting electron revealed that the center lamellas were partly eliminated by and *Pleurotus eryngii* and *C. subvermispora*; the secondary cell walls apparently removed by *P. radiata*; whenever these fungi had been expanded in straw. Countless researchers have optimized various environmental conditions such as “time of cultivation,” “nutrients,” “pH,” and “oxygen level” to achieve maximum lignin degradation (Hatakka et al. 2010). The dilapidation of lignin by white-rot fungi results from actions of ligninolytic oxidative enzymes that degrade lignin. Carbon and nitrogen source regulate these enzymes (Isroi et al. 2011).

White-rot fungi lessen lignin in biomass, named “selective” and “non-selective” declination. All three constituents (lignin, hemicellulose, and cellulose) have been almost equivalently degraded for non-selective degradation, while selective degradation mostly involved the degradation of hemicellulose and lignin. *G. applanatum* and *H. annosum* are capable of degrading selective and non-selective wood with both types of attack (Fernandez-Fueyoa et al. 2012).

For example, *Pleurotus ostreatus*, *Pycnoporus cinnabarinus*, *Pleurotus eryngii*, *Phlebia tremellosa*, and *Dichomitus squalens* are examples of selective degradations. In the pretreatment of different lignocelluloses, selective have a potential role in achieving the substantial amount of feed in the production of biofuels. Certain species conveniently remove lignin than carbohydrates. Several more white fungi colonize luminous cells and cause erosion of cell walls. The eroded areas develop with decay and large mycelium-filled vacuums. This category of rot is recognized as non-selective or concurrent rot. Simultaneous rot fungi are typical *Trametes Versicolor*, and *Fomes fomentarius*. The need for non-selective fungi is therefore drastically decreased and thus can be applied to organic pretreatment through its "non-selective degradation" of the plant cell walls.

6.7.3 Brown-Rot Fungi

Hemicellulose and cellulose degrade brown-rot fungi more quickly than lignin in forests. Lignin is reformed to firm point and leftward over residue of "brown lignin"; thus, collectively referred to as brown-rot fungi. A variation of brown-rot fungi are used in different investigations including *Coniophora puteana*, "*Laetiporus sulphureus*, *Ganoderma trabeum*, *Meruliporia incrassata*, and *Serpula lacrymans* (Monrroy et al. 2011). "Brown-rot fungi" have an exceptional wood breaking appliance. In comparison to "white-rot fungus" that only depolymerize the carbohydrates of the cell wall to the degree of using a degraded product in the metabolism of fungi, "brown-rot fungi" accrue the decay of the cell wall, "cellulose" and "hemicellulose" since all products of metabolism are not used in the fungus. These brown-rot fungal hyphae permeate through extant pores in wood cell walls from one cell into another primary in the deterioration procedure. "Brown-rotted lignin" is used as an adherent because it is earlier than instinctive lignin meanwhile of an enormous level of phenolic hydroxyl group. *G. trabeum* is the furthermost frequently used mushroom for the conduct of woodchips.

Pinus radiata wood-chips are pretreated by (Monrroy et al. 2011). The treatment with organosolv with various "ethanol-water blend" ratios at pH-2 and the solvent accessibility was significantly improved and the H factor for obtention of 161 g ethanol per kilos in *P. radiata* wood was reduced from "6000 to 1156." Brown-rot fungi have quality amenities as white-rot fungi to degrade lignocellulose. Both types of fungi have a wood decay mechanism based on "low pH," "radical formation," and "organic acid production" such as "oxalic acid." Radical lignin formation could maximize solutions in alkaline and the downward trend is an oxidation reaction that can thus improve downturn through slightly elevated supply of oxygen. Needless to say, many proposed mechanisms were not conclusively proven quantitatively (Hatakka 2001).

6.7.4 Soft-Rot Fungi

“Type-I” soft-rot fungi comprising of cylindrical or biconical cavities are made within secondary walls, and “Type-II” soft-rot fungi is a degrading erosion (Blanchette 1995). *Daldinia concentrica*, for example, is the most efficient type II fungus, mainly affecting hardwood (Nilsson et al. 1989). Xylariaceous ascomycetes of genres such as *Xylaria*, *Daldinia*, and *Hypoxylon* were often considered white-rot fungi when the various wood-rotting fungi are classed in the early stage of classification; nonetheless, these mushrooms are categorized as “soft-rot fungi” as effects typical type II soft-rot in wood. For coniferous timber, weight loss was very small and more guaiacyl units were considered to be present in this type of timber in mid-lamella inhibiting soft-rot fungi growth. The microfungi is detected in a soil enriched sample and can mineralize grass lignins to up to 27% of some species (*Penicillium chrysogenum*, *Fusarium oxysporum*, and *Fusarium solani*). Most soft-rot fungi, however, is readily cost-effective during invasion and is less suited to biological pretreatment applications (Hatakka 2001).

6.8 Hydrolytic and Oxidative Enzymes Convoluted in Lignin Dilapidation

A series of enzyme complications occur in macromolecular lignin degradation. Since the medium is a large polymer, it is very difficult to decompose the microbial substrate. Lignin does not retain hydrolyzable links in enzymatic form and is efficient in stereo applications. The enzymes or agents should be highly reactive for degradation of lignin. The following describes several enzymes in which the lignin is demeaned.

(a) **Laccase**: The enzyme laccase belongs to the “oxidase family” or “blue Cu-protein.” The main laccase producers are fungal kingdoms, the variability of which is found in ascomycetes and basidiomycetes; in soil, pathogens and freshwater (Baldrian and Snajdr 2006). Lac has a molecular weight of about “60 kDa” and “pH (3–6),” which is typically superior to peroxidases. Lac catalyzes four individual “electron oxidations” of “aromatic amines” and “phenolic compounds” such as lignin phenolic substructures that coincide with O_2-H_2O reductions (Have and Teunissen 2001). Consequently, white-rot fungi should indeed be produced by the natural mediator for the complete oxidation of lignin. It appears to have a certain number of “Lac-coded” genes and isoforms. Lac has varying levels of enzymes with four copper atoms, and each has a various surface oxidation component. The substrate is implicated in the initial response of type I of copper. The “copper type I” gives the enzyme a maximum absorption of “610 nm”; thus, adding a typical blue color to its enzymes. The “type II copper” and the “type III copper” clusters are existed in triangular shape.

The binding, reduction of O_2, and storage of electrons from the reduction substrates are part of copper II and III complexes (Fig. 6.2). The absorbent range is not visible for type II copper, while the maximum absorbent range for type III copper is "330 nm"; and therefore the "copper II- and III-complexes" have no color. The entire crystalline laccase structure with four copper atoms was studied from *T. versicolor* (Piontek et al. 2002). The white-rot fungus *T. versicolor* produces two isozymes of laccase (I and II) (Bourbonnais et al. 1995). Various white-rot fungi, in addition to copper ions, may be used for the effective biological pretreatment of lignocellulose to induce Lac secretion. Lac may also induce aromatic compounds such as "veratryl alcohol" and "2–5 xylidine" in some particular cases. Lac oxidizes phenolic lignin residues typically and oxidizes non-phenolic lignin compounds with addition of "ABTS." Thus, a special catalyst can be added to biological pretreatment to induce Lac action quite far. Lac production could be accelerated by the presence of lignocellulosic materials for certain fungi, such as *C. subvermispora* and *Ganoderma lucidum* (Isroi et al. 2011).

(b) **Lignin peroxidase:** Lignin peroxidase was revealed in the "extracellular medium" of *P. chrysosporium*, which is cultivated under nitrogen limitations (Tien and Kirk 1983). The enzyme uses hydrogen peroxidase as cofactor and activity mediator that allows lignin/lignin models to be oxidized. Some fungi produce enzyme lignin peroxidase are *P. chrysosporium*, *T. versicolor*, and *Bjerkandera* sp. and many more. Indeed, LiP was found to only play a minor role in *T. versicolor* lignin degradation by biological pulp bleaching. LiPs are a monomeric glycol and homo-protein of the oxidoreductase family that precisely acts as an acceptor for peroxide (peroxidases). The weight of such enzymes is 40 kDa and isoelectrical points (pI) between 2.8 and 5.3 (Have and Teunissen 2001).

Fig. 6.2 Laccase cycle

LiPs collaborate with their substrates by means of a ping pong mechanism. LiPs are oxidized to “two electrons” oxidizing mediates along with “Fe^{4+}” and hydroxyl radical filtrates of tetrapyrrole. “LiP- I” oxidizes the donor substrate by an electron in a certain oxidation state, i.e., “Fe $^{+\ 4}$.” Moreover, the “heme tetrapyrane” and the radical cation, in which it is identified in a very identical oxidation condition, do not have “oxygen radicals” substance. “LiP-II” oxidizes the second donor substrate molecules (VA) and gives a further radical cation and a native “LiP” form. The revision of the native LiP is mainly dependent on the abatement step “LiP-II,” which constitutes a catalytic cycle rate limit. This leads to an inactivation of the complex receptor and forms “LiP-III” complex for “LiP-II” complex, which is again capable of interacting with “hydrogen peroxidase” (Fig. 6.3).

Veratryl alcohol radical cations serve as redoublers and can reduce the complex “LiP -III” to its original form, “LiP.” VA radical (VA•+) cations after their oxidation reaction. Veratryl alcohol plays an important role in this catalytic cycle reaction. Up to now, three key VA functions were studied—

1. In electron-transfer responses, VA acts as a mediator.
2. For compound II, VA is a good substratum, so VA is crucial to complete the LiP catalytic cycle during terminal substratum oxidation. Furthermore, when “LiP- III” is inactive, advanced VA•+ will reduce “LiP- III” sophisticated to its original LiP-like form (Fig. 6.3).

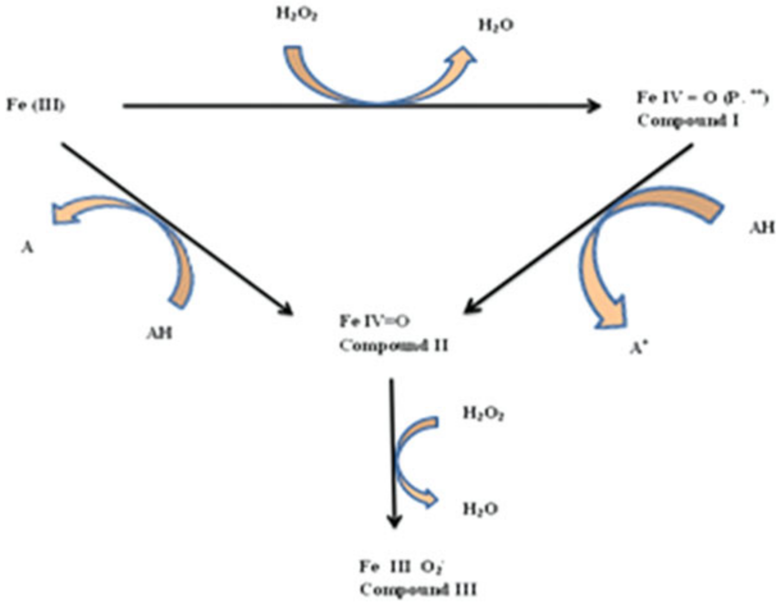


Fig. 6.3 LiP cycle

3. VA prevents H_2O_2-dependent “LiPs” from being inactivated by minimizing the “LiP- II” complex to their indigenous LiP.

Almost every white-red fungal in the initial point of secondary metabolism synthesizes VA through “de novo-glucose path” in sequential with “LiP.” “LiPs,” by removing one electron and generating free radicals that cause the polymer to disintegrate chemical, oxidize “non-phenolic” and “phenolic” lignins. It has been demonstrated that “LiP” oxidizes completely methylated lignin, lignin models, and diverse hydrocarbons (Have and Teunissen 2001).

(c) **Manganese peroxidase**: In the catalytic response dependent on Mn, in which “Mn^{2+}” is converted into “Mn^{3+}”; manganese peroxidase also requires H_2O_2 as an oxidant. Mn^{3+} oxidizes phenolic rings into phenoxylactic radicals, resulting in compound breakdown. Manganese peroxidase plays a crucial part in “lignin depolymerization,” “chlorolignine,” and “lignin de-methylation.” MnPs consequently play a vital role in lignocellulosic biomass biological pretreatment. Several investigators have recounted that *P. chrysosporium*, *P. ostreatus*, and *Trametes* produce manganese peroxidase. MnPs include one molecule of heme as “protoporhyrin-IX” and consist of “~357 amino acid residues,” “3 sugar residues,” “2 structural calcium and manganese ions,” and “~478 solvent molecules.” In MnP, the manganese-binding residues are “two glutamic acids,” “aspartic acid,” and “acidic amino acids” (Isroi et al. 2011). The native MnP form is therefore oxidized to form an “MnP- I” complex by adding hydrogen peroxidase (Fig. 6.4). Belatedly, Mn^{3+} metabolizes and attacks the lignin compounds in the lignified cell wall. This oxidation response clarifies that the phenolic part of lignin is oxidized by “MnP” ions indirectly. As they just don’t have a residue of “tryptophan” which is necessary for transfer of electrons into non-phenolic substrates. It is therefore obvious that adding Mn^{2+} could increase the oxidation of “phenolic lignin” amalgams and persuade manganese peroxidase assembly in fungi (Have and Teunissen 2001).

(d) **Cellobiohydrogenase (EC 1.1.99.18):** Cellobiose dehydrogenase is an extracellular flavocytochrome, released into cellulolytic culture by “white-rot” and

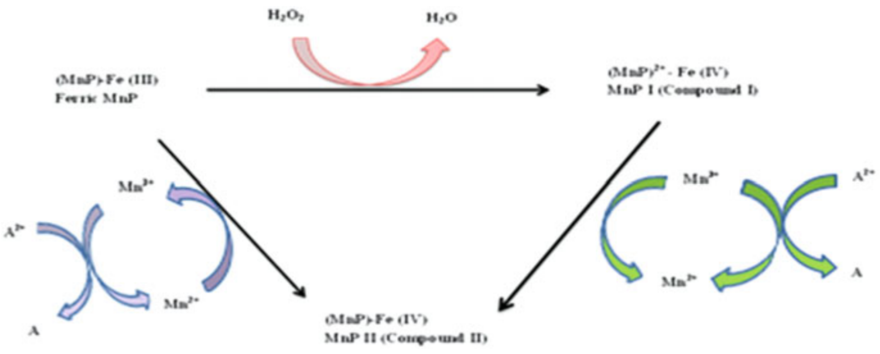


Fig. 6.4 MnP catalytic cycle

"brown-rot" fungi. This enzyme has been sequestered from the white-rot fungi: "*Trametes versicolor*, *Schizophyllum commune*, *P. cinnabarinus*, and *P. chrysosporium*; the brown-rot fungus: *Coniophora puteana*; and the soft-rot fungi: *Myceliophthora thermophila* and *Humicola insolens*. Far from *C. subvermispora* cultures, no CDH activity has been reported although it is the delignment. It has been found that cellobiohydrogenase has consistently proved its participation in white-rot fungal ligninolytic metabolism in the presence of hydrogen peroxidase. Henriksson et al. summed up the results of several researchers on cellobiose dehydrogenase in ligninolysis that Fe^{3+} was reduced to Fe^{2+}, and cello-oligosaccharides were reduced to hydrogen peroxidase. The reactant causes the formation of hydroxylic radicals created by the "Fenton reagent" in the production of hydrogen peroxidase. This highly reactive radical hydroxyl is recognized to outbreak "lignin" and "cellulose." In addition, Henriksson et al. (2000) conferred the assumption/concept of cellobiose dehydrogenase activity as follows:

- Cellobiose dehydrogenase provisions the dilapidation of lignin by lessening aromatic radicals produced by lignin peroxidase and laccase during lignin oxidation reaction. Enzyme response is reversible; consequently, in vitro polymerizations of radicals can be favored by lignin degraders. By minimizing the radicals produced by lignin peroxidase and laccase, CDH may inhibit polymerization.
- Cellobiose dehydrogenase decreases phenols lethal quinones that can be used by ligninolytic enzymes as redox mediators.
- Cellobiose dehydrogenase minimizes the use of lignolytic enzymes toxic quinones to phenols as redox mediators.
- Throughout the utter lack of the peroxidase substratum, CDH reduces "compound–II" of lignolytic peroxidases and completes the catalytic cycle.
- Cellobiose dehydrogenase downgrades and alters "celluloses," 'hemicelluloses," and "lignin" by producing "hydroxyl radicals" in a Fenton type reaction.

While the overhead postulate is imprecise, many types of CDH features over the last step on hydroxyl radicals are clearly explained, and this could be CDH's best recommendation. Furthermore, Dumonceauxa et al. (2001) suggested that cellobiose dehydrogenase is not momentous for deprivation of lignin, at least for delignment of T. versicolor. They indicated that some enzymes can disguise the impacts of lack of CDH through reduction. Consequently, the CDH-inadequate mutant may still reduce or modify lignin as the mutant strain, but cellulose really doesn't disintegrate.

(e) **Aryl alcohol oxidase:** Aryl alcohol oxidase (AAO), "FAD" containing enzyme belonging to the family oxidoreductases of glucose-methanol-choline oxidase (GMC) was formerly labelled in *Polystictus versicolor* during 1960s. White-rot fungi have been observed to be elaborate in effectual deterioration of lignin and the development of H_2O_2 and fuel for ligninolytic peroxidases have been shown

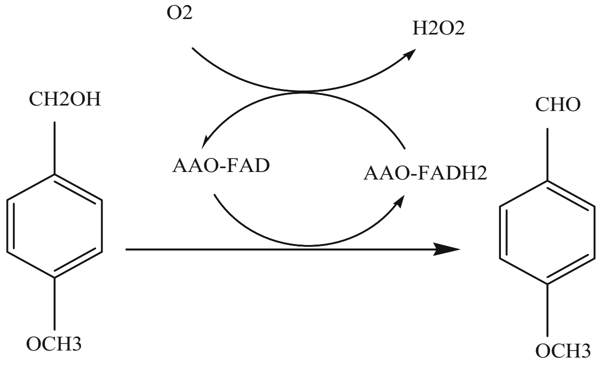


Fig. 6.5 Hydrogen peroxidase production by extracellular aryl alcohol oxidase

to be involved in the depolymerization process for the lignin (Ferreira et al. 2005).

AAO isolated from *P. eryngii* structural and functional studies shows assortment of substrates, catalyzing prime and poly-unsaturated alcohol oxidation (Guillen et al. 1992). An "oxidative" and "reductive" reaction can discern the precise aryl alcohol oxidase rejoinder mechanism, catalyze the oxidative de-hydrogenation of the substrate; the O_2 re-oxidized the FAD and produces H_2O_2 (Ferreira et al. 2005). Meta analyses on AAO substratum specificities showed that it catalyzes the oxidation of aromatic alcohol in the correlating aldehydes by aromas such as "aliphatic alcohols" and 'p-anisyl alcohol" (Guillen et al. 1992).

Phenolic hydroxyls have been reported to strongly inhibit AAO enzymes. The "p-anisaldehyde" redox cycling entails intracellular dehydrogenase of the aryl alcohol, together with aryl alcohol oxidase, which results in the production of H_2O_2 (Fig. 6.5). AAO might seem equally catalytic to "choline oxidase" that catalyzes alcohol substrates that outcome in aldehyde production. Previous *P. eryngii* AAO studies show that the reversion of primary alcohols with various structural properties is catalyzed.

(f) **Versatile-peroxidase:** VA may oxidize lignin in addition to "Mn^{2+}" phenolic and non-phenolic compounds. The catalytic mechanism is analogous to lignin peroxidase (Fig. 6.3). For instance, non-phenolic models, like "veratrylglycerol" and "β-guaiacyl ether" oxidize versatile-peroxidase and produce veratraldehyde. VP also oxidizing "$Mn^{2\ +}$ to $Mn^{3\ +}$" and "p-benzoquinone to p-veratraldehyde and p-dimethoxybenzene" (Wong 2009).

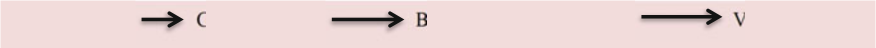
6.8.1 Mediators Involved in Lignin Degradation

Laccase and peroxidase enzymes are more explored and therefore have no close contact with lignin than cell walls pores. Throughout the system of white-rot-ligninolytic enzymes, various compounds of low molecular weight can be identified.

The influence of intermediaries or cofactors was explored in numerous in-vitro studies showing adequate levels of “hydrogen peroxidase,” “lignin,” “oxygen,” and “pertinent mediators” (Hammel et al. 1994). Therefore, fungi and cofactor for the biological removal of components of lignin of lignocellulosic biomass need not be abandoned bereft.

(a) **Veratryl alcohol**

In bioligninolysis, the function and significance of veratryl alcohol is crucial. In parallel with LiP production, de novo is usually synthesized from $C_6H_{12}O_6$ via the “shikimate pathway” at the initial stage. With 14 C isotopical trapping experiments on *P. chrysosporium* ligninolytic fungus (ATCC 34541), the VA biosynthesis pathway was performed and it was concluded that this was the pathway (Shimada et al. 1981).



The production of VA is due to nitrogen limitations in *P. chrysosporium* while the nitrogen element certainly not have any significant regulatory consequences on “veratryl alcohol” synthesis in *Bjerkandera* (Mester et al. 1995). Lignin peroxidase can also be increased by adding veratryl alcohol to the biological pretreatment of lignocellulose for non-phenolic residue of lignin. Veratryl alcohol is a catalytic reaction that protects lignin peroxidase against H_2O_2-mediated inactivation reaction (rate limiting stage) and is proposing veratryl alcohol in vivo as an enzyme stabilizer (Fig. 6.2) (Hammel et al. 1994).

(b) **Oxalate**

The synthase of oxalate is attributable respectively to enzymes, namely “oxaloacetase” and “glyoxylate oxidation” which catalyze oxaloacetate hydrolysis and glyoxylate oxidation. One important aspect is that in the proximity of “veratryl alcohol” or “Mn^{2+},” “lipids,” and “MnPs” can decompose oxalate. A breakdown in oxalate leads to the development of CO_2 and superoxide (O^+ or HOO^{++}), which are further oxidized by O_2, under aerobic environment. It is suggested that active oxygen species actively participate in lignin oxidation. Consequently, oxalate can be viewed as an inactive sink for “H_2O_2” production. The mineralization frequency of lignin is adversely affected only if oxalates reduce the VA^{+-} and Mn^{3+} ions (Figs. 6.3 and 6.4). The VA^{+-} and Mn^{3+} compounds for the effective degradation of lignin should both be reduced by phenolic or non-phenolic. The inordinate action of VA^{+-} and Mn^{3+} oxalate is essential for optimal biological treatment (Heinzkill et al. 1998).

(c) **Manganese**

All through fungal decay on woody materials, the importance of “Mn^{2+}” can clearly be found as it proliferates under the form of “manganese oxide.” Consequently, at the initial stages of growth and infestation, the insoluble “Mn^{4+}” bonds at the gradient of innovative fungal hyphae (Hames et al. 1998). “Mn^{2+}” stimulates “MnP” production and improves the oxidation reaction deterioration of lignin components, when “Mn^{3+}” is produced through “MnP,” as the oxidation mediator of different phenolic compounds. Adding “Mn^{2+}” will thus increase the rate of biological oxidation of lignocellulose pretreatment. Incorporating “Mn^{2+}” on the other hand inhibits “LiPs” activity and production. It is therefore very important to optimize concentrations of “Mn^{2+}” for biological treatment. In fact, the gradient for manganese concentration naturally establishes in decaying wood that allows soluble manganese forms “(Mn (I1)” and “Mn (III)” (Roy et al. 1993).

(d) **2-Chloro-1,4-dimethoxybenzenez**

A broad range of organohalogens are generated by white-rot fungi. “Chlorinated anisyl metabolites (CAM)” and “chlorinated hydroquinone metabolites (CHM)” are the utmost commonly generated halogens. CAM has a substantial physiological part in the deprivation of lignin, which helps to produce extracellular H_2O_2, as substrates for AAO. Chlorinated 2, 4-dimethoxybenzène, such as “tetrachloro1,4-dimethoxybenzene” and “tetrachloro-methoxybenzene” are identified among CHM’s metabolites. The other LiP substrate, “2-chlorine 1,4-dimethoxybenzene” indicates a promising dynamic utility in the process of the board degradation. This can act as a redox mediator, analogous to veratryl alcohol (Teunissen and Field 1998).

6.9 Upshot of Biological Treatments on Lignocelluloses

Biomass physical-chemical features reform lignocellulose biomass biology pretreatment. Lignin degradation is the most appealing and examined of the changes. The loss of lignin in wheat straw, for instance, occurred within 25% within 1 week for “canola straw” with a fungal strain of *Trametes versicolor* and “cellobiose dehydrogenase strain”. Maize straw “lignin” concentrations have been found in a range from “75.67–80%” for maize stalk treated with *Irpex lacteus* after 30 days of pretreatment (Canam et al. 2011).

Lignin deprivation is usually triggered by an “oxidative non-specific reaction” which results in ample oxidation of the lignin. Alterations in relation between “p-hydroxyphenyl (H),” “lignin syringe (S),” and “guaiacyl (G)” were investigated using the “pyrolysis-gas mass spectrometry (PyGC–MS).”

The attack on fungal biomass also involves hemicellulose and is easier to degrade hemicellulose from component biomass. Hemicellulose degradation with lignin loss was observed in white-rot fungi such as *P. chrysosporium*, *P. florida*, *Trame ochracea*, *C. subvermispora*, and it has demonstrated several activities in the area of endoxylanase. This approach minimizes recalcitrance of lignocellulose but increases chances of cellulose loss or during bioconversion decreases the whole operation of sugar recuperation. During the biological treatment of lignocellulose, white-rot fungus also separates the cellulase enzyme with various special properties and synergistic characteristics. The non-selective white fungi equally mineralize all lignocellulosic components. Selective white-rot fungi generally deteriorate an insignificant level of celluloses and play a proactive approach in the biotreatment of

Table 6.3 Impact of biological treatment on lignocellulosic constituents

S. no.	Raw material	Microorganism	Lignin loss (%)	Cellulose loss (%)	Hemicellulose loss (%)	Reference
1	Sugarcane trashes	*Cellulomonas cartae*	5.5 ± 0.26	25.4 ± 0.66	–	Singh et al. (2008)
2	Corn stover	*Irpex lacteus*	17.8 ± 1.0	31.5 ± 0.8	16.8 ± 0.9	Ma et al. (2010)
3	Bamboo clums	*Ganoderma lucidum*	10.86	12.83	29.22	Zhang et al. (2007)
4	Wheat straw	*Fomes fomentarius*	35 ± 1	45 ± 1	51 ± 2	Salvachua et al. (2011)

lignocellulose. In the crystallinity index, the loss of cellulose may be analyzed using "x-ray diffraction (XRD)." The amount of crystalline biomass treated by the maize stove has grown from "33.22 to 46.06%" and crystals from "59.96 to 94.96%" with preference for *Fomitopsis* sp." to degrade the amorphous structure preferentially (Zeng et al. 2011). The biological pretreatment of the "Japanese red pine" with three white-rot fungi reduced up to approximately "65%" (Lee et al. 2007).

Xu et al. (2010) investigated morphological changes to the surface during a white-rot fungus "lactum CD2" outbreak on the "corn stove" through "scanning electron microscopy (SEM)." The SEM imageries disclosed particular physical fluctuations after biological treatment and led to the asymmetrical tropics in the maize. "Wheat straw" degradation by *P. chrysosporium* (Singh et al. 2001) and "bamboo culms," which were treated by *E. taxodii* 2538 and *T. versicolor* G20 and catalogued the functioning group modifications of the bonds through "Fourier Transformation Infrared (FTIR)" (Zhang et al. 2007).

A more configuration area procured from *P. chrysosporium* treated with inorganic "Tween 80" salts demonstrating lignin depletion and making the hemicellulose or cellulose surface more available (Zeng et al. 2011). Xu et al. (2010) also dumped *I. lacteus* CD2 for improving the dimension distribution and average aperture of a maize stove, resulting in much more populated regions of enzyme sugaring surface. Table 6.3 outlines the influence of biotreatment on "cellulose," "hemicellulose," and "lignin.'"

6.10 Steps on Ethanol Production from Lignocellulosic Feedstock

Bioethanol's major renewable energies are lignocellulosic biomasses including "grass," "crop residues," "forest residues," "other biological emits" without effecting food and fiber crops. Global production of "49.1 gallon" of bioethanol can reach between 73 and 106 tons of dry waste (Kim and Dale 2004). Lignocellulose is transitioned to ethanol in various phases: (1) biological pretreatment, (2) hydrolysis,

(3) fermentation, (4) product recovery (Saini et al. 2015). Increasing bioethanol production is crucial throughout each step in a cost-effective and productive way.

(a) **Biological Pretreatment of Lignocellulosic Substrates:** Lignocellulosic feedstock biological pretreatment is an essential and precarious step in the processing of ethanol. Biomass pretreatment requires varying the wide cellulose structure, hemicellulose-lignin matrix in order to limit crystalline cellulose and enhance amorphous cellulose (Furusato et al. 2018). It is therefore an essential milestone to obtain greater yields from the desired products in the ethanol production from lignocellulose feedstock. In biological pretreatment processes, microorganisms are being used to pretreat the substrate. Comparable with common treatments for lignocellulose, physical or chemical, the method is inexpensive and greener, using specific enzymes from a microorganism such as bacteria and fungi. This method is used to degrade the substratum (Maurya et al. 2015). The hydrolyte process typically involves biological pretreatments (Hendriks and Zeeman 2009). Multiple clusters of fungi have been observed to have lignocellulose undignified enzymes and are precise efficacious in degrading grazing (Amin et al. 2017). Therefore, a comparatively inexpensive, more proficient, and environmentally friendly basis of enzymes in biological pretreatment, and thus an extremely large prospects in industrial applications.

(b) **Hydrolysis:** The pretreatment process, which is enforced by a number of aspects such as "pH," "temperature," "incubational time," "substratum quality," and "enzymatic substratum proportion" is cognized for enzymatic hydrolysis of "hemicellulose" and "cellulose." The use of diluted or concentrated acid (sulfuric acid) as acidic hydrolysis, however, is also familiar for breaking down the polymer. "Acid hydrolysis" has countless constraints such as the output of noxious combinations such as phenols which are not preferable for efficacious bioethanol fermentation (Achinas and Willem 2016). A number of research studies have been conducted using cellulolytically/lignocellulolytic enzymes for the isolation of the sugar molecules which can be used in in the conversion of ethanol in the process of effective hydrolyzing (Jessen et al. 2015). Lignocellulosic substrate pretreatment is associated with enzymatic hydrolysis that contributes to an amended penetrability and approachability of the substratum by oxidative/ligninolytic enzymes (Limayem and Ricke 2012).

(c) **Fermentation:** Carbohydrates are utilized for the production of "gases," "organic acids," and "alcohol" under anaerobic conditions by bacteria or yeasts released after hydrolysis (Mussatto et al. 2010). In order to reduce the production of inhibitory substances and achieve high ethanol yields, the effectiveness of the fermentation process depends on an effective hydrolysis and selector of appropriate microorganisms (Achinas and Willem 2016). Table 6.4 gives a description of fermentation methods. Either "SHF (separated hydrolysis and fermentation)" or "SSF (saccharification and fermentation)" are used as a fermentation process but glucose accumulation reduces cellulase efficiency. In SSF, a single reactor produces cellulose hydrolysis and hexose fermentation to minimize cellulose inhibitor responses which surmount such a daunting fermentation in SHF

Table 6.4 Comparative analysis of fermentation process (Singh et al. 2017)

S. no.	Fermentation process	Advantages	Disadvantages
1	SSF (Saccharification and fermentation)	• Low cost • Less inhibitory effects • Less contamination	• Difficult in process controlling • Fermentation or hydrolysis can be done under optimized conditions
2	CBP (Consolidated bioprocessing)	• Cost-effective • Energy-efficient	• Processing is difficult
3	SSCF (Simultaneous saccharification and combined fermentation)	• Brief time period • Higher ethanol yield • Lower contamination	• Elevated loading of enzyme
4	SHF ('Separate hydrolysis and fermentation)	• Low quantity of enzyme loaded • Higher bioethanol yield • Both fermentation and hydrolysis can be ruled out under optimized conditions	• Increased contamination • Inhibitory effects
5	SHCF ('Separate hydrolysis and co-fermentation)	• Higher bioethanol yield • Both hydrolysis and fermentation can be accomplished underneath raised circumstances	• Highly concentrated enzyme loading • Effective inhibition • Drastic contamination

(Devarapalli and Atiyeh 2015). *Saccharomyces cerevisiae* is one of the most commonly used strain for fermentation for maize and sugar-based biofuel industries. Proper fermentation also helps to condense ethanol cost-effectively. A whole other pertinent and more cost-effective area is bacterial fermentation for the production of ethanol. Bacteria such as *Corynebacterium glutamicum* and *Zymomonas mobilis* are commonly used in industrial sugar metabolization production in order to produce ethanol (Kang et al. 2014). The cellulolytic and ethanologenic properties in *Clostridium Thermocellum* are reported (Ibraheem and Ndimba 2013). One other challenge for researchers using genetic engineering approaches is an increase in ethanol yield (Jessen et al. 2015).

6.11 Impeaches in Biological Treatment

In biological pretreatment progressions, the reduction of sugar and the reasonably long pretreatment duration are main hurdles compares favorably with physical/chemical pretreatment. "Brown-rot fungi" are the main users of fermentable sugar organic pretreatment. In addition, the hazard of contamination increases for prolonged periods with biological pretreatment. This increases the value of the goods considerably. The process of addressing these problems and improving the cost-effectiveness of the process should include a specialized microorganism, when lignocellulose recalcitrance may be limited with lowest possible sugar loss or short incubation time.

1. strain must be highly lignin-affinity
2. more lignin degradation rate
3. enriched with nitrogen source
4. requires efficient micronutrients

Numerous scientists have previously augmented and instigated these factors in their biological pretreatment method for innumerable applications. In order for the upfront outlay, the period of incubation and efficient organic preparation with a benchmark fermenting sugar forfeiture, the next strategies can be executed in the imminent forthcoming:

1. Cumulative biological and chemical or physical therapies can be operative for the treatment of lignocelluloses.
2. Efficient use of sophisticated technology like bio-informational tools, metagenomics can be used for the process.
3. Metagenomic technologies could be used to segregate new varieties or new enzymes for both the superlative deterioration and changeover of lignocelluloses.
4. The inhibitor or mediator of a specific enzyme could be used to prohibit the cellulolytic enzyme's impact or enhance the effects of the cellulolytic enzyme.

6.12 Conclusion

Plant cells predominantly entail of "cellulose," "hemicellulose," and "lignin." Pretreatment of lignocellulosic biomass already when hydrolysis enhances the hydrolyzing efficacy owing to the elimination of "lignin" and "hemicellulose" and the diminution of cells. Microorganisms, specifically fungi, can deteriorate the plant cell wall. White-rot fungi have dual kinds of enzymatic extra cells: "hydrolytic and oxidative." Hydrolytic systems produce "hydrolases" and the ligninolytic system degrades "lignin components" and unties phenyl structures. The fungi are operational for biodegradation because it is wider and faster to degrade lignin than other microorganisms. The noticeable lignin demeaning by white-rot fungi with limited xylanase and cellulose activity may significantly minimize the chemical or enzymatic hydrolysis of the substrates efficiently and eventually.

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Chapter 7
Agricultural Lignocellulosic Waste to Biofuels

Sachin Kumar, Shasta Kalra, Tanvi Sahni, Sukhpreet Kaur Sidhu, and Loveleen Kaur Sarao

7.1 Introduction

It is important to accept the truth that the human population is going to upsurge continuously at least for the next few decades. The increasing human population creates a cascading effect that led to an increase in demand for food, water, and shelter putting extra pressure on already stressed natural habitats. Population boom will also create an inevitable accelerating demand for energy and present strategies based on non-renewable sources may lead to cataclysm events in the human world. Scientists are working to trap alternative sources of energy and got succeeded to a large extent. These sources include almost all forms of renewable sources available to earth like solar energy, wind energy, tidal energy, etc. The solutions provided by these sources may seem very attractive on the first look however implementation of these technologies in an economically profitable manner always remains a challenge. Even after applying all available alternative resources, we still are under energy-deficient condition. The other big challenge is the increasing demand for food. The agricultural land holding is increasing and they are being converted into agricultural lands. The process is not going to halt in the coming decades.

Agricultural intensification harms climatic factors including air, water, and soil quality. An intensive cropping system provides a narrow period between harvest and the next sowing season. Crop residue burning provides a convenient option being a simple, easy, and one-shot solution for the farmers. While several management practices are suggested, some of them involve costly equipment while others involve microbial residue management strategies, none of them were successful on large-scale fields (Bhattacharya et al. 2017). The crop waste includes a large quantity of lignocellulose content which might be the solution for problem crop waste management and energy crisis at the same time. In general, plants convert and store the

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energy from sunlight into chemical bonds in the form of organic matter known as biomass. This biomass serves as an energy source for humans for various purposes including food, shelter, and fuel. The demand for fuel is increasing in an accelerated manner and dealing with the demand with a simple combustion reaction will not solve the problem. Therefore, the current investigations are working on converting biomass into higher energy value fuel as a substitute for petroleum. The production of biofuels has been categorized into generations where first-generation biofuels include ethanol, biodiesel, and a modicum of biogas. However, the current biofuel market is diverting towards fuels derived from food sources, which has started debates regarding land-use changes, competition with food crops, and impact on biodiversity (Gnansounou 2010; Merklein et al. 2016). Under all discussions, the next-generation fuels are getting discussed including the use of lignocellulose-based residues of crops, woody plants, grasses, etc. to produce bioenergy. Although the production of second-generation biofuels is not cost-competitive as commercial products; however, the chapter will discuss the various dimensions of lignocelluloses conversion to biofuel driver from agricultural waste specifically from major crops including wheat, rice, maize, and sugarcane. Because food crops have always been evaluated against land-use changes can leading to the loss of natural ecosystems and fuel competition (Kim and Dale 2004; Kluts et al. 2017). Lignocellulosic crops used only for biofuel production may compete with food crops as areas are needed to produce those plants (Kluts et al. 2017) whereas lignocellulosic waste of food crops could be a beneficial and promising option with a beneficial greenhouse gas balance for the production of sustainable biofuels. Like all lignocellulosic materials, straw is recalcitrant and requires thermochemical and enzymatic pretreatment to enable access to the three major biopolymers of straw—the polysaccharides cellulose and hemicellulose and the polyaromatic compound lignin. Straw is used for commercial ethanol and biogas production. Considerable research has also been conducted to produce biobutanol, biodiesel, and biochemicals from this raw material, but more research is required to establish them on a commercial scale (Passoth and Sandgren 2019). In contrast, food crop lignocellulose waste may represent an ideal resource for biofuel production, as it is a by-product of food production, does not compete with food generation (Townsend et al. 2017), does not alter the land-use system and have a positive impact on the supply of raw materials for biofuel production (Jørgensen et al. 2018). Biofuel production from the residue of crop lignocellulose can add value and reduce the consumption of fossil resources. Various factors may impact the sustainably of this idea including the availability of straw, cultivation conditions, grain cultivar, weather conditions, and soil quality (Panoutsou et al. 2017; Townsend et al. 2017). This chapter has been designed to understand the various structural aspects of lignocelluloses, techniques available for biofuel conversion from agricultural wastes.

7.2 Structures in Lignocellulose Biomass

Lignocellulose biomass is composed of three major polymers: lignin, hemicellulose, and cellulose while other polymers (pectin, minerals, ash, proteins, salt, extractives) are present in the smaller amount (Van Dyk and Pletschke 2012). Cellulose is a polymer of glucose and its structure favors the sequencing of the polymer chains into tightly packed, crystalline structures that are water-insoluble and resistant to depolymerization (Mosier et al. 2005). Crystalline cellulose consists mainly of cellulose, with a small proportion of messy cellulose chains to form amorphous cellulose (Kumar et al. 2009). Hemicelluloses are derived primarily from chains of pentose sugars and work as the cement material holding together the cellulose micelles and fiber (Demirbas and Dincer 2008). The hemicellulose chain can be a homopolymer (consisting of a single sugar unit) or a heteropolymer (a blend of different sugars). The most essential sugar of the hemicellulose constituent is xylose (Demirbas 2009a, b). The third aromatic polymer "lignin" is obtained from phenylpropanoid precursors (Demirbas and Dincer 2008). These precursor units are bonded together by linkages that form a complex matrix (Demirbas 2009a, b) that consists of various functional groups, viz. hydroxyl, methoxyl, or carbonyl, which provides a high polarity to the lignin (Feldman et al. 1991). Second-generation biofuel production led to an emphasis on the structural characterization of biomass. Hence, the major composition along with substituents of agricultural waste biomass is provided in Table 7.1.

Cellulose is the most abundant polymer in biomass followed by lignin and hemicellulose in consequence present as a major constituent of the plant, fungal, and algae cell wall (20–40% dry matter) (Ding et al. 2012). Thousands of β-D-glucopyranose residues with the molecular formula $(C_6H_{10}O_5)_n$ and n is the degree of polymerization. These were linked by Beta-(1,4)-glycosidic linkages joined by intra-, intermolecular hydrogen, and van der Waals bonding (Chundawat et al. 2011) as shown in Fig. 7.1. Smaller units were hydrogen-bonded to form larger unit microfibrils which were observed by electron and atomic force microscopy (Atalla et al. 2008; Davison et al. 2013; Ding and Himmel 2006; Jarvis 2003). These microfibrils were further covered by hemicellulose and lignin. It displayed two regions crystalline and amorphous. The amorphous form is considered disturbances, known as micelles. The crystalline structure has two forms I_α (one-chain triclinic structure) and I_β (two-chain monoclinic structure) (Atalla and Vanderhart 1984).

Table 7.1 Percentage of lignocellulose polymers in agricultural wastes and residues (Sun and Cheng 2002)

S. no.	Agricultural waste	Cellulose %	Hemicellulose %	Lignin %
1	Wheat straw	30	50	15
2	Wheat bran	24	40	6
3	Rice straw	30–45	20–25	15–20
4	Sugarcane bagasse	40–50	25–35	17–20

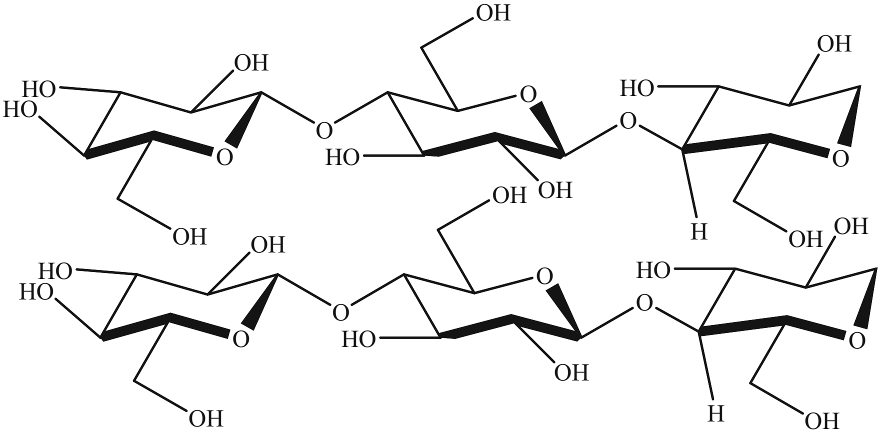


Fig. 7.1 Structure of Cellulose

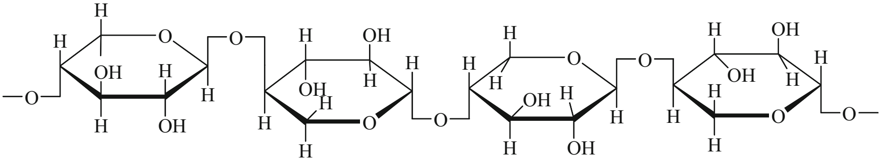


Fig. 7.2 Structure of Xylan

Hemicellulose is a heterogeneous, branched polymer made 20–50% of cellulose biomass. It contains 500–3000 sugar units comprising short lateral chains (Gibson 2012). Different types of sugars present as monomers like hexoses (mannose, glucose, galactose, rhamnose), pentoses (xylose and arabinose), uronic acids (4-O-methyl glucuronic, D-glucuronic, and D-galacturonic acids), and acetylated sugars. Not only this, the backbone of hemicellulose contains homo- or heteropolymers with short branches linked by beta-(1,4)-glycosidic bonds and occasionally beta-(1,3)-glycosidic bonds. Inter- and intramolecular hydrogen bonding is present between hemicellulose and lignin while ether and ester bonding with lignin. Different lignocellulose plants having different types of hemicellulose which differed in composition. Xylan (Fig. 7.2) which are heteropolysaccharides having backbone chains of 1,4- linked β-D-xylopyranose units which were accompanied by arabinose, glucuronic acid, or its 4-O-methyl ether, acetic acid, ferulic and p-coumaric acids. Xylan and arabinoglucuronoxylan (Fig. 7.4) are present in agricultural waste and grasses while glucomannan (Fig. 7.3) is present in softwood.

Lignin is hydrophobic, a three-dimensional aromatic polymer of *p*-hydroxy phenylpropanoid units connected by β-O-4, β-5, β-1, β-β, 5–5, and 4-O-5 linkages. Lignin is categorized based on monomer alcohol. First is guaiacyl lignin having coniferyl alcohol unit and second is guaiacyl syringyl lignin having coniferyl and sinapyl alcohol (Fig. 7.5). Structural characterization study of wheat straw lignin was

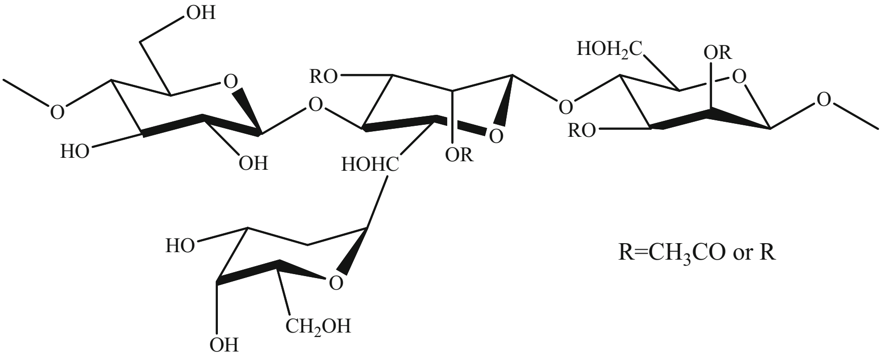


Fig. 7.3 Structure of Galactoglucomannans

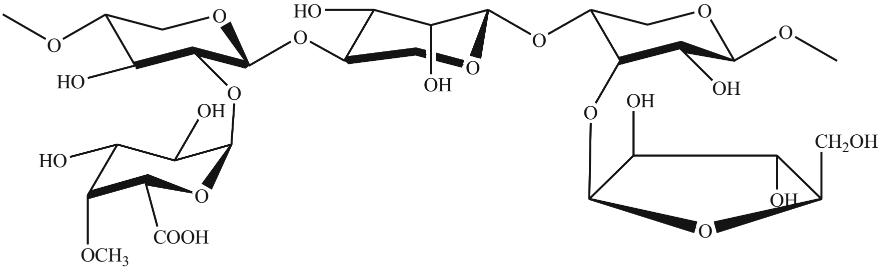


Fig. 7.4 Structure of arabinoglucuronoxylan

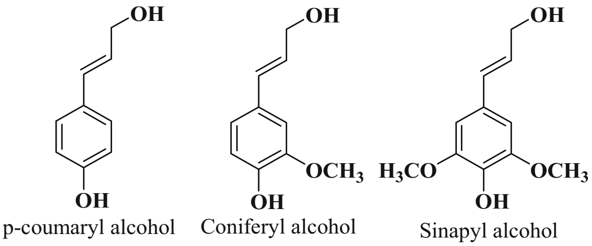


Fig. 7.5 Alcohol units present in lignin

carried out by Río Andrade et al. (2013) where the main substituent along with other monomers was identified by 2D NMR and DFRC which were drawn in the figure below (Fig. 7.6).

Agricultural wastes contain different sugar molecules including glucose, xylose, mannose, galactose, arabinose, etc. Diversity in structure makes this more vulnerable to acid, thermal, and biological hydrolysis. Sugar composition of various agro-wastes given in Table 7.2 (Lee 1997).

The structure characterization of lignocellulose has been studied by analytical pyrolysis of polymers, viz lignin, hemicellulose, and cellulose by different researchers. The studies provided various structural monomers and substituents

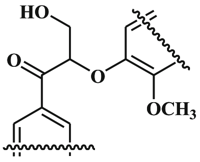
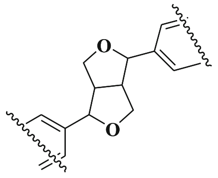
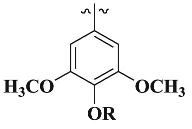
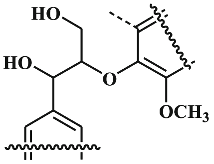
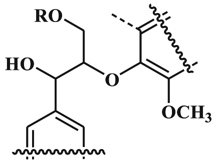
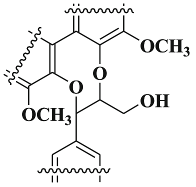
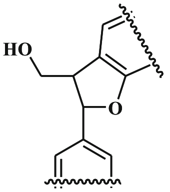
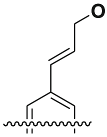
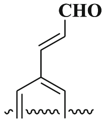
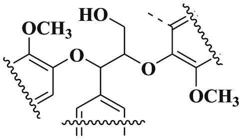
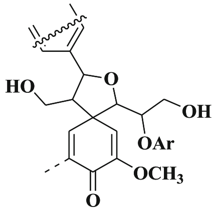
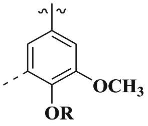
		
Cα-oxidised β-O-4’	Resinols	Syringyl units
		
β-O-4’ alkyl-aryl ether	β-O-4’ alkyl-aryl ethers with acylated γ-OH	Dibenzodioxocinons
		
Phenyl coumarins	Cinnamyl alcohol end groups	Cinnamyl aldehyde end groups
		
α,β-diaryl ethers	Spirodienones	Guaiacyl units

Fig. 7.6 Phenols Present in Lignin

present in the lignocelluloses. These lignocelluloses were further characterized by spectroscopic techniques like 2D NMR, FT-IR, SEM, X-ray. Some important substituent units present in the waste of major crops are given in Table 7.3.

Table 7.2 Sugar composition of agro-wastes

S. no.	Agricultural waste	Glucose	Xylose	Mannose	Galactose	Arabinose	References
1	Wheat straw	38.8 ± 0.5	22.2 ± 0.3	1.7 ± 0.2	2.7 ± 0.1	4.7 ± 0.1	Erdei et al. (2010), Lee (1997)
2	Rice straw	41–43.4	14.8–20.2	1.8	0.4	2.4–4.5	Karimi et al. (2006a, b)
3	Sugarcane bagasse	38.1	23.3	NA	1.1	2.5	Lee (1997)

7.3 Agricultural Wastes for Biofuels

Waste materials originating from varied human actions are the main hazards to the use of natural resources that includes air, soil, water, and natural resources in a balanced manner (Demirbas et al. 2009). The term “waste” implies that the substance is unusable and undesirable, though, most of the waste products can be recycled, and hence can be used as a fuel for manufacturing or energy storage if they are recycled appropriately (Tchobanoglous et al. 2000). Waste-to-energy (WTE) technologies transform these discarded resources to innumerable forms of fuel which is used as a source of energy (Demirbas and Balat 2010). WTE technologies that yield fuels are identified as waste-to-fuel technologies. Such technology can be utilized to make biogas (CO_2 or methane), syngas (CO or hydrogen), liquid fuels (bioethanol or biodiesel), or pure hydrogen; afterward, these fuels can be used to generate energy again. Biowaste fuel’s probably comprises wood, agricultural and animal wastes, short-rotation woody and herbaceous plants, as well as a variety of other ingredients. Biomass can be viewed as the ideal alternative which possess the greatest capacity for meeting these needs and ensuring power supplies in the future (Bakis 2008; Balat 2009). In developed nations, biomass contributes to approximately 35% of total primary energy consumption, bringing the global average to 14% of primary consumption (Balat et al. 2009). Biowaste fuels deliver significant aids as far as the environment is taken into consideration. During its development, biomass absorbs CO_2 and releases it while combustion. As a result, biomass aids to recycle CO_2 in the atmosphere and does not add to the global warming. Furthermore, biomass is a CO_2-neutral source, so net CO_2 emissions can be reduced.

The term biofuel refers to solid, liquid, or gassy fuels which are largely formed from biomass. Liquid and gassy biofuels are highly distinguished in recent times due to their environmental welfares. These are pollutant-free, readily available, long-term, and dependable fuels attained from inexhaustible sources. Shortly, energy production via biofuels is thought to be an appealing process. Biomass integrated gasification, which has high energy conversion efficiencies, is the way of the future for biomass electricity generation (Demirbas 2009a, b). There are many reasons why both developing and developed countries should recognize biofuels as viable

Table 7.3 Substituents present in waste of major crops

S. no.	Agricultural waste		Substituents
1.	Wheat bran	Cellulose (Anderson and Ydesdale 1980)	Consist of D-glucose bonded together with Beta-(1,4)-glycosidic linkages
		Hemicellulose (Adams 1955; Sun et al. 2000; Anderson and Ydesdale 1980)	Arabinoglucuronoxylans (arabino-4-O-methylglucuronoxylans) Xylose as the main sugar, arabinose, glucose, and galactose were present in small amounts, and rhamnose and mannose were identified as minimal quantities Phenols: Vanillin, syringaldehyde
		Lignin (Merali et al. 2015)	*p*-hydroxy phenylpropanoid units
2.	Wheat straw	Lignin (Río Andrade et al. 2013; Del Río et al. 2012; Crestini and Argyropoulos 1997; Sun et al. 2005)	*p*-hydroxyphenyl-guaiacyl-syringyl lignin with coumarate and ferulates The main units are present
		Hemicellulose	Arabinoglucuronoxylans (arabino-4-O-metylglucuronoxylans)
		Cellulose	Consist of D-glucose bonded together with Beta-(1,4)-glycosidic linkages
3	Rice straw	Lignin	Phenylpropane units are linked by ether, ester, and various other bonds
		Hemicellulose	Xylan hemicellulose
		Cellulose	Consist of D-glucose bonded together with Beta-(1,4)-glycosidic linkages
4	Sugarcane bagasse	Lignin	Phenylpropane units are linked by ether, ester, and various other bonds
		Hemicellulose (Bian et al. 2012)	4-O-methyl-glucuronoarabinoxylans consisting of a linear (1 → 4)-β-d-xylopyranosyl backbone decorated with branches at O-2 and O-3 of arabinofuranosyl or at O-2 of 4-O-methylglucuronic acid unit
		Cellulose	Consist of D-glucose bonded together with Beta-(1,4)-glycosidic linkages

technologies. Energy safety challenges, ecological concerns, foreign interchange savings, and socioeconomic problems affecting all countries' rural sectors are among them (Demirbas and Dincer 2008). Developing nations desiring economic and trade opportunities are particularly interested in the increasing international demand for biofuel. Due to higher land accessibility, favorable weather conditions for agriculture, and lesser labor expenses, developing nations have a competitive benefit in biofuel production. However, there may be other socioeconomic and environmental consequences that limit developing countries ability to profit from better global biofuel demand (Forum for Agricultural Research in Africa (FARA) 2008). Large-scale biofuel production offers a chance for some emerging economies to decrease their reliance on oil imports. There is an increasing trend in developed countries to use new technology and effective bioenergy transformation using a variety of biofuels that are turning out to be cost-effective with fossil fuels (Demirbas 2008). First-generation biofuels (FGBs), second-generation biofuels (SGBs), third-generation biofuels (TGBs), and fourth-generation biofuels are the four categories of biofuels based on their technological innovations. FGBs are biofuels prepared from sugar, starch, vegetable oils, or animal fats that are traditionally grown. Primary feedstocks for the development of first-generation biofuels include seeds or grains, for example, wheat, that produces starch that is converted into bioethanol, and sunflower seeds, that are hard-pressed to create a vegetable oil to be utilized in the production of biodiesel. Second- and third-generation biofuels are referred to as innovative biofuels. SGBs are prepared with advanced technology from non-food crops such as wheat straw, corn, wood, and energy crops. Algae fuel, also known as third-generation biofuel, is an algae-based fuel. Algae are low-input/high-yield feedstocks for advanced technology to generate biofuels (30 times the amount of energy per acre as field). A modern fourth generation, on the other hand, is focusing on using cutting-edge technologies to convert vegetable oil and biodiesel into biogasoline (Demirbas 2009a, b).

Due to inefficient burners used, agricultural wastes (or residues) only provide an insignificant proportion of the potential energy when used as fuel via direct combustion (Osman et al. 2006). Current crop residue disposal practices have sparked extensive environmental issues. For example, open-field burning of rice and wheat straw pollutes the air (Demirbas 2008). The method of anaerobic biological treatment of agrarian solid waste has gathered a lot of consideration in recent years. Converting these litters to methane generates energy and has a positive impact on the environment; however, bacteria in the compost are eliminated. During the digestion process, which is beneficial to environmental health. Straws, nutshells, molasses, fruit skins, fruit seeds, and green leaves are examples of agricultural residues that could be used to generate renewable energy. A large range of agricultural residues is abundant in many developing countries. Agricultural plant residues are produced in large quantities every year around the world and are largely underutilized (Demirbas 2001). Rice straw is an ample and mostly underutilized agricultural by-product. East and Southeast Asian developing countries produce 90 percent of the world’s straw, which is the primary feed for livestock (Hameed and El-Khaiary 2008). Straw can be utilized as animal feedstuff, bedding, a mushroom cultivation substrate, or a fuel source (Panoutsou et al. 2017; Townsend et al. 2017). Thorough elimination of the straw from the ground is not ideal because it reduces the volume of soil carbon in the fields over time (Karlsson et al. 2017; Townsend et al. 2017). Wood and organic crop remains containing lignocellulosic biomass are being regarded as possible bioethanol and biodiesel raw materials (Kaparaju et al. 2009). Fuels made from these raw resources are a likely alternative to fossil fuels, which are a chief cause of contamination. Water-soluble carbohydrates (fructans, sucrose, glucose, and fructose) may gather in the stem and leaf sheath of cool-season cereals (C3 plants) during their development (Xue et al. 2008). Rice has a well-documented phenomenon of non-structural carbohydrate accumulation, where stem serves as a basis for sugar transport to the crop (Park et al. 2011). Carbohydrates are temporarily stored in wheat stalks throughout the initial reproductive development process, often as water-soluble carbohydrates, and then remobilized in grain filling. Under abiotic stress, carbon buildup becomes critical for grain produce in cereal crops. The carbon supply from photosynthesis is decreased in drought-stressed wheat plants owing to stomatal closures in the leaves and downregulation of Calvin Cycle genes (Xue et al. 2008). The limitations stemmed primarily from depending solely on biowaste as a fuel, considering biowaste's highly varying properties. Biowaste fuels' high moisture and ash content can cause ignition and combustion issues (Demirbas 2005; Oliveira and Franca 2009).

7.3.1 Biofuel from Wheat Straw

Wheat straw, a by-product of the wheat harvest that has enormous commercial potential for the production of bioethanol fuels around the world. In 2012, global wheat grain production was reported to be 670 million tonnes (FAOSTAT 2019), and it continues to rise each year. The residue weighs 887 million tonnes, assuming a 1.3 ratio of residues (straw) and grains. When other uses of wheat straw are taken into account, it is assessed that partial of this volume, or 400 million tonnes, would go idle and could be used as biomass for ethanol production (Talebnia et al. 2010). Conferring to the biofuels-OECD-FAO Agricultural Outlook 2013–2022, ethanol manufacture is projected to rise by 67% over the next 10 years, reaching 168 billion liters by 2022, with the majority of it coming from sugarcane and grains. The possibility of producing bioethanol from these starch/sugar-rich crops adds to the food vs. fuel debate (OECD-FAO Agricultural Outlook 2014). Unlike several other first-generation biofuel feedstocks, the feedstock for second-generation biofuels derived from lignocellulosic biomass of crops has the advantages of being cheap and plentiful, and its production does not compete with agricultural lands or food.

7.3.1.1 Ethanol Production

The most intensive application of produced glucose is probably the ethanol production using wheat straw. Bacteria such as *Zymomonas mobilis, Brettanomyces bruxellensis,* and *Saccharomyces cerevisiae* are the perfect microbes to use in the industrial production of ethanol because they transform hexose and glucose to ethanol (Blomqvist and Passoth 2015; Gupta et al. 2016). Bioethanol made from lignocellulosic biomass will help meet some of the world's rising mandate for liquid fuels. It could be used as a fuel in vehicles that do not need engine modifications (Talebnia et al. 2010). Three key steps are needed to convert lignocellulose biomass into ethanol. (1) pretreatment, which decomposes the carbohydrates-lignin bond, depolymerizes and solubilizes hemicellulose polymers, and subjects the cellulose and hemicellulose to enzymatic degradation; (2) saccharification, which entails the enzymatic hydrolysis of cell wall carbohydrates to sugar monomers; and (3) bacteriological fermentation of the six-carbon sugar monomers into ethanol (Kristensen et al. 2008).

7.3.1.2 Methane Production

One of the most efficient applications of agricultural waste is wheat straw methane production. Methane is generated by anaerobic oxidation of lignocellulosic biomass, that is more energy efficient than ethanol production using wheat straw. This anaerobic molecule degradation is divided into four stages. Biopolymer degradation, acetogenesis, acidogenesis, and eventually methanogenesis that produce methane gas (Börjesson and Mattiasson 2008).

7.3.1.3 Butanol Production

Wheat straw can be used to make butanol in a variety of ways, and both the iso-butanol and n-butanol forms of butanol reflect the activity of fuels. *Clostridium beijerinckii* P260 is used to generate acetonebutanolethanol from wheat straw, and the process is divided into five steps (1) separate straw hydrolysis and fermentation, (2) simultaneous straw hydrolysis and fermentation without mix, (3) fermentation and hydrolysis with supplementation, (4) fermentation and hydrolysis of straw with gas stripping mixing, and (5) ultimately, fermentation and hydrolysis of straw to acetonebutanolethanol, which is more appealing and less expensive (Qureshi et al. 2008).

7.3.2 Biofuel from Maize

Maize has considered a leading candidate for biofuel production due to its ability to carry photosynthetic action via. C4 pathway. This aids maize in achieving high carbon fixation, water, and nutrient utilization efficiency. Maize stands out among the C4 grasses because of the abundance and diversity of germplasm available for crop enhancement, as well as its capacity to acclimatize to a variety of environments (Ragouskas et al. 2006). In contrast to corn grain starch, which is the only carbon form that can be harvested, maize can contain three different forms of biomass feedstocks: sugar, starch, and lignocellulosic biomass. As a result, the rising bioenergy industry requires maize as a bio-refinery feedstock because it serves two purposes—as a sugar feedstock that can be used instead of sugarcane in temperate climates, and as a lignocellulose feedstock that can be used instead of corn grain for ethanol production (White et al. 2011). As a result, maize will provide us with a wide range of items. Starch-based ethanol development setups or installations could be used as bases for cellulose-based ethanol production, aiding in the early stages of the lignocellulose-based economy. The key components of the cell wall (cellulose, hemicellulose, and lignin) add complexity to lignocellulosic content and necessitate pretreatment and hydrolysis to recover cellulosic ethanol. By disrupting the cellulosic structure, pretreatment aids in the fractional elimination of hemicellulose, allowing enzymes access to a larger surface region. Hydrolytic enzymes aid in the breakdown of cellulosic and hemicellulosic chains into monomers that are then fermented by natural or engineered yeast to generate ethanol (Mosier et al. 2005; Wyman 1999).

One approach for progressing lignocellulosic feedstock is to improve the comparative content and efficiency of cellulose that will help obtain more harvestable energy per unit of land. Cellulose is a durable substrate with properties including high polymerization and crystallinity index that make it almost impossible for enzymes to degrade (Park et al. 2010). Modifications to the ultrastructure of cellulose to facilitate enzymatic depolymerization would not only increase processing efficiency but also improve economics and cell-wall digestibility as compared to the bare form, all without upsetting growth and fitness.

7.3.3 Biofuel from Rice

Rice straw is a residue of the rice crop that is a valuable sustainable bioresource for biofuel creation. Rice straw is thought to be capable of producing approximately 205 billion liters of ethanol/year, which would account for around 5% of global ethanol consumption. Carbohydrates, namely glucose, mannose, xylose, arabinose, and galactose can be found in rice straws (Roberto et al. 2003; Yoswathana et al. 2010).

Biofuels can be extracted from rice residues' cellulosic content by altering them to fermentable sugars, which can further be converted into fuel using microorganisms or enzymes. The lignin existence in the plant cell wall hinders the supply of carbohydrates in rice residues, which must be extracted. Several pretreatment methods for degrading lignin materials and solubilizing hemicellulases (Fan et al. 1982; Schultz et al. 1983; Hormeyer et al. 2009; Hahn-Hagerdal et al. 2001; Bollock 1999; Soni et al. 2010) to produce fermentable sugars have been developed. When compared to wheat straw, rice straw varieties with higher enzymatic digestibility react better to different chemical pretreatments (Wu et al. 2013). Rice straws are revealed to be a more effective biofuel processing substitute. Instead of being burned, rice straw could be used as a feedstock for bioethanol processing, making it the global prime feedstock for the development of second-generation ethanol (Harun et al. 2013; Karimi and Taherzadeh 2016; Kim and Dale 2004).

7.3.4 Biofuel from Sugarcane

Sugarcane tops (SCT) may be used as a bioethanol feedstock. Saccharum officinarum, or sugarcane, is a group of high perennial true grasses in the Saccharum family, Andropogoneae (Canilha et al. 2012). Sugarcane's key product is sucrose, which accumulates in stalk internodes and can be extracted and distilled in specialized sugar factories before being used in the food industry or fermented to generate ethanol. Sugarcane stalks make up about 75% of a fully grown sugarcane plant, while leaves and tops make up about 25% (Sherpa et al. 2017). SCT, like leaves, is high in cellulosic materials and contains sugar as cellulose. As a result, ethanol can be extracted from SCT by using its abundant cellulosic matter and massive biomass supply. The extraction of ethanol from SCT and leaves does not affect the food supply and will not interfere with sugar-based foods or juice derived from sugarcane stalks. SCT is abundant during harvest, but it is burned in the field (Sukumaran et al. 2010), and the leaves are normally used as animal fodder until they rot. During the burning process, polyaromatic hydrocarbons are released, and some of the compounds emitted to the atmosphere may be carcinogenic or mutagenic. According to the Food and Agricultural Organization, nearly 1700 million tonnes of sugarcane are processed globally each year. This results in a large number of postharvest residues, mostly SCT, which are a cheap and easy source of LCB (lignocellulosic biomass). When 1 MT of sugarcane is harvested, 0.250.30 MT of SCT is usually made (Sindhu et al. 2011). Measures can be implemented to use SCT as a bioethanol processing substrate. Sugarcane is a popular renewable energy crop that is abundantly available and widely grown in countries like Brazil, China, India, Thailand, and Australia (Phalan 2009; Demirbas 2010).

7.4 Bio-Renewable Liquid Fuels

The following liquid biofuels are currently being considered around the world: (a) edible oils and biodiesels, (b) bio alcohols, and (c) biocrude and bio-synthetic oils. Liquid biofuels for transportation have lately fascinated a lot of interest in numerous countries around the world due to their recyclability, affordability, widespread accessibility, regional expansion, countryside trade employment, lessening of greenhouse gas releases, and biodegradability (Demirbas 2009a, b).

7.4.1 Vegetable Oil/Biodiesel

Transesterification is a chemical process that transforms vegetable oils, animal fats, and grease into biodiesel fuel. Biodiesel is an ecologically safe fluid fuel which can be castoff with any diesel engine without modification. The production of biodiesel started in earnest in the early 1990s, and it has gradually grown since then (Balat and Balat 2008). To make a biodiesel blend, biodiesel can be mixed with petroleum diesel at any proportion. These savings will grow when the volume of biodiesel mixed into diesel fuel surges. Biodiesel's high price is perhaps the utmost significant obstacle to its commercialization. The rate of producing biodiesel is significantly more than that of petroleum-based diesel fuel. Once such factors, like plant ability, process technology, cost of raw materials, and chemical costs, are known, the commercial output of a biodiesel plant can be known (Zhang et al. 2003). The price of biodiesel fuels differs subject to the base stock, location, crop produce fluctuations season-wise, cost of crude petroleum, etc. (Demirbas and Karslioglu 2007). The price of feedstock is a significant determinant of biodiesel production viability. Raw material costs account for 70–95% of the overall cost of biodiesel production (Krawczyk 1996). Approximately 95% of global biodiesel generation is currently made from edible oils that are readily accessible on a wide scale from the agriculture business (Gui et al. 2008). There are issues that biodiesel feedstock would clash with the food supply. The usage of a "less valued" feedstock, such as oily agricultural and food remains, could mitigate these disadvantages (Oliveira and Franca 2009). Biodiesel production from various inedible oilseed crops has been widely researched in recent times (Sharma et al. 2010). In developing countries, inedible oils are readily obtainable and cost less than edible oils (Darici and Ocal 2010). This low-cost oils and fats are difficult to process since they often comprise elevated quantities of free fatty acids (FFA), which is impossible to be turned into biodiesel that used an alkaline catalyst. In a one-hour reaction at 333 K, each step was carried out with a 0.30–0.35 v/v methanol-to-oil ratio with an acid catalyst, sulfuric acid. To produce biodiesel, *M. indica* oil was pretreated and transesterified with a 0.25 v/v methanol-to-oil ratio (6:1 molar ratio) and 0.7% w/v KOH as an alkaline catalyst. *M. indica* oil yielded 98% biodiesel after going through this procedure. Zullaikah et al. (2005) analyzed two acid-catalyzed methanolysis for rice bran oil with a high FFA content that generates more than 98% fatty acid methyl ester (FAME).

7.4.2 Bio-Oil

It is a renewable liquefied fuel provided by the rapid pyrolysis of biomass. It has a lesser heating charge of nearly 16 MJ/kg than diesel, that has a heating value of 43 MJ/kg (Brammer et al. 2006). Pyrolysis of biomass is the thermal breakdown of the organic matrix without oxygen, resulting in a variety of solid, liquid, and gas products (Yaman 2004). The pyrolysis process is thought to hold a lot of promise for turning biomass into compounds and higher-value fuels (Balat 2008). The liquefied and gaseous products could be utilized to generate energy in engines and turbines. Based on the operating situations, pyrolysis processes are categorized as carbonization (very slow), traditional (slow), quick, or flash (Demirbas 2009a, b). Quick pyrolysis is recommended if our goal is to produce mostly liquid and/or gaseous products. Recently, the quick pyrolysis method for biomass has gotten a lot of consideration because it can maximize liquid yields (Pütün 2002). Quick pyrolysis/thermolysis is a mechanism in which biomass is quickly warmed to higher temperatures without the presence of air (specifically oxygen). At stumpy temperatures (675–775 K), fast pyrolysis is related with tar, and at high temperatures, with methane. Depending on the feedstock used, quick pyrolysis processes generate 60–75% liquid bio-oil, 15–25% solid char, and 10–20% noncondensable gases (Mohan et al. 2006). Sugarcane bagasse, rice hulls and straw, peanut hulls, wheat straw and wood are only some of the forest and agricultural waste materials that can be used to make bio-oil. Bio-oil is made from forest remains in North America and Europe (sawdust, bark, and shavings). It is made from sugarcane bagasse and other agricultural wastes in Central and South America. Wheat straws, rice hulls, coconut fiber, and other plentiful potential feedstocks are just a few examples (Mohan et al. 2006). Bio-oil derived from wood has an extraordinary heating value (HHV) of about half as compared to heavy fuel oil. Bio-oil yields from wood, paper, and other biomass ranged from 60 to 95% by weight, depending on the feedstock composition. Based on the comparative amounts of cellulose and lignin in the material, bio-oil yields from wood vary from 72 to 80% by weight. Elevated lignin content, as that contained in the bark, tends to result in lesser liquid yields (60–65%) (Mohan et al. 2006). Zheng et al. (2008) investigated quick pyrolysis of the cotton stalk in a fluidized bed at temperatures ranging from 753 to 803 K, obtaining the highest yield of bio-oil (55%) at 783 K. Demiral (2006) investigated the pyrolysis of hazelnut bagasse in a fixed-bed reactor using a slow pyrolysis procedure. At a final temperature of 773 K, with a heating rate of 283 K/min, the particle size range of 0.425–0.600 mm, and a sweep gas flow rate of 150 cm^3/min, the maximum bio-oil yield of 34.4% was obtained. 25–30% water-insoluble pyrolytic lignin, 20–25% water, 5–12% organic acids, 5–10% nonpolar hydrocarbons, 5–10% anhydrosugars, and 10–25% other oxygenated compounds are the main constituents of bio-oil (Shaw 2006). The biochemical conformations of the bio-oils are comparable to the feedstock compositions that are documented. Park et al. (2004) used gas chromatography mass spectroscopy (GC–MS) to examine the constituents of bio-oils derived by pyrolysis of rice straw. Some common components identified in the sample were acetic acid, phenol and alkylated phenols, furan derivatives, furfural, and anhydrosugars. According to GC–MS review, the bio-oil obtained from sawdust is mostly made up of oxygen-comprising aromatic mixtures. Bio-oil cannot currently be used for transport fuel because of its high viscosity, acidic composition, poor heating charge, higher content of water and oxygen and inconsistency with conventional fuels.

7.4.3 Bioalcohols

Alcohols are oxygenated fuels in which the alcoholic molecule contains single or multiple oxygen molecules that reduces the combustion heat. In theory, every organic molecule in the alcohol family can be used as a fuel. Bioethanol (C_2H_5OH), biomethanol (CH_3OH), propanol (C_3H_7OH), and biobutanol (C_4H_9OH) are alcohols which can be utilized as motor fuels. Only bioethanol and biomethanol fuels, on the other hand, are economically appropriate for internal combustion engines (Demirbas 2007).

7.4.3.1 Bioethanol

It is perhaps the utmost popularly used biofuel for transportation on a global scale. The United States is the biggest bioethanol fuel producer, corresponding for nearly 47% of world's bioethanol produce (Balat and Balat 2009). It can also be used straight way in models produced to operate on pure ethanol, or it can be combined with gasoline to produce "gasohol." Blending with gasoline necessitates the use of anhydrous bioethanol. In most cases, no engine modifications are required to use this mixture. Bioethanol is an oxygenated fuel with a 35% oxygen content that aids in the reduction of particle and NOx emissions during combustion. It also has a greater octane number (108), a wider range of flammability limitations, faster flame speeds, and greater vaporization temperature than gasoline. These possessions enable a greater compression ratio, a lesser burn time, and a leaner burn engine, resulting in speculative efficacy benefits over gasoline in a combustion engine (Balat 2007, 2009). Bioethanol has a lesser energy density than gasoline (but 35% higher than biomethanol), is corrosive, has a poor flame luminance, low vapor pressure, is miscible with water, is detrimental to environments, increases acetaldehyde exhaust releases, and increases vapor pressure when mixed with gasoline (Smith 2008). The amount of raw materials for bioethanol manufacture is a significant issue. The availability of bioethanol feedstocks can differ greatly season-wise and depending on geographic location. The raw materials are also extremely unstable that can have a considerable impact on bioethanol production costs (Yoosin and Sorapipatana 2007). The price of feedstock accounts for 60–75% of the total rate of bioethanol production (Balat and Balat 2009). Manufacture technology for sugar or starch crops is comparatively developed, and it is unlikely that it will be improved to reduce production costs (Demirbas et al. 2009). Lignocellulosic biomass is likely to contribute a substantial share of the raw materials for bioethanol manufacturing in the medium and long term because of its low rate and abundant obtainability. The usage of food crops for bioethanol production poses serious dietary and moral concerns. Because approximately 60% of the world's population is now malnourished, there is a significant need for grains and other fundamental commodities (Pimentel et al. 2009). One of the key reasons why bioethanol has failed to gain momentum as a fuel source is the high expense of manufacturing bioethanol from lignocellulose. Numerous environmental and food-versus-fuel difficulties that hamper bioethanol derived from crops like sugar or corn may be overcome by bioethanol manufactured from lignocellulosic materials. Delignification, vapor burst, and diluted acid pre-hydrolysis are used to delignify the lignocellulose, which is then accompanied by enzymatic hydrolysis and fermentation into bioethanol (Demirbas 2010).

Hydrolysis is most easily accomplished with feedstocks that are rich in starch and sugar. Cellulosic feedstocks, such as the majority of organics in MSW, are extra problematic to hydrolyze, necessitating added pretreatment (Alodali 2010). Any pretreatment method intends to maximize the rate of enzyme hydrolysis and yields of fermentable sugars by modifying or eliminating structural and compositional hydrolysis barriers (Mosier et al. 2005). If the pretreatment is insufficient, the resulting residue is difficult to hydrolyze by cellulase enzyme, and if it is more serious, toxic compounds are produced, inhibiting microbial metabolism (Kodali and Pogaku 2006). According to Silverstein (2004), an ideal lignocellulose pretreatment should: (1) enhance formation of sugar or the capacity to form sugars later through hydrolysis; (2) prevent degradation of carbohydrates or its loss; (3) avoid the development of byproducts that hinder associated hydrolysis and fermentation processes; and (4) be economically efficient. If cellulose and hemicellulose both are hydrolyzed, the supernatant from enzymatic lignocellulose hydrolysis will comprise both the hexoses and pentoses sugars (Keshwani and Cheng 2009).

7.4.3.2 Biomethanol

Methanol is generally derived from natural gas, but it can also be formed from biomass (biomethanol). Synthetic gases (H_2 and CO) are generated by gasification. Syngas can manufacture a variety of commercial fuels and compounds, such as synthetic diesel, methanol and lower carbon alcohols, acetic acid, dimethyl ether, and others (Demirbas 2010). Biomethanol is generated from synthesis gas formed by traditional biomass gasification at elevated temperatures (1073–1273 K) and catalytic processing of the resulting blend of CO_2 and H_2 with a 1:2 molar proportion at high pressures (4–10 MPa) (Demirbas 2009a, b). It can be manufactured from any carbon-rich renewable resource, namely seaweed, waste wood, or garbage. This is a feasible strategy, with a wide range of fuel submissions that have been recognized to favor the environment, economy, and consumers (Demirbas 2009a, b). Biomethanol can be partially generated from waste. Methanol produced from agriculture is currently more costly than methanol produced from natural gas. The engine's thermal efficiency is higher, and there are no emissions issues. Biomethanol is the perfect fuel for high-compression engines due to its high octane number (106) (Corlett 1975). With a higher octane level, some engine design factors like compression ratio and valve timing can be changed to improve fuel efficiency and strength (Demirbas 2009a, b). Biomethanol has a low energy density than gasoline when measured in mass units. Biomethanol has a lesser heating value of 19.9 MJ/kg, while C_8H_{18} has a greater heating value of 44.4 MJ/kg (Kar and Deveci 2006). It is most commonly used as a fuel in the M85 (85% biomethanol/15% gasoline) mix although it can also be used in its almost pure form (M100) (Balat et al. 2009).

7.4.3.3 Biobutanol

Although bioethanol is presently the most popular alternative for replacing gasoline as a transport fuel, biobutanol has now gained popularity (Nair et al. 2008). Because of its high energy content and greater air-to-fuel ratio, biobutanol is thought to have superior fuel properties to bioethanol. It is much less unstable and destructive than bioethanol, with a high flash point and low vapor pressure, making it a safer substance to work with (Pakkila et al. 2009). Isobutanol (a branched isomer of straight-chain butanol) may be mixed up to 15% volumetrically with petrol, compared to ethanol. Butanol, on the other hand, has an octane value similar to gasoline but lower than ethanol. Butanol, as a result, cannot be utilized as an octane enhancer. The major drawback of butanol appears to be its toxicity (Kavalov 2009). Latex surface coatings, enamels, nitrocellulose lacquers, adhesives/scalants, elastomers, textiles, superabsorbents, flocculants, fabrics, and plastics all require butyl acrylate and methacrylate esters, which account for roughly half of world manufacturing. Biobutanol, like bioethanol, can be produced in a fermentation or petrochemical process. The biotechnological method is once again economically viable due to current crude oil prices (Dürre 2007). The fermentation process is divided into two phases: (1) acidogenesis, which is characterized by cell growth combined with acid production, and (2) solventogenesis, which is characterized by least growth, solvent making and acid change into solvents. Over the last decade, a hyper-butanol-producing strain and an integrated acetone–butanol–ethanol (ABE) fermentation system for the continuous synthesis and exclusion of butanol from the fermentation broth have been developed using molecular approaches applied to solventogenic clostridia and recent advances in fermentation techniques (Ejezi et al. 2007). Annual crops, namely corn, rice, barley, etc. can be used to make biobutanol. Due to price and obtainability constraints, there is considerable curiosity in using wood and agricultural waste as feedstock for ABE manufacturing. Solventogenic ABE-producing clostridia have a benefit over many other cultures in that they can produce ABE from both hexose and pentose sugars that are unconstrained by hydrolysis of wood and agricultural remains (Qureshi et al. 2008). Marchal et al. (1992) used *Clostridium acetobutylicum* to manufacture ABE from corncob hydrolysate. Wheat straw hydrolysate and *Clostridium beijerinckii* P260 were used by Qureshi et al. (2007) to turn this agricultural waste into ABE.

7.4.4 Biogas

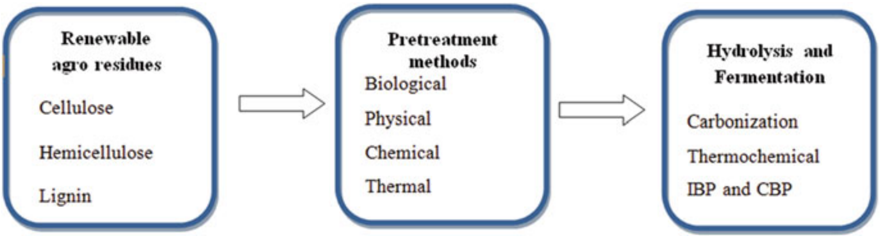
This pollution free and renewable type of energy has the potential to replace traditional energy sources (fossil fuels, oil, etc.) that are initiating environmental degradation while also rapidly depleting (Santosh et al. 2004). Biogas is principally made of methane (CH_4) and carbon dioxide (CO_2), with lower quantities of sulfur (H_2S). Biogas usually contains 55–70% CH_4, 30–45% CO_2, 0–2% N_2, and 500 ppm

H_2S. (Monnet 2003). Methane is the most essential of its constituents, mainly for the combustion in vehicle engines. If released into the environment, methane is a valued renewable energy source, but it is also a dangerous greenhouse gas (Kuwahara et al. 1999). After proper gas cleaning, biogas can be used as a fuel for generators, gas turbines, fuel cells, boilers, industrial heaters as well as for chemical industry. Biogas may be utilized straightaway in spark-ignition gas engines (SIGEs) and gas turbines. When utilized as a fuel in SIGE to generate mainly energy, the complete conversion efficiency to electricity from biomass is around 10–16%. Anaerobic digestion is now the extensively used technique for treatment of organic leftover material owing to its great performance in volume reduction and stability, as well as the creation of biogas. Animal waste like manure and industrial waste streams caused by agricultural, animal, and other food production actions are samples of traditionally low-valued waste produce (Rutledge 2005). The biogas generated in anaerobic digestors comprise approximately 80% methane v/v, and its excellence would be determined by its source (Benito et al. 2007). Biogas and digestate, a moist solid that is usually dewatered to create a liquid stream and a drier solid, are the end products of anaerobic digestion (Ostrem 2004). Approximately 30–60% of the solids are transformed to biogas during anaerobic digestion; by-products include undigested fiber and various water-soluble materials (Veringa 2004). The first phase of anaerobic digestion, which is a multi-stage process, is hydrolysis. Organic compounds, such as carbohydrates, amino acids, alcohols, and long-chain fatty acids, are hydrolyzed into smaller units. The rate-limiting step in the digestion of organic wastes anaerobically is extracellular hydrolysis. In this process, particulate matter is dissolved and organic polymers are biologically decomposed into monomers or dimers. A range of mechanical, thermal, chemical, and biological pretreatment strategies have been explored to increase hydrolysis and anaerobic digestion efficiency (Ferrer et al. 2008). These pretreatments trigger cell lysis or disintegration, releasing intracellular materials that anaerobic microbes prefer, resulting in better anaerobic digestion (Demirer and Othman 2008). Anaerobic fermentation decreases total waste mass, produces solid or liquid fertilizer, and producing energy (Vindis et al. 2009). In recent decades, anaerobic digestion has been evaluated in the hopes of developing a technology that combines waste stabilization with resource retrieval (Nguyen et al. 2007). The composition of MSW varies based on the waste source; although, the main constituents of MSW are all organic, accounting for more than half of MSW. Agricultural leftovers produce just a slight fraction of their potential energy when burned directly as fuel due to poor burners. As a result, one of the alternate possibilities for altering the agricultural waste usage pattern is anaerobic fermentation to generate a combustible, safe, stable, and cost-effective gas. The most of agricultural wastes are lignocellulosic, which signifies they have a low nitrogen concentration, which makes anaerobic fermentation of crop leftovers difficult (Osman et al. 2006). The carbon-to-nitrogen (C/N) ratio represents the connection between the quantity of carbon and nitrogen found in organic materials (Verma 2002). Agricultural residues are low in nitrogen, with C/N ratios ranging from 60 to 90 (Demirbas 2009a, b). A high C/N ratio indicates that methanogens consume nitrogen quickly, resulting in lower gas production. A small C/N ratio, on the other hand, induces ammonia accumulation and pH values above 8.5 that are deadly to methanogenic bacteria (Balat and Balat 2009). For anaerobic digestion, a C/N ratio of 25–35 is ideal (Hills and Roberts 1981). Nitrogen can be supplemented in two forms: inorganic (ammonia) and organic (livestock manure, urea, or food wastes). N_2 is converted to ammonium, which is water-soluble until it is released from organic matter. The amount of nitrogen needed is reduced by recycling N_2 in the digested liquid (Demirbas 2009a, b). Wheat emerged as first, barley second, and corn third in developing countries, with 68% of cultivated land producing grains. Wheat straw wastes, if appropriately and biologically converted to methane, provide a promising energy resource. They are green and produce no net CO_2 emissions into the atmosphere. Biogas sources including manures and manure-straw combinations have been comprehensively researched. Demirbas et al. (2009) focused into the digestion of wheat straw-manure mixtures anaerobically in order to create a methane-rich gas combination. The methane yields from the products used ranged from 10.4 to 14.7%. For the runs, the biogas contained between 73 and 79% methane, with the remaining being mostly carbon dioxide.

7.5 Processing of Biomass to Ethanol

The method of converting lignocellulosic materials into the biofuels consists primarily of three stages.

1. Pretreatment
2. Hydrolysis
3. Fermentation process



7.5.1 Pretreatment

Pretreatments are essential for effective breakdown of the barrier to lignin and extraction of cellulosic material that is then supplied with hydrolysis to be transformed to simple monosaccharides. Delignification can be accomplished by a variety of physical, mechanical, biochemical, and physiochemical processes. This move is critical for making feedstock susceptible to microorganisms by reducing indigenous crystallinity, particulate size, and polymerization. Chemical pretreatment methods include hydrothermolysis with acid, alkali, and solvents (e.g., H_2O_2, glycerol, dioxane, phenol and ethylene glycol, ozone); ball milling, commination (mechanical reduction of the size of particles of biomass), and compression milling are physical pretreatment processes.

7.5.1.1 Milling

Milling may be done to make lignocelluloses more amenable to cellulases based on the intrinsic cellulose ultrastructure and crystallinity level. Cellulases are enzymes which catalyze the cellulose disintegration, so for the enzymes to act optimally, substrate supply must be increased. Lignocellulosic matter should be milled and reduced in size before submitting it to enzymatic hydrolysis. Examples of milling processes include ball milling, hammer milling, colloid milling, vibro-energy milling, and two-roll milling. Colloid mills, dissolvers, and fibrillators are good for wet materials, whereas hammer mills, extruders, cryogenic mills, and roller mills are good for materials that are fully dried. Both wet and dry products may be used for ball milling. Hammer milling is the best pretreatment method for waste paper. Milling improves enzyme degradation by reducing the crystallinity and size of substrate. Particle size reduction by up to 0.2 mm can be achieved by milling and grinding. Up to a certain extent, biomass particle size reduction is possible; after that, particle size reduction has no effect on the pretreatment process. Corn stover with little granules, such as 53–75 μm, is more efficient than corn stover with big particle sizes, such as 475–710 μm. Because of the size difference between the particles, efficiency has a major impact on the pretreatment method. Ball milling reduces the crystallinity index of straw from 4.9 to 74.2%, making it more ideal for saccharification under moderate hydrolytic conditions and the processing of fermentable sugars (Walpot 1986; Sidiras and Koukios 1989; Bondy et al. 1998; Taherzadeh and Karimi 2008). To boost hydrolysis results, milling can be combined with enzymatic hydrolysis. Mechanical activity, mass transfer, and enzymatic hydrolysis will all be performed at the same time when two systems are merged. In comparison, multiple ball perforations on the reactor of the bill mill play a critical role in cellulose hydrolysis, in contrast to biotreatment without using the milling process, when a lower energy charge is required and 100% hydrolysis can be achieved. After cutting, steam explosion and pulverization, rice straw was mounted on a fluidized bed in opposition to a jet mill to fine grind to achieve the maximum hydrolysis rate and reduction in sugar yield.

Vibratory ball milling is an excellent method for increasing digestibility and decreasing crystallinity. Wet disk milling has a significant benefit in terms of energy consumption because it produces fibers that boost cellulose hydrolysis, while hammer milling produces finer bundles. As a result, when wet disk milling is available, milling isn't the best option (Zhu et al. 2009a, b). The results of other ball and disk milling analyses are compared. Top xylose and glucose yields of 54.3 and 89.4%, respectively, were obtained using traditional ball milling (Hideno et al. 2013). Wet milling produces less results, but it avoids the formation of inhibitors and wastes less energy. When wet milling was combined with alkaline pretreatment, enzymatic hydrolysis improved by 110 percent. 10 mm diameter 20 steel balls, a solid-to-liquid ratio of 1:10, a speed of 350 rpm/min, and a particle size of 0.5 mm are the best conditions for wet milling pretreatment of corn stover (Lin et al. 2010).

7.5.1.2 Microwave

Microwave irradiation is a popular method for plant biomass pretreatment. This pretreatment approach has many benefits, including ease of use, improved heating power, fast processing time, limited inhibitor production, and lower energy requirements. A team of researchers from the University of Kyoto, Japan, carried out the first thesis on microwave irradiation in a sealed container in 1984. They microwaved the bagasse of sugarcane, rice paw, and rice husks in the presence of water. Microwave treatment requirements include 50 mL glass vessels, 2450 MHz capacity, and 2.4 kW microwave irradiation (Azuma et al. 1985). Typical pretreatment techniques have been used at high pressures and temperatures. Chemical interactions among lignocellulosic materials collapse as a result of the high temperatures and increased availability of substrate to enzyme. In traditional heating processes, lignocellulosic materials are heated with high pressure steam injection or indirect heat injection at temperatures between 160 and 250 °C. However, to avoid temperature gradients, lignocellulosic material must be crushed into small fragments. A microwave is a safe option for avoiding high-temperature gradients because it evenly distributes heat and prevents lignocellulosic substrate degradation into humic acid and furfural. The combination of microwave irradiation with moderate alkaline therapy is necessary for successful oxidation. The sugar content was 70–90% obtained through alkaline pretreatment and irradiation by switching grass (Hu and Wen 2008). Because of the high temperature of microwave radiation, a closed container is necessary to achieve this temperature. Microwave demonstrates three properties: penetration, reflection, and absorption. Microwaves are absorbed by water and biomass and pass through plastic and glass, while metals reflect microwaves. Two groups can apply to microwave reactors based on these characteristics: those that allow microwaves to pass through and those that reflect them. The first kind of microwave reactor is made of glass or plastic, while the second kind is made of steel. Microwaves will penetrate the reactor through quartz windows, which are installed in the reactor. For microwave irradiation pretreatment, a locked, sealable, pressure-resistant tube glass container with a Teflon gasket may be used at a high temperature of 200 °C. Sensors are used for microwave temperature control and maintenance. Sensors with Teflon coating are a good choice because of their thermal stability, corrosion resistance, and zero absorption properties. Some scientists use Teflon vessels in microwave ovens because of their favorable properties (Azuma et al. 1984; Komolwanich et al. 2014). Aside from glass vessels and steel tanks with controls on temperature and pressure, a microwave feedback control system and a mechanical stirrer are also used.

7.5.1.3 Mechanical Extrusion

When the materials pass into a die on a certain cross-section, a definite profile is applied. This is the method of extraction of sugar from the biomass. Mechanical extrusion pretreatment has many benefits, including ability to adapt improvements, products that do not degrade, a controlled environment, and high throughput. Extruders are divided into two types: single screw and twin screw. The forward kneading and reverse screw parts make up a single screw extruder. Bulk content of varying pitches and different lengths can be transmitted by forwarding screw parts with minimal shearing and mixing. The use of enormous blends and shears requires material which is pushed back by reverse torn elements, while materials that are pushed back by kneading torn elements with a poor forward conveyor effect are used for prominent mixing and shearing. A screw-configuration is described by the arrangement of different angles, heights, spacing, pitches, and positions. A twin-screw extruder can conduct multiple blending, cutting, mixing, reaction, draining and separation functions simultaneously. Single and twin-screw extruders are used to achieve high enzymatic hydrolysis speeds. Different parameters such as screw speed, temperature of the barrel, and compression ratio may all have a major impact on sugar recovery. Short-time extruders allow for rapid heat transfer, careful mixing, and improved shear. The composition of the biomass is disrupted as it passes through the extruder barrel, exposing more surface for enzymatic hydrolysis (Amalia et al. 2010; Karunanithy and Muthukumarappan 2011; Zheng and Rehmann 2014). Lignocellulosic material can be treated during the extrusion process to increase sugar recovery using alkali and acid. Acidic treatment is less beneficial than alkaline therapy due to degradation caused by acid in the extruder material. The use of AL6XN alloy for manufacturing barrels and extrusion screws will prevent corrosion. Alkali treatment is appropriate for lignocellulosic content because it reduces the deterioration of glucose and plays a part in delignification. Sodium hydroxide is most widely used to dissolve lignins and hemicelluloses and sever ester bonds. Alkali treatment can be done in two ways: adding alkali to the extruder using a volumetric pump, or soaking the lignocellulosic substance at room temperature in the alkaline (Morrison 1988; Morrison 1991).

7.5.1.4 Pyrolysis

Pyrolysis is used in the manufacture of bio-oil from biomass. Pyrolysis is the thermal oxidation of lignocellulosic without the use of an oxidizing agent at extremely high temperatures. Pyrolysis was performed between 500 and 800 °C at temperatures. The rapid decomposition of cellulose generated products such as charcoal and pyrolysis oil (Kilzer and Broido 1965). Pyrolysis pretreatment classified into two types based on temperature: rapid and low pyrolysis. Various factors, such as biomass properties, reaction conditions, and pyrolysis type, affect the end products. Due to high-value energy-rich product formation, fast transport management retrofitting, combustion, packaging, and flexibility in usage and marketing, thermal industries are adapting to the pyrolysis process. The use of oxygen and a lower temperature increase the performance of this process. The bond cleavage rate of cellulose was studied in the presence of nitrogen and oxygen. During the pyrolysis step at 25 °C, 7.8109 bonds/min/g cellulose is broken in the presence of oxygen and 1.7108 bonds/min/g cellulose in the presence of nitrogen (Kappe 2004). Three thermochemical conversion approaches for biomass into biofuels are gasification, pyrolysis, and direct combustion (Yin et al. 2010). Different forms of pyrolysis result in different yields of pyrolysis materials. Bio-oil is made up of water and polar organics. When bio-oil production is needed, pyrolysis is used. In a regulated atmosphere, rapid pyrolysis results in the formation of liquid materials (fuels). Torrefaction, also known as mild pyrolysis, is a relatively new procedure. It varies from pyrolysis in that it is a thermochemical process that takes place at temperatures between 200 and 300 °C. This method results in partial decomposition of biomass, with the final product being terrified biomass. During the pyrolysis process, plant biomass breaks down into vapor, aerosols, and char. Torrefaction is divided into two types: dry and wet.

Torrefaction of dry biomass necessitates the presence of an inert atmosphere, normal atmospheric pressure and fully dry biomass. Biochar is the key byproduct of this form of biomass pretreatment. Other terms for wet torrefaction include hydrothermal carbonization and hydrothermal torrefaction. In contrast to dry torrefaction, the pretreatment is carried out in a pressurized vessel of water. Since the biomass used in wet torrefaction retains moisture, this form of torrefaction necessitates a drying process after torrefaction. A pressure range of 1–250 MPa is needed for wet torrefaction. Hydro-char is the most common biomass component used in wet torrefaction pretreatment (Chen et al. 2018).

7.5.1.5 Pulse Electric Field (PEF)

Pores are produced in the cell membrane as a result of this process, exposing cellulose to agents that penetrate the cell and cause it to break down. In a nano- or millisecond blast, a high voltage varying from 5.0 to 20.0 kV/cm is applied to biomass. The sample was placed between two parallel plate electrodes, and the electric field amplitude was calculated using the formula $E = V/d$, where V and d refer to the voltage and distance between the plate electrodes, respectively. The amount of mass permeability and tissue rapture improved significantly when an electric field was applied. Electric signals are used, which are typically in the form of square waves or exponential decay. A pulse generator, a monitoring system, a data collection system, and material handling equipment were all part of the pulse electric field setup (Kumar et al. 2009). At room temperature, the procedure can be carried out with little electricity. Another drawback of this treatment is the instrument's basic construction. The short length of the pulse period saves effort and energy (Kumar and Sharma 2017). Pig manure and waste-activated sludge were pretreated with a pulse electric field by Author et al. (2009). In comparison to untreated manure and sludge, the analysis discovered 80% methane from manure and a twofold rise in methane production from sludge. A PEF setup was designed and developed by Kumar et al. (2011), A high-voltage power supply, a switch circuit, a work generator, and a sample keeper were among the components. To explore the variations in cellulose structure created by PEF pretreatment, the neutral red dye was used. The function generator powers the transistor in the switching circuit, and the switching circuit switches on when the function generator sends a pulse to it. Around the sample holder, the switching circuit is switched to high voltage. As a result, a function generator may be used to apply pulses of the desired shape, distance, and high voltage to the sample. This rig was used to study the effects on switch grass and timber. The results revealed that switch grass had a fast neutral red uptake at 8 kV/cm. Structure shifts are less likely to occur at low field strength. Pulse length and electric field power, have a significant impact on electroporation via a pulsed electric field. Irreversible electroporation was observed in Chlorella vulgaris at >4 kV/cm with millisecond pulse duration and 10 kV/cm with microsecond pulse duration, demonstrating that pulse duration differences in the micro- and millisecond range can affect electroporation (Fig. 7.7). A pulse electric field increases the rate of hydrolysis by introducing cellulose to catalytic agents (Kumar et al. 2009; Luengo et al. 2015).

Chemical pretreatment with dilute sulfuric acid is the most popular process (Mosier et al. 2005). It efficiently hydrolyzes hemicellulose to sugars, improves lignin composition, and increases cellulosic surface area (Wyman et al. 2005). Grethlein and others pioneered a pretreatment method that can split the lignin–hemicelluloses shield in agricultural residues and woody biomass, which is normally followed by hemicellulose degradation.

The acid-catalyzed process has been extensively evaluated from a variety of perspectives, including performance optimization, kinetic review, and cost-effectiveness. This mainstream method, on the other hand, could have some

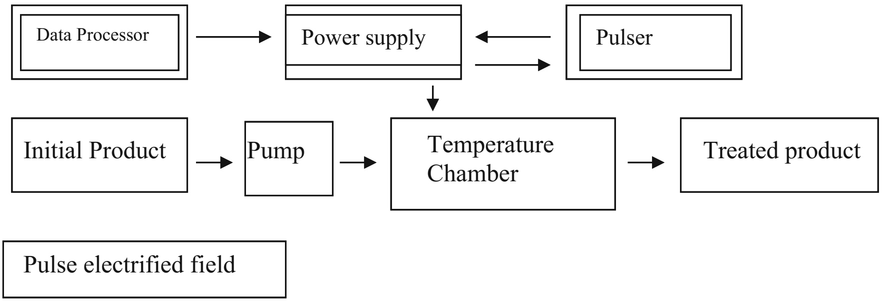


Fig. 7.7 Basic process of Pulse electric field

unfavorable consequences. Excessive degradation of the formed monosaccharide, for example, results in the development of aldehydes like furfural, lowering the polysaccharide conversion yield and inhibiting the ethanol fermentation process. Another drawback with this method is that it uses a corrosive acid, such as sulfuric acid, which requires downstream neutralization in addition to requiring specific reactor materials. The recycling of expended acid adds to the complexity of downstream production. Ammonia fiber/freeze explosion (AFEX) is a process in which anhydrous ammonia reacts with lignocellulose to increase surface area, decrease crystallinity, melt part of the hemicellulose, and eliminate lignin. The pretreatment of lignocellulose in a less concentrated ammonia solution is known as ammonia recycled percolation (ARP). The AFEX pretreatment is a novel alkaline pretreatment process that physicochemically changes the ultra and macro composition of lignocellulosic biomass. When compared to untreated lignocellulosic biomass, AFEX pretreatment increases biomass enzymatic digestibility by many times according to studies (Teymouri et al. 2005). The AFEX pretreatment causes cellulose decrystallization (Gollapalli et al. 2002), partial hemicellulose depolymerization, deacetylation of acetyl groups, cleavage of lignin–carbohydrate complex (LCC) linkages and lignin C–O–C bonds, an increase in functional surface area due to structural disruption (Turner et al. 1990), and an increase in wettability (Sulbaran de Ferrer et al. 1997). The AFEX approach has proved to be economically appealing as compared to some other leading pretreatment technologies, according to a recent study using an economic model (Eggeman and Elander 2005) for measuring bioethanol conversion of corn stover.

7.5.1.6 Ozonolysis

The oxidant ozone has been shown to digest LCB. This pretreatment process takes place at room temperature and does not result in the formation of inhibitory compounds (Sun and Cheng 2002). However, it necessitates a significant volume of ozone, rendering the process commercially unviable.

7.5.1.7 Organosolv

Various organic or aqueous solvent mixtures, such as methanol, ammonia, acetone, ethylene glycol, and tetrahydrofurfuryl alcohol, are used in this pretreatment. These mixtures remove lignin (Zhao et al. 2009a, b). A potential advantage of organosolv over other pretreatment methods is the recovery of relatively pure lignin as a by-product. Solvent removal is needed for this pretreatment process because solvents can interfere with enzymatic hydrolysis and fermentation (Sun and Cheng 2002). As a result, because of their low boiling points and ease of separation, low-molecular-weight solvents such as ethanol and methanol are favored. Others suggested a two-stage fractionation using organosolv and acid hydrolysis to separate hemicelluloses and lignin. The biomass is treated first with acid to hydrolyze the hemicellulose selectively, then the organosolv delignment stage is taken. This was followed by high lignin elimination with low cellulose reduction (Papatheofanous et al. 1995). However, a large amount of chemicals will be needed to succeed with this procedure, which will increase both the cost of operation and the process risk.

7.5.1.8 Ionic Liquids (ILs)

The use of ionic liquids (ILs) as solvents is a comparatively new approach to pretreatment and is widely investigated. They consist of huge organic cations and small inorganic anions, melted salts at melts below 100 °C (35 °F). They are low vapor, chemical and heat stable, non-flammable, and generally non-toxic (Alvira et al. 2010). Dissolving biomass in solvent at different temperatures of about 90–130 °C at ambient pressures, and for different time periods, is used for pretreatment with ILs (1–24 h). After that, water is added to the biomass precipitation, which is then cleaned before being subjected to enzymatic hydrolysis (Samayam and Schall 2010; Zhu et al. 2006). IL splits the crystalline cellulose structure by creating a hydrogen connection between cellulose and anion IL (Brodeur et al. 2011). In addition, the chemistry of certain ILs allows lignins and hemicelluloses from biomass selectively to be removed (Pu et al. 2007; Binder and Raines 2009; Lee et al. 2009).

7.5.1.9 Uncatalyzed Steam Explosion

Masonite process is used for an uncatalyzed steam explosion to dissolve hemicellulose for the manufacture of fiber board and other similar materials (Mosier et al. 2005). High-pressure steam is applied for a few minutes to woodchips without the use of additives. Without decrystallizing the cellulose, this procedure increases the wood surface area and improves cellulose digestibility greatly.

7.5.1.10 Hot Water Treatment

Elevated temperatures and pressures using subcritical water (200–250 °C) and supercritical water (higher than 374 °C and above 22 MPa) is used to raise biomass surface area and dissolve hemicelluloses (Mosier et al. 2005; Wyman et al. 2005). The three types of reactors used for heat-water pretreatment are co-current (lignocellulose and water flowing in the equal sense), counter-current (water and lignocellulose flow in opposing directions), and flux reactors (hot water passes over a stationary bed of lignocellulose).

7.5.1.11 Carbon Dioxide Explosions

CO_2 is used as a supercritical fluid is carbon dioxide explosions, as gas is compressed to create a liquid-like mass at temperatures close to its critical stage. CO_2 reacts to carbonic acid with water, which facilitates hydrolysis polymer. CO_2 molecules are identical in size to water and ammonia, but, like water and ammonia, they move though LCB pores. The strain is reduced to allow for the devastating emission of CO_2 in the CO_2 molecule. This publication, which increases the available surface area, interrupts the arrangement of cellulose and hemicelluloses. The supercritical CO_2 method could be too expensive for commercial size because both hardwood and softwood biomass, subjected to supercritical CO_2, demonstrated an efficient enzyme hydrolysis.

7.5.1.12 Wet Oxidation

It is an effective pretreatment process for wheat straw and wood; the hemicellulosic fraction dissolves and makes a solid cellulosic fraction susceptible to enzyme hydrolysis and fermentation. Hot water under pressure is used in the WO operation, along with oxygen. The method is a hydrothermal pretreatment that is equivalent to the well-known steam pretreatment until oxygen is not added. The addition of carbonate during hydrolysis results in degradation of sugar and reduced formation of 2-furfural (Bjerre et al. 1996) and phenol aldehydes (Klinke et al. 2002). Sugar monomers are formed during steaming and dilute acid hydrolysis pretreatments, while the alkaline WO treatment of wheat straw only produces soluble polymeric hemicellulose sugars (arabinoxylan).

7.5.1.13 Biological Pretreatment

Standard physical and chemical pretreatments necessitate expensive reagents, materials, and a significant amount of resources. Biological pretreatment treats lignocellulosic material with live microorganisms, and it is a more environmentally sustainable and energy-efficient approach. Cellulolytic and hemicellulolytic capacities are seen in certain microorganisms found in nature. White-rot, soft-rot, and brown fungi are well-known for removing lignin and hemicellulose without affecting cellulose. White rot can degrade lignin due to the presence of lignin-degrading enzymes such as peroxidases and laccases. Carbon and nitrogen sources affect the regulation of these decaying enzymes. Brown rot mostly targets cellulose in plant biomass, while white- and soft-rot target both lignin and cellulose. *Pleurotus ostreatus, Ceriporiopsis subvermispora, Ceriporia lacerata, Pycnoporus cinnabarinus, Cyathus cinnabarinus, and Phanerochaete chrysosporium are some of the most commonly used white-rot fungi. Bjerkandera adusta, Ganoderma resinaceum, Trametes versicolor, Fomes fomentarius, Irpex lacteus, Lepista nuda,* *and Phanerochaete chrysosporium* are among the basidiomycetes species studied, and these species showed high delignification ability.

Pretreatment with *Pleurotus ostreatus* converted 13% of wheat straw into sugars in 5 weeks, while *Phanerochaete sordida* and *Pycnoporus cinnabarinus* converted about the same amount of wheat straw into sugars in less time. The fungus has developed a cellulose-free mutation. Sporotrichum pulverulentum can also be used to degrade lignin thereby avoiding cellulose degradation in woodchips. Ceriporiopsis subvermispora and Cyathus stercoreus, both white-rot fungi, can be used to delignify Bermuda turf, with delignification rates of 29–32 and 63–77%, respectively. During secondary metabolism in the fungus P. chrysosporium, two lignin degrading enzymes, lignin peroxidase and manganese-dependent peroxidase, are produced in response to carbon and nitrogen limitation. These two enzymes can be used in multiple white-rot fungi's extracellular filtrates.

7.5.2 Hydrolysis

During the stage of hydrolysis, the pre-treated biomass is converted to fermentable glucose. The hydrolysis caused by pretreatment is catalyzed by dilute acid (Saha et al. 2005), concentrates or ideally by cellulase enzymes. In order that oligomers can converted into glucose and xylose with general reactions with water:

$$(C_6H_{10}O_5)n + nH_2O \rightarrow nC_6H_{12}O_6 \tag{7.1}$$

$$(C_5H_8O_4)n + nH_2O \rightarrow nC_5H_{10}O_5 \tag{7.2}$$

The reaction of hydrolysis in the dilute acid phase takes place at a temperature of between 160 and 230 °C and an acidic acid content of between 2 and 5% (10 atm), resulting in small quantities of cellulose biomass glucose molecules; hence, the yield of the end products is low. The concentrated acid hydrolysis produces more ethanol and transforms cellulose and hemicellulose in sucrose by around 95–98% due to longer retention times. Lower operating temperatures (50 °C) and air pressure with concentrated acid (concentration of 10–30%) are required during concentrated acid hydrolysis (Shahbazi and Zhang 2010; Kim et al. 2011; Bensah and Mensah 2013). Furthermore, microbial enzymes catalyze lignocellulosic biomass dealignment and depolymerization in its component sugars under relatively mild conditions (50 °C and pH 5). Enzyme hydrolysis is the most common process for the production of ethanol from lignocellulosic residues without the aggregation of by-products to hinder enzymes (Álvarez et al. 2016; Waghmare et al. 2018).

7.5.2.1 Physical Methods for Hydrolysis

Hydrolysis Using Water or Steam Under Pressure

In the fatty acid industry, batch and continuous high-temperature–pressure systems are used to hydrolyze fats and oils. The "Twitchell cycle" refers to batch hydrolysis of fats and oils at high temperatures and pressures, while the "Colgate-emery technique" refers to continuous mode. In a batch operation, oil or fat is heated with water at 150–270 °C and 10–45 bar pressure. Depending on the kind of triglyceride, hydrolysis takes 6–10 h. The hydrolytic reaction is slowed as the triglyceride's molecular weight increases. After two changes of water to extract the glycerin by-product, a standard industrial batch operation performs at 230 °C and 400 psig, yielding about 96% hydrolysis of oils and fats.

The fat and water are currently fed into a continuous flow column at a temperature of 260 °C and a pressure of 60 bar. Water (sweet water) removes the glycerin by-product, bringing the reaction equilibrium closer to completion. The high temperature ensures that in the water process fat or oil is fully dissolved. The oil process flows from under to above through the column with the vacuum volume of the column acting as a reaction space. The water pass into the combination of fat or oil and fatty acids, remove the by-product of glycerin from the bottom outlet. Heat is transferred from the materials to the incoming reactant sources via the top and bottom portions of the column reactor. The correct temperature and stress ratio, use a little water, and continually remove the by-product of glycerin, will perform a hydrolysis of up to 99% of oils and fats in 1–3 h (Chupa et al. 2007).

Hydrolysis Using Subcritical and Supercritical Water

Every day, significant volumes of biomass waste can be spontaneously created or produced with high value-added components by industrial processes such as waste hydrolysis. The two most common methods of industrial hydrolysis for biomass wastes are chemical (acid or alkaline) and enzymatic hydrolyses. Chemical hydrolysis, on the other hand, necessitates violent reaction conditions and often pollutes the atmosphere. Enzymatic hydrolysis is costly and takes a long time to produce. As a result, identifying and developing a new environmentally sustainable approach to address the limitations of chemical and enzymatic hydrolysis is critical.

In super- or subcritical water, the majority of biomass waste can quickly be hydrolyzed. Tc = 374 °C, Pc = 24.2 MPa, and c = 0.32 g Ml1 have the necessary properties for (highly critical) SC-H2O. Water has a structural deviation from standard liquid water and some impressive properties in supercritical and almost supercryptical regions (subcritical: Firstly, it is used as a nonpolar organic solvent (like acetone) which allows some organic solvents to be replaced and used as a smooth medium for chemical reactions; secondly, it can dissolve a broad range of organic solutes and its dielectric constant (permissibility) can be modified to represent temperature and environmental pressure so that even the most nonpolar, hydrophobic solutes can be dissolved. The reaction rate in super subcritical water can also be increased in the absence of atmospheric pollution, making hydrolysis a renewable technology in super- or subcritical water. Biomass and waste can be used for hydrolyzing the amino acids, unsaturated fatty acids, polysaccharides, hydrogen, and methane and other high value manufacturing raw materials (King et al. 1999). While super- and subcritical water has not yet been used commercially to hydrolyze biomass, research conducted over the last decade has shown that it can be used to hydrolyze substrates including vegetable oils to produce fatty acids, protein-rich biomass to produce amino acids, and cellulose to produce oligosaccharides.

Hydrolysis of Vegetable Oils

Subcritical water at 270–280 °C will hydrolyze vegetable oils such as soybean oil, linseed oil, and coconut oil with a high yield of more than 97% in just 15–20 min (Holliday et al. 1997). At temperatures below 300 °C, most saturated fatty acids, such as caproic, caprylic, capric, lauric, myristic, palmitic, and stearic acids, are stable. At these temperatures, the unsaturated fatty acids oleic and linoleic acid are both largely unchanged. Under comparable conditions, a small amount of linolenic acid is degraded, while a large amount is isomerized from the cis, cis, cis form to the trans, trans, cis and trans, cis, cis forms. Hydrolysis of linolenic acid-rich oils like linseed oil can be carried out at slightly lower temperatures (i.e., at 260 °C) to reduce isomerization reactions; however, this increases the time taken for hydrolysis. The time taken to hydrolyze various vegetable oils to more than 97% at various temperatures has been tabulated in Table 7.2.

Hydrolysis of Protein-Rich Biomass

Protein-rich biomass, including oils and fats, takes a long time to hydrolyze (Cheng et al. 2008). Traditional hydrolytic and enzymatic methods take hours to break down protein or protein-rich biomass, while subcritical water breaks down protein-rich biomass in minutes. Hydrolysis of biomass such as fish waste, chicken waste, hair, and feather under subcritical conditions has recently yielded amino acids. Controlling the hydrolysis time and reaction temperature is critical for obtaining high amino acid yields; most amino acids yielded their highest yields when the reaction temperature was between 200 and 290 °C and the reaction time was between 5 and 20 min. The reaction environment, which involves sunshine, nitrogen, and carbon dioxide, affects the yields of the same amino acid. This is due to chemical variations between reaction atmospheres; for example, nitrogen is an inert gas, while air contains active oxygen, and carbon dioxide will significantly enhance acid catalysis. As a result, selecting suitable reaction atmospheres will result in the highest yield of necessary amino acids. The effect of reaction atmosphere on yields of four amino acids, leucine, isoleucine, serine, and tyrosine, from fish waste has been recorded at various subcritical temperatures (see Fig. 7.1 for illustration). Isoleucine yields were found to be highest when the reaction atmosphere was nitrogen, and slightly lower when the reaction atmosphere was air or 260 °C with carbon dioxide. Similarly, the highest serine yield was found at 240 °C with air as the reaction atmosphere, while the highest tyrosine yield was found at 240 °C with nitrogen as the reaction atmosphere.

Corn stalks may be a source of lignocellulosic waste (Zhao et al. 2009a, b). Ethanol processing technology, a common resource technology for lignocellulosic waste, has received a lot of attention due to its feasibility and useful products. However, there are already bottlenecks in the efficient conversion of lignocellulose to ethanol. To begin with, because of its large molecular structure, cellulose is difficult to hydrolyze, resulting in crystallinity and low solubility. Second, the presence of lignin around the cellulose fibers prevents the cellulose from direct interaction with the hydrolyzing solvents. To address these obstacles, a number of methods for the pretreatment and hydrolysis of lignocelluloses have been developed, including acid therapy, steam explosion, and enzyme hydrolysis. In addition, under critical and supercritical water treatments were examined and some of the benefits, such as the high rate of reaction, no demand of catalysts and no inhibition of products, were found.

Cellulose has been reported to hydrolyze glucose in 2 min at 300 °C and 8.9 MPa, but glucose takes just 30 s in the same state for later degradation. This means that in subcritical water, cellulose hydrolysis is much slower than glucose decomposition into several smaller molecules, making the processing of high fermentable sugars difficult. To solve the above-listed problems, lignocellulose pretreatment and hydrolysis have been proposed using a hybrid supercritical/subcritical technology. This strategy involves two main methods. To remove the lignin and produce cellulose oligosaccharides, the lignocelluloses are first pretreated and hydrolyzed in supercritical water. The oligosaccharides are subsequently hydrolyzed to generate mainly glucose and fructose in the subcritical water. At the same time, this process can efficiently produce a high level of fermentable sugars and avoid glucose further decomposition into unwanted products. A subcritical state (at 280 °C, 40 MPa) of the oligosaccharide-water mixture for around 15–45 s will then occur, after which there will be a hydrolysis of glucose oligosaccharides. These conditions of the reaction are comparatively milder than those of the supercritical level, which reduces glucose degradation of unwanted compounds afterward to a minimum.

Chemical Methods for Hydrolysis

Under normal conditions, only a few reactions exist between water and organic compounds (Morrison and Boyd 1995). Solid acids or bases must usually be added as catalysts that speed up reactions. Acids and bases accelerate both hydrolysis, as energy substitutes can exist for both the h+ and the hydrolysis ions. Acid catalyst generates H+ ions which speed up hydrolysis rates by deleting nuclear density and making them more vulnerable to H_2O nuclear attacks. The base catalyst produces

OH ions that are much stronger than water, speeding up the hydrolysis process. Nucleophilic replacement reactions are hydrolytic reactions that can take two paths: SN1 and SN2. The SN1 and SN2 pathways are capable of acid-catalyzed substratum hydrolysis, and base-catalyzed hydrolysis happens only by an SN2 pathway.

Mechanism of Acid-Catalyzed Hydrolysis of Esters

Acid-catalyzed ester hydrolysis is reversible and takes place via the SN1 route. Acid catalysts speed up the reaction by the protonation of CO_2 and thus increase the susceptibility of carbonyl carbon to nuclear attack. The acid-catalyzed hydrolysis mechanism of esters is described by different reaction balances.

Mechanism of Base-Catalyzed Hydrolysis of Esters

The foundation facilitates ester hydrolysis by the supply of stable hydroxide nucleophile ions. The baseline and catalytic ester hydrolysis occurs along the SN2 path, which is irreversible because it involves alcohol and ion carboxylation in the base catalyst ester hydrolysis (and not carboxylic acid). In the following various reaction balances, the basic catalyzed hydrolysis mechanism of esters is defined.

Enzymatic Hydrolysis

Biomolecules are enzymes that catalyze almost all of the biochemical reactions in a live system. Most enzymes are in natural proteins, except for a few RNAs which catalyze unique biochemical reactions. Six main groups can be categorized as enzymes. Each class is the general kind of reaction caused by this class's enzyme.

1. Oxidoreductase: enzymes which catalyze reactions from oxidation to reduction
2. Transfers: enzymes which catalyze the functional group transmission
3. Hydrolases: hydrolysis-catalytic enzymes from different substrates
4. Lyases: enzymes that catalyze water, ammonia, carbon dioxide, etc. addition or elimination
5. Isomerases: enzymes which catalyze reactions of isomerization
6. Ligases: enzymes which catalyze synthetic reactions, which combine two molecules and use ATP

Class is divided into many subclasses in turn. A four-digit Committee of Enzymes assigns enzymes covering the class (first digit), subclass (second digit), subclass (third digit), and human enzymes (fourth digit) (EC). For the six classes of enzymes, selected examples are shown in Table 7.4.

Table 7.4 Classification of enzymes

Enzyme class	Type of reaction catalyzed	Example with EC numbers
Oxidoreductase	Oxidation-reduction	Alcohol dehydrogenase (alcohol NAD+ oxidoreductase, EC 1.1.1.1)
Transferases	Group transfer	Hexokinase (ATP: D-hexose 6-phosphotransferase, EC 2.7.1.1)
Hydrolases	Hydrolysis	Lipase (triacylglycerol acyl hydrolase, EC 3.1.1.3)
Lyases	Addition–elimination	Aldolase (ketose 1-phosphate aldehyde lyase, EC 4.1.2.7)
Isomerases	Isomerization	Triosephosphate isomerase (D-glyceraldehyde 3-phosphate ketoisomerase, EC 5.3.1.1)
Ligases	Condensation	Glutamine synthesis (L-glutamate ammonia ligase, EC 6.3.1.2)

7.5.3 *Microbial Fermentation*

Fermentation is the biochemical mechanism by which various types of microalgae, including bacteria, yeast, fungus, or mold, convert hexose and pentose into ethanol (Heeres et al. 2014; Okamoto et al. 2014). The final step leads to the generation of ethanol from hydrated disaccharides divided mainly into two phases: (1) the conversion of simple sugars to ethanol and (2) distillation and adsorption of distilled ethanol. The hexoses (C6) and pentoses (C5) conversion reaction is as follows:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

$$3C_5H_{10}O_5 \rightarrow 5C_2H_5OH + 5CO_2$$

At 20 °C, there was a general theoretical yield of ethanol at 0.719 and 0.736 L/kg of hexoses, for example, glucose and xylose; (Elshahed 2010). The most widely used yeast in ethanol production by fed batches and multi-stage fermentation is the *Saccharomyces cerevisiae* (Liu et al. 2008). In addition, the fermentation of glucose and even xylose through solid-state fermentation has been identified to filamentous white-rot fungal strains such as *Phanerochaete chrysosporium, Flammulina cellules, Peniophora cinerea,* and *Trametes suaveolens* via digestion of cellulose, but its conversion is slow due to the formation of acetic acid as a by-product (Bak et al. 2009; Okamoto et al. 2010, 2011, 2014).

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Chapter 8
Mixed Lignocellulosic Feedstocks: An Effective Approach for Enhanced Biofuel Production

Diksha Singla and Monica Sachdeva Taggar

Abstract Additional energy needs in today's world have led to the exploitation of fossil fuels like gasoline. Fossil resources are not only on the verge of extinction but also create environmental and economic problems. For these reasons, the ethanol production has been promoted as sustainable alternative to address the crisis related with increasing global warming, rising prices of crude oil and declining fuel stores. The lignocellulosic biomass leads to the production of second--generation (2G) ethanol through its hydrolysis, followed by bacterial fermentation and regeneration of product. Agricultural biomass produced as waste during or subsequent to the processing of the agricultural crops is one of such renewable sources and lignocelluloses of rich biomass sources found in abundance for ethanol production. Lignocellulosic biomasses are potentially sustainable feedstocks for the production of biofuels due to its availability, low price and high sugar content. Nonetheless, the costly processing necessities of lignocellulosic materials and the high cost of feedstock supply hamper the growth of biorefinery. A mixed feedstock system usually involves simultaneously handling and conversion of two or more than two different lignocellulosic feedstocks in equal or varying ratios for production of an interested product instead of using a single feedstock. This chapter aims to reveal the significance of the usage of mixed lignocellulosic feedstocks along with its potential advantages and limitations for enhanced biofuel production.

Keywords Biofuel · Lignocellulosic biomass · Mixed feedstocks · Bioethanol · Paddy straw

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8.1 Introduction

Today, the global transportation system relies heavily on the provision of mineral oil in spite of the quick development of other technologies, for example, (CNG) compressed natural gas vehicles, electrical vehicles, or biofuels (mainly ethanol and biodiesel) (International Energy Agency 2018). The utilization of fossil fuel-oils has led to the number of issues like environmental concerns, reduction of crude oil stores, and local disputes of source management (Oke et al. 2016; Ge and Li 2018). Carbohydrate polymers of lignocellulosic feedstock are renewable energy sources in petroleum-based fuels. The transition to renewable carbon from fuel-oils is largely determined by the shocking global demand for energy, which is being cut off by 80% by burning fuel, while 58% order comes from the transport sector only (Zabed et al. 2016). In such approach, lignocellulosic materials, i.e., grasses, energy crops, industrial wastes, agricultural crop, and forest residues are expected to be considered as the potential raw supplies for the marketable production of 2G bioethanol. The supply of these materials is inexpensive as compared to 1G biomass (starchy and sugar-rich materials) and are basically not consumed by human beings because of extremely uneatable lignocellulosic substances. As a result, lignocellulosic waste materials do not interfere with human food stores and therefore avoid food versus energy clash. Also, some types of lignocellulosic waste biomass are highly poisonous and therefore cannot be utilized as fodders. Such indigestible varieties prevail over food, fodder versus energy conflict, and could therefore supply as an important feedstock in producing bioethanol in domestic and international markets.

A key to mass biofuel production based on lignocellulosic waste biomass is stable and constant, year-round trade of lignocellulosic feedstocks from a diversity of resources (Shi et al. 2015). Nevertheless, in actual, the delivery of feedstocks in the United States reflects variations from area to area, year to year, or season to season. In a particular area, the quantity, quality, and cost of lignocellulosic feedstocks differ depending on climatic conditions, management, storage, and variety of crops (Milbrandt 2005). As of an economic viewpoint, biorefinery have to be capable of effectively converting whichever waste residues offered at reasonable prices and indispensable levels to maintain profitability and productivity (Oke et al. 2016). The amount of feedstock energy plays major function in estimating the price and energy for the production of biofuel. Low-energy density waste biomass is less efficient to convert it into biofuels than high-energy ones as a result of higher energy necessities for the transport, storage, and allocation of the waste lignocellulosic biomass from the grassland to the gateway of biorefinery.

As accounted by “Turkish Republic Ministry of Energy and Natural Resources” (TMENR 2011) (Imamoglu and Sukan 2014), overall utilization of fuel-oil was 22 million tons, out of which was three million tons of benzene and 160 thousand tons of bioethanol. According to Turkish Statistical Institute (TUIK) 900,000 tons of rice was collected from 99,000 hectares of plantations as well as 180,000 tons of its hulls were removed. Besides this, 2.60 million tons (MT) of cotton was produced from 481,000 hectares of plantations and 15.50 MT of its stalks were achieved in Turkey. Thus, as an outcome, the ratio of waste into product (W/P) was 6/1 for stalks of cotton and 1/5 for rice hulls in Turkey. Lim and Lee (2013) reported chemical composition of rice husks and cotton straw with cellulose content of 28.60% and 47.10%, hemicellulose content of 28.6% and 24.1%, lignin content of 24.4% and 22%, and extractive matter of 18.4% and 6.3%, respectively. Thus, both of these feedstocks can be effectively used for enhanced biofuel production.

Till date, bulk of the existing studies on conversion of lignocellulosic biomass has paid attention on the use of single feedstock, and very less consideration for the effectiveness of converting combinations of different substrates to fermentable sugars as well as biofuels. This would necessitate re-examine as well as enhancement of current technology that is primarily based on utilization of single biomass feedstock. This chapter thus aims to focus on the probable advantages plus possible drawbacks about the use of mixed lignocellulosic feedstock approach for enhanced biofuel production. Different measures are also proposed to overcome the challenges and improve the processing of mixed lignocellulosic feedstocks (MLF) for the production of biofuels.

8.2 Biofuels

The vast raise in air contamination, shortage of fuel resources as well as rising global oil prices have sparked international interest in exploring renewable energy resources. The transport zone is the one that can apply renewable energy resources through replacement of fuel-oils with biofuels (Fig. 8.1). Biofuels can thus be

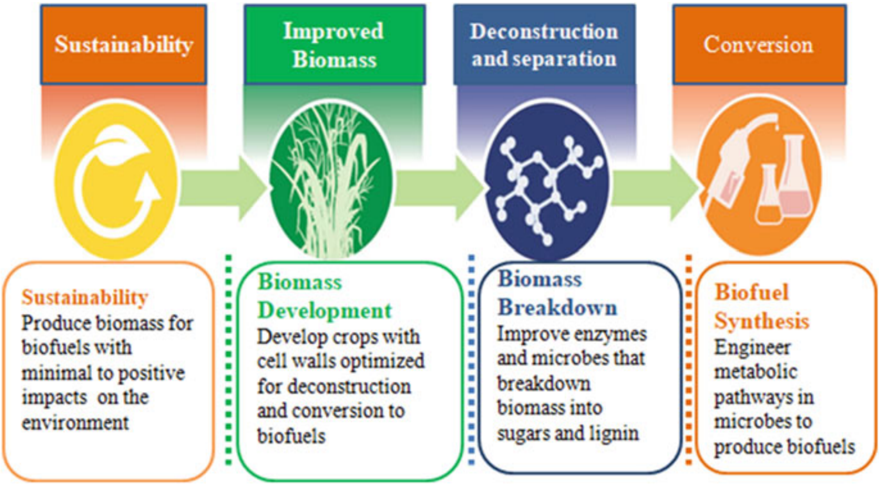

Fig. 8.1 Concept of biomass to biofuel

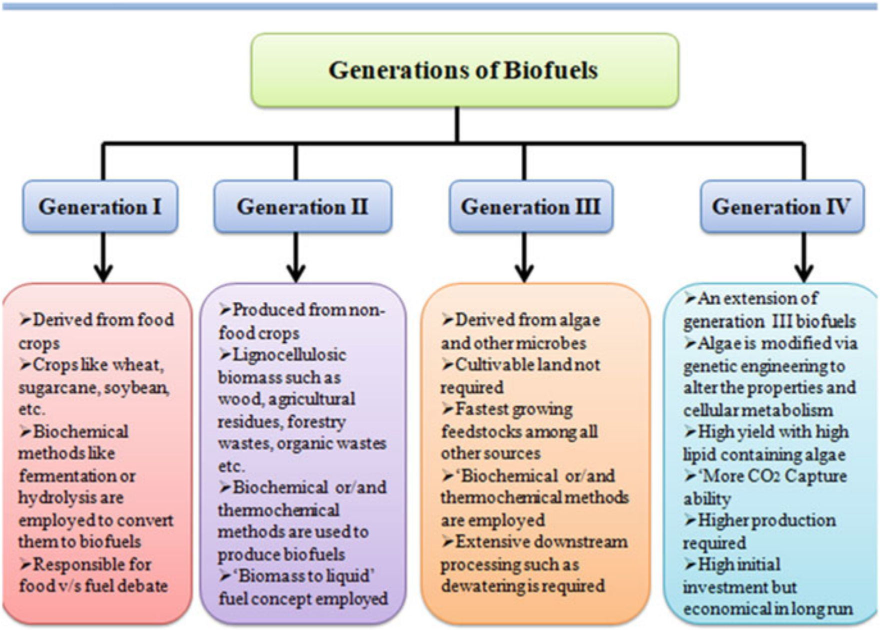

Fig. 8.2 Generation of biofuels

categorized into biodiesel, bioethanol, biohydrogen, biomethanol, and biogas. Bioethanol as well as biodiesel are the popular biofuels which are produced on industrial scale (Rodionova et al. 2017). Biodiesel and bioethanol are the main commodities in the world biofuel trade with an expected 25% biodiesel and 75% bioethanol of the total sales of biofuel. Five percent of the globe's bioethanol is provided by Europe, 39% by Brazil, and 50% by the United States (Heinimo and Junginger 2009). Bioethanol is ethanol formed through biochemical conversion of waste biomass through saccharification followed by fermentation. The different feedstocks which can be utilized are starchy grains, lignocelluloses, and microalgae that can be ultimately used to convert them into biofuels. There are four generation of biofuels which are shown in Fig. 8.2. The most expensive pretreatment method finds the yield of sugar that waste biomass can generate in the process of enzymatic saccharification, and this yield is generally less than 20% without prior treatment, while it can raise by more than 90% with pretreatment (Galbe and Zacchi 2007). After pretreatment, the next step is saccharification followed by fermentation; both of which can be performed separately or concurrently. The technology for the production of bioethanol from lignocellulosic waste biomass has been developing quickly. Nonetheless, there are number of uncooperative buttonholes like complexity in pretreatment, production of highly resistant yeast inhibitors, and attempts to lessen the cost of enzyme and principal costs in producing complex manufacturing process that hinders trade (Banerjee et al. 2010; Talebnia et al. 2010). The method to decrease the expenditure of bioethanol production on industrialized level is by decreasing the cost of untreated material, growing effectiveness, and promoting improved production systems (Jonker et al. 2015). Pretreatment is a major challenge to find the most excellent sugar raw substance for the process of saccharification and fermentation of lignocellulosic feedstock. The resultant outcome is not just on the point of lignocellulosic constituent, but also at the level of tissue as well as lignocellulosic biomass cells (Hendriks and Zeeman 2009). Efforts are being made to improve the pretreatment method so as to get the lignocellulosic feedstock with higher porosity and larger surface area which ultimately makes cellulose largely available to enzymes as a result of removing disturbing substances (Agbor et al. 2011). Different pretreatment methods have their benefits and drawbacks for their use at the industrial level. According to the relevant studies available, the effectiveness of pretreatment is to check the equilibrium between the inhibitor's production and the dissolution of feedstock (Parawira and Tekere 2011). In addition, pretreatment is the major cost-efficient process in terms of obtaining reducing sugars (Chandel et al. 2007). So to commercialize the production of biofuels at the industrial level, pretreatment is necessary.

8.2.1 Bioethanol

Bioethanol represents a closed carbon-dioxide (CO_2) sequence as after the ethanol is burned, the released CO_2 is recycled reversely into the plant matter as they utilize CO_2 to produce cellulose during the photosynthesis cycle and thus, no net CO_2 is added in the atmosphere (Singh and Tiwari 2013). Also the toxicity of released emissions from bioethanol is lesser than that of the fossil fuel sources (Wyman and Hinman 1990). Bioethanol does not contain any mono-aromatic or poly-aromatic hydrocarbons, making bioethanol a clean and environment friendly fuel. Other advantages of bioethanol include its use as an octane enhancer in unleaded gasoline and as an oxygenated mixture of fuel for cleaner gasoline combustion, thereby dropping tailpipe pollution and improving ambient air quality (Kang et al. 2014).

8.2.2 Biobutanol

For blending of gasoline, a 4-carbon alcohol, namely butanol is much more attractive than bioethanol because of its elevated energy density, lesser Reid vapor pressure and hygroscopicity, enhanced mixing capacity, and utilization in conventional fire engines devoid of any alteration (Karimi et al. 2015). Apart from the fuel extender, this biofuel can be utilized as an ultimate feedstock for the production of various marketable products (Mascal 2012). Fermentative production pathway, for example, by means of microorganisms under *Clostridium* genus attracts more attention environmentally and renewably than the petro-chemical path. These microorganisms usually produce combination of various liquid chemicals, primarily consisting of acetone, butanol, and ethanol; therefore, the process is thus known as "acetone-butanol-ethanol" (ABE) fermentation (Karimi et al. 2015) Conversely, the key ultimatum in microbial butanol production is its low titer due to product inhibition. A number of approaches have been recorded to tackle these issues like metabolic as well as genetic alteration of microorganisms and significant integrated continuing culture technologies with proficient product revival techniques, for example, utilizing frameworks of metal-organic (Cousin et al. 2011), gas stripping (Qureshi and Blaschek 2001), liquid–liquid extraction (Sreekumar et al. 2015), and pervaporation technique (Liu et al. 2014). Butanol can be produced through different engineered and metabolic ways using several different substrates. Starch or sugars be able to convert into biobutanol through clostridial pathway which involves "pyruvate: ferredoxin oxidoreductase", "glycolysis", "crotonase", "3-hydroxybutyryl-CoA dehydrogenase", "thiolase", "butyraldehyde/butanol dehydrogenase" as well as "butyryl-CoA dehydrogenase" The conversion of waste biomass to butanol also follows similar pathway after their conversion to pentoses and hexoses in the foregoing pretreatment and the enzymatic hydrolysis steps. The productions of lignocellulosic butanol have gained lots of attention, and more recently it has become the focal point of many studies (Morone and Pandey 2014). However, the low titer and yield of butanol and necessity of additional pretreatment and hydrolysis steps are various key challenges in the lignocellulosic biobutanol formation. Likewise, CO_2/H_2 or syngas also could be fermented to butanol through clostridial route (Bertsch and Müller 2015).

8.2.3 Biodiesel

Biodiesel is a combination of "fatty acid methyl esters" (FAMEs) which can be synthesized via trans-esterification of animal fats or edible oil. It has recently received much interest as a renewable energy resource (Talebi et al. 2013). However, this production source does not meet up the high demands for the transport fuel and requires renewable and sustainable energy source. On the other side, the oleaginous microorganisms can accumulate intracellular lipids, commonly called single cell oil (SCO), mainly triacylglycerols (TAGs). Microbial oils, such as unprocessed feedstocks for production of biodiesel, are advantageous as compared to vegetable oils due to shorter life cycle, are less labor intensive, less sensitive to location, climate, and season, and are easier to expand. Several oleaginous microorganisms, like yeasts, bacteria, microalgae as well as fungi, have been shown to produce considerable quantities of SCO with 20–50% dry cell mass) (Garay et al. 2016). Nevertheless, it is likely to enhance the accumulation of lipids in such oleaginous microorganisms through the technology of metabolic engineering, which involves different approaches, viz. enrichment of fatty acid and TAG synthesis, control of associated TAG biosynthesis circumvent, blockage of competitive routes, and multigene pathway (Satari et al. 2019). An array of carbon resources from lignocellulosic-based carbohydrates along with other low-priced wastages from industries like foodstuff processing wastes, glycerol, and contaminated water has been incorporated by oleaginous organisms to make lipids. Supplementary nutrients like nitrogen (N) and phosphorous (P) are found in the waste streams. Conversely, accumulation of lipids in such organisms is often caused through deficiency of nutrients, for example, N or P, which is related to the carbon source (Jin et al. 2015). The production of lipids from lignocellulosic waste has drawn considerable interest in present years and much research has been centered on its trade though major method enhancements plus reductions in production costs is necessary (Satari et al. 2019).

8.2.4 Biogas

In addition to aqueous biofuels, feedstock with higher organic contents is able to convert into biogas by anaerobic metabolism. In this method, the organic stuff decomposes naturally by the variety of microorganisms in the O_2-deprived state and produces biogas (approximately 25–50% CO_2 and 50–75% CH_4) (Kashi et al. 2017). The process of anaerobic digestion can be categorized into four stages: (1) breakdown of proteins, lipids, and carbohydrates into amino acids, long chain fatty acids and sugars, respectively; (2) conversion of these formed products and monomers to "volatile fatty acids" (VFAs) and other small products, for example, alcohol by acidogenic bacteria; (3) conversion of VFAs to acetate, CO_2, as well as H by acetogenic microbes; and (4) synthesis of methane through methanogenesis from the other phase products (Zheng et al. 2014).

8.2.5 Biohydrogen

Hydrogen has found significant coherence as a substitute to fossil fuels due to several benefits of higher energy density of about 143 kilo joules per gram, with no carbon emissions plus numerous storage forms (Aruwajoye et al. 2020a). Besides fuel compliance, hydrogen product has significant industrialized uses in synthesis of ammonia (NH_3) and methanol. Biohydrogen has currently become of great significance as a carrier of renewable source, as the use of hydrogen intended for combustion, electricity production, or in fuel cell does not produce carbon emissions. Biohydrogen can be synthesized by photo-fermentation, bio-photolysis, and dark fermentation methods (Priya et al. 2020; Cárdenas et al. 2019). During dark fermentation process, biohydrogen is formed by fermentation of whole organic matter like lignocellulosic waste as well as industrial wastewater with thermophilic and mesophilic organisms. This process uses renewable raw stuffs and is not as much of energy intensive when comparing it to the thermo-chemical pathway and has therefore received a lot of consideration as the most favorable way for biohydrogen formation. However, fermented dark biohydrogen formation is still a major challenge due to low yield, low production rate, and low substrate conversion efficiencies (Pandey et al. 2019; Sekoai and Daramola 2015).

8.3 Lignocellulosic Biomass (LB)

Lignocellulosic biomass (LB) refers to the plant biomass consists of cellulose, hemicellulose, lignin, and many other constituents like silica, ash, and pectins. The biomass is more gradually recognized as an important material, as it is a substitute to petroleum for the biofuel production. Bioethanol from renewable energy sources has been of great interest in current decades as an alternative to the existing fuel-oils (Belal 2013). The lignocellulosic materials are potentially sustainable feedstocks for biofuel production due to its accessibility, higher sugar content, and lower price (Saini et al. 2015). On an average, lignocellulosic waste biomass consists of 40–50% cellulose, 20—30% hemicellulose, and 10–25% lignin (Shahzadi et al. 2014). Cellulose is a main plant storage polysaccharide containing a linear sequence of D-glucopyranose units joined by β→(1,4)-glycosidic bonds to each other and accountable for mechanical power, whereas hemicellulose macromolecule polymers are repeated polymers of pentoses (C5), hexoses (C6), and a variety of sugar acids. Lignin is an aromatic polymer of three alcohols, namely sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol) produced by biosynthetic processes and forms a protective covering around cellulose and hemicellulose (Iqbal et al. 2013).

The lignocellulosic waste biomass can be utilized for the production of biofuels only after a pretreatment process which helps in weakening the natural recalcitrant structure to open up the accessible fermentable sugars (Bosma et al. 2013) in the shape of monomeric sugars (C5 and C6). Pretreatment methods include chemical, physical, and biological processes or a combination of all these (Fig. 8.3). Among these pretreatments, the chemical treatment of dilute sulfuric acid is very efficient in opening the recalcitrant arrangement of agricultural biomass (Brodeur et al. 2011). In this pretreatment, numerous inhibitory compounds are produced, as well as hydrolyzed sugars, which usually inhibit cell growth and fermentation. These inhibitory compounds are different salts, furfurals, acetic, ferulic, phenolic compounds, glucuronic acid, coumaric acid, and hydroxymethyl furfurals (HMF). Thus, their formation and removal becomes a vital parameter that needs to be performed for any aspect of lignocellulosic waste biomass in production of biofuels. In present years, extensive studies have been done on biobutanol production (Zhen et al. 2020). Biobutanol is a better-quality fuel than bioethanol due to its higher energy content, improved air-to-fuel proportion, more explosive, less volatility, higher ash point, and lower vapor pressure. Commercial butanol is usually chemically synthesized from fuel-oil. However, with the reduction in fossil fuel and environmental barriers emerging, production of biobutanol through fermentation has become more beneficial.

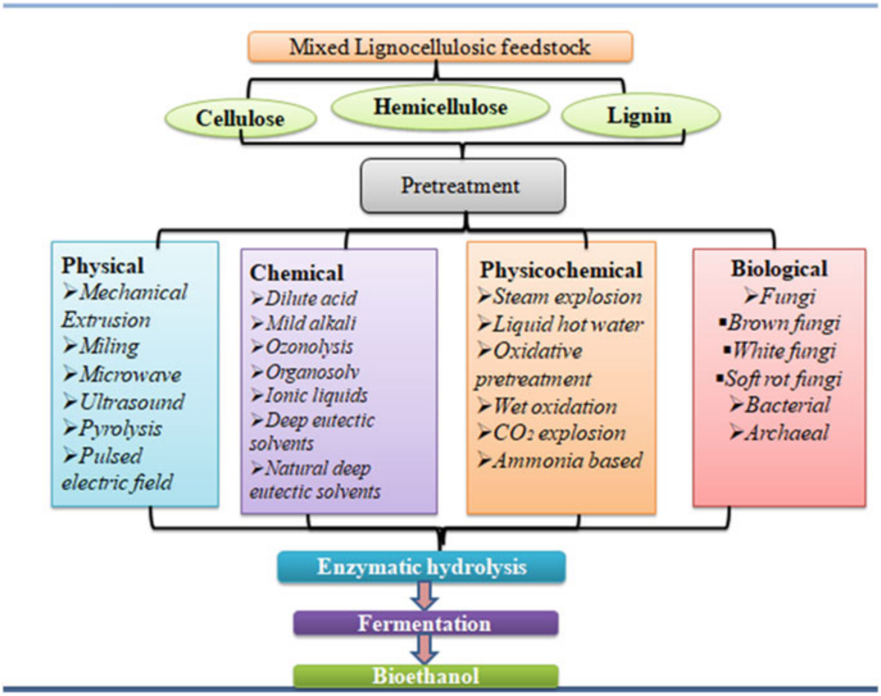

Fig. 8.3 List of pretreatment technologies for lignocellulosic feedstock conversion

8.3.1 Lignocellulosic Biomass (LCB) Sources

Lignocellulosic biomass is divided into different categories according to its source as follows: shrubs; wood, for example, hardwoods as well as softwoods; non-food agricultural crops like rapeseed, kenaf; agricultural residues, viz. maize cobs, paddy straw, its hulls and husk, wheat straw, maize cobs, sugarcane tops and bagasse, as well as municipal solid wastages (MSW) related to gardening, tapering, road repairs, etc. The waste biomass involved in the generation of bioethanol chiefly involves agricultural wastes (Niju et al. 2020). The majority of organic products is formed while processing the by-products during the harvest of agricultural crops and in addition is classified as primary along with secondary residues. The primary ones are the remaining elements obtained during crop harvesting in the field (e.g., wheat straw and sugarcane tops) whereas secondary remains are massed while the procedures are described (e.g., sugarcane bagasse). Although the primary ones are utilized for animal feed as well as fertilizers, their use in energy generation is very little and restricted. In the meantime, the secondary ones found in bulk on its affluent place; in addition, it can be stored as energy sources. A lot of agricultural remains are not used and burned openly, which has a huge effect on the atmosphere with significant energy loss. Agricultural wastes, viz. wheat straw, paddy straw and husk, maize cobs, sugarcane bagasse, dry sugarcane tops and leaves, etc. is widely available in the grassland and is believed as a key source of bioethanol production.

8.3.1.1 Paddy Straw: The Most Abundant Lignocellulosic Feedstock

Paddy, a monocotyledon belongs to the *Oryza* genus consists of two cultivable species, namely *Oryza glaberrima* as well as *O. sativa* commenced from Africa and Asia, respectively (Khush 1997), the former is limited to only West African area while the later that has enhanced yield which is cultivated nearly in 112 countries. In most of the Asian countries, paddy is the main staple food, and it generates a large amount of paddy straw as agricultural crop residue in the fields (Singh et al. 2016). In terms of total production in the world, paddy is ranked third important agricultural crop after wheat and corn (Binod et al. 2010). India produces 100 million metric tons (MMT) paddy per year against the global manufacturing of 727 MMT (Kocher and Kalra 2013). About 1–1.5 kg of paddy straw is formed in every kilogram of grain harvested (Maiorella 1985).

Among different states of India, rice is a major crop grown in Punjab on an area of 29.75 lakh hectares with total production of 177.34 lakh tons of paddy (118.23 lakh tons of rice). The average yield in terms of paddy in Punjab is 59.61 quintal per hectare (23.84 quintal per acre) (Anonymous 2017). Punjab alone produces 17 million tons of paddy straw yearly, from which around 15 million tons is cleaned off from the grounds by burning (Anonymous 2014). Farmers remedy to the activity of open field burning of paddy straw because of the following reasons: (1) short period between harvesting of paddy and wheat plantation; (2) to kill soil-borne deleterious pests and pathogens; (3) lack of harvesting machinery; (4) high transportation costs; (5) high processing cost; (6) high labor charges for the handling of straw (Singh et al. 2016). The uncontrolled burning of paddy straw in the open field causes greenhouse gas emissions like methane (CH_4), CO_2, carbon monoxide (CO), nitrous oxide (N_2O); emissions of other gaseous contaminants like sulfur dioxide (SO_2), nitrogen oxides (NO_x), HCl and, to some level, furans and dioxins (Oanh et al. 2011). These pollutants have notable toxic properties and can be potential carcinogens (Gadde et al. 2009). Furthermore, emissions of CO_2 from open burning entail severe risk to the atmosphere as it adds to the issue of global warming to the greater level (Mandal et al. 2004). Burning of paddy straw causes loss of nutrients, reduction of soil organic material, and decrease in valuable soil biota. The brutality of harm caused by such pollutants can be experimented from the reality that paddy straw burning causes almost complete loss of nitrogen, phosphorus losses of about 25%, potassium losses of 20%, and sulfur losses of 5–60%. The amount of nutrients lost depends on the method used to burn the straw. The huge quantity of heat released through burning of straw have a direct effect on the properties of soil by reducing the humidity level as well as microflora. Therefore, the adverse impact of burning the straw calls for its management and utilization.

There are several options which are being practiced and/or being tried for management of straw such as fuel for power generation in brick kilns, biofuel production, surface retention and mulching, incorporation in soil for improvement of soil health, use as feedstock, mushroom cultivation, bailing, and removing the straw (Mandal et al. 2004). In 2016–2017, to attain the above-mentioned aims, the state government had set the target of utilization of 5.73 million tons of rice straw (Anonymous 2014).

Rice straw can be converted into various forms of biofuels. Thus, there is a requirement to “deoxygenate” the lignocellulosic waste and the most important methods for conversion of paddy straw to synthetic fuels are: (1) hydrogenation to produce pure hydrogen, (2) pyrolysis to produce bio-crude, (3) anaerobic digestion for biogas production, (4) gasification for syngas, and CO production, (5) biochemical conversion to bioethanol (Demirbas et al. 2011). Among these, the ethanol production from paddy straw is an attractive option because the straw has higher contents of cellulose and hemicelluloses which can be easily hydrolyzed to fermentable sugars (Binod et al. 2010). Thus, the paddy straw can be mixed in different proportions with other lignocellulosic feedstocks for enhanced and efficient bioethanol production.

8.3.1.2 Rice Husk

In 2005, the rice consumption in Indonesia arrived 54 million tons. Of such amount, rice husks of about 10.8 million tons can be separated (Rahardjo et al. 2021). According to other theory, the process of grinding rice typically yields about 50–63% of the milled rice; 20–30% of the husk; and 8–12% of the bran. The husk generally consists of cellulose, hemicellulose, lignin, and ash with value of 42.20%, 18.47%, 19.40%, and 15%, respectively.

8.3.1.3 Coconut Husks

Coconut is tropical plant mainly found in almost all countries, especially in Indonesia where its production reaches around 28 lakh tons per annum. This highest production is associated with the higher waste biomass production in the type of coconut husks. The coir is the outmost part and when the fruit of coconut is removed from its coir, this will obtain 35% of the coconut weight (Khatiwada et al. 2016). It is thus expected that the coir production is around 10 lakh tons in 2016. Coir of coconut is a waste lignocellulosic feedstock consisting of crude fiber. The cellulose as well as lignin content in husks is extremely high, with value of 26.72% cellulose and 41.19% lignin, while the hemicellulose content is only about 17.73% (Sangian et al. 2015).

8.3.1.4 Sugarcane Bagasse (SCB)

Saccharum officinarum (sugarcane) is the agricultural crop commonly originated in Indonesia, principally on the Java Island. It belongs to the tall evergreen true grasses of family Andropogoneae. Out of the top ten manufactures of sugarcane worldwide, its production in Indonesia was 29 million tons in 2012 (Rahardjo et al. 2021). It is raw product for sugar derived through the extraction of sugarcane plants. It consists of three key components, i.e., extract of sugar, bagasse, and molasses. Molasses is an integrated sugar produce that can be utilized in the production of ethanol. Five percent sugar and 90% of bagasse content is found in sugarcane. Sugarcane bagasse consists of cellulose, hemicellulose, and lignin with content of 52%, 20%, and 24%, respectively (Wahono et al. 2014).

8.3.1.5 Sugarcane Tops (SCT)

Sugarcane plant is a renewable energy source and is widely grown in countries like Australia, Brazil, Thailand, India, and China. Sucrose is the most important produce of sugarcane that accumulates in the stalk's internodes and thus able to be extracted as well as refined in particular sugar industries, followed by its utilization in the food industry or fermentation for ethanol production. An entirely full-grown plant of sugarcane has about 75% stalks plus 25% of the tops and leaves (Sherpa et al. 2019). Sugarcane tops (SCT) include leaves that consist of sugar in cellulose form and thus are cellulosic-rich substances. Thus, ethanol could be extracted from the tops through its higher cellulosic potential and massive scale feedstock accessibility. The production of bioethanol from the leaves and tops of sugarcane will not have any effect on food supply and also not adversely affect the juice extorted from the stalks. The tops of sugarcane are found in abundance during collection but are burned in the ground itself (Sukumaran et al. 2010) and are generally utilized as an animal fodder prior to the leaves begin to rot. "Polyaromatic hydrocarbons" are released in the process of burning, while other matter released into the atmosphere can be mutagenic or carcinogenic. In 2010, the production of sugarcane is around 1700 million tons per year globally as documented by the "Food and Agricultural Organization" (FAO). This produces a large number of post-harvest residues, especially SCT, which is a cheap and easily accessible resource for lignocellulosic feedstock. Typically, 0.30 million tons of the sugarcane tops was produced during harvesting of one million tons of sugarcane (Sindhu et al. 2011). Attempts can thus be made to use the tops as an easily available substrate for enhanced ethanol production. The cellulose, hemicellulose, and lignin content in the sugarcane tops is 29.85%, 18.85%, and 25.80%, respectively (Sindhu et al. 2013) while in the sugarcane leaves the content is 36%, 21%, and 16%, respectively (Moodley and Kana 2018). In addition, the capacity of dry SCL is equivalent to ten tons of coal per hectare. The tops are rich in cellulose which contains higher glucan and xylan contents and is found as a prominent raw material that can be utilized for bioethanol production.

8.3.1.6 Maize Stover

Maize (*Zea Mays*) is an important food crop worldwide. In Indonesia, the area under harvest was 3.5 million ha with the average manufacturing of 3.47 tons per hectare, whereas the national corn production was about 11.7 million tons in 2006. The stems as well as dry leaves are the wastes from these agricultural crops have the production of 3.46 tons per hectare. The total agricultural wastage varies from 12.10 million tons. The chemical composition of maize stover is as follows: 37.10% cellulose, 22% hemicellulose, 2.5% arabinan, 1.6% galactan, 20.70% lignin, 7.8% protein, and others (Rahardjo et al. 2021).

8.3.1.7 Palm Oil Empty Fruit Bunch

Elaeis guineensis is the central raw substance for the production of palm oil. The world's second leading producer of palm oil is Indonesia where number of its fields reaches around 67 lakh ha that reach across 22 zones. The world can generate around 310 lakh tons of palm oil per annum. Around 26% weight of the whole palm oil production is from its empty bunches which is a waste product and are abundantly present. Only 10% of bunches are utilized as petroleum for compost and boilers; accordingly, there is still much of the lignocellulosic waste left which is capable of being converted into useful products. The chemical composition of the empty bunches is 33.25% cellulose, 23.24% hemicellulose, 25.83% lignin, 56.49% holocellulose, 4.19% extractive matter, and 8.56% water (Rahardjo et al. 2021).

8.4 Mixed Lignocellulosic Feedstock (MLF) Theory

The theory of mixed lignocellulosic feedstock (MLF) usually entails the simultaneous handling as well as conversion of mixture of two or more than two different substrates in equal or varying ratios for the formation of an interested product instead of utilizing single lignocellulosic feedstock (Fig. 8.4). The substrates can have the identical or different origins (resource as well as supply chain), might comprise similar or contradictory features, and may have need of same or different handing methods in their conversion.

The concept of combining two or more different substrates in the mixed lignocellulosic feedstocks approach can ultimately enhance the production of biofuels (Oke et al. 2016). The preference of substrates should be primarily based on the necessity to avoid additional nutrient uptake, the proximity of various feedstock to the collection hub or processing capability, and in general economic performance

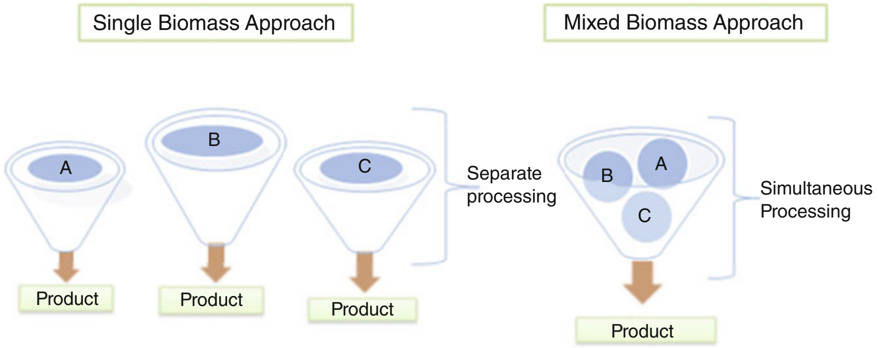

Fig. 8.4 Single biomass v/s mixed biomass approach to lignocellulosic bioprocessing

depending on the quantity associated with the lower feedstock costs (Fan et al. 2019). Table 8.1 represented the different studies using mixed lignocellulosic biomass for bioethanol production. A combination of different lignocellulosic compounds was investigated by mixing substrates listed either as under similar class (e.g., mixed hardwood) (Lim and Lee 2013), grasses mixtures (Martín et al. 2008), or different class (sugarcane bagasse and straw (Moutta et al. 2014) paddy straw and wheat bran (Qi et al. 2007)). Meanwhile, the incorporation of starch or sugar-based constituents in the bioethanol production has also been investigated, in which part of the mix includes first-generation lignocellulosic feedstock (e.g., corn kernels, wheat meal, and starch or sugary wastes (e.g., extracted residue of *Dioscorea composita* (DER), sugarcane molasses). Thus, this method helps us to lessen production costs and enhance cellulosic ethanol production.

Fan et al. (2018) studied integrated molasses in the production of sugarcane-based ethanol which ultimately improved the final production of ethanol and showed that the optimal ratio for the fermentation of molasses and sugarcane bagasse was 1: 1. The productivity ratio inconsistency makes molasses unable to meet the conditions of bagasse-based ethanol production. To prevail over this issue of feedstock inequality, DER and cassava were thought to replace half of the molasses because they both are rich in starch and are grown worldwide in tropical and subtropical climates. Nevertheless, cassava as one of the mainstays for the industrial production of starch is used as a staple crop in a number of areas such as Latin America and South Asia, thus eliminating its high demand for biofuel production as feedstock.

Singla et al. (2018) evaluated cellulase production using different agricultural biomass for hydrolysis of rice straw. In their experiment, they used different ratios of soybean pod husk and paddy straw. The main focus of their study was to make use of paddy straw due to its abundance and the health problems linked with paddy straw burning. The combination of soybean pod husk and paddy straw as substrates in equal ratio showed higher enzyme activities as compared to 3:1 ratio and paddy straw alone as substrate under solid-state fermentation at different incubation time. The addition of soybean pod husk to the rice straw, thus, stimulated *Aspergillus fumigatus* for high cellulolytic enzyme production. Soybean pod husk was observed

Table 8.1 Different studies using mixed lignocellulosic biomass feedstocks for bioethanol production

Mixture constituents	Configuration/ Fermenting microorganisms	Mixture pretreatment	Objective	Results	Source
Ricotta whey and sugarcane bagasse	Simultaneous saccharification and fermentation; *Kluyveromyces marxianus* CCT 7735	Separate and acid pretreatment given to sugarcane bagasse	Optimization of bioethanol production	Highest ethanol yield of 49.65 g/L was observed at optimum conditions	Ferreira et al. (2015)
Wheat straw and waste paper	Simultaneous saccharification and fermentation (SSF); *Saccharomyces cerevisiae* "NCYC 2826"	Joint pretreatment of steam explosion	Effect of waste paper as co-substrate on pretreatment as well as production of ethanol	Decrease in the levels of inhibitor and high yield of ethanol after 24 h	Elliston et al. (2015)
Wheat straw; wood wastes, and waste papers	Separate hydrolysis and fermentation (SHF); *Saccharomyces cerevisiae*	Combined pretreatment of acid-assisted steam explosion	Effect of pretreatment on ethanol production	Theoretical ethanol yield of 80%	Nguyen et al. (1999)
Cotton stalks and rice hull	SHF; *Escherichia coli* "KO11"	Separate acid pretreatment	Effect of single versus different substrate mixtures on bioethanol production	7:3 ratio of rice hulls and cotton stalks gave highest ethanol yield with value of 0.44 g ethanol/g sugar)	Imamoglu and Sukan (2014)
Wheat straw and municipal household waste	SSF; *Saccharomyces cerevisiae*	Combined pretreatment of wet oxidation	Effect of pretreatment as well as enzyme loads on bioethanol production	60–65% yield of bioethanol obtained at optimized conditions and with reasonable enzyme loadings	Lissens et al. (2004)
Sugarcane residues (hops, straw, and bagasse)	SHF; *Saccharomyces cerevisiae* "CAT-1"	Joint acid pretreatment	Bioethanol production on single versus combined biomass	25% high ethanol yield on mixed residues as compared to sugarcane bagasse only	Pereira et al. (2015)

to possess high crude protein content and therefore, the supplementation of soybean pod husk with paddy straw resulted in high enzyme titer with balanced proportion of different enzyme activities. The carbon-to-nitrogen (C:N) ratio of paddy straw is very high, i.e., about 80:1 (Goyal and Sindh 2011) as compared to other agricultural waste biomass. Therefore, addition of soybean pod husk to paddy straw declined the C:N value of the resulting mixture, thus improving the conditions for fungal growth and cellulase production (Delabona et al. 2013). As a result, C:N ratio is an essential factor to find out the efficiency of solid-state fermentation process for enzyme production (Krishna 2005). Soybean pod husk residue was found to provide nearly all necessary nutrients for the growth and production of enzymes by *A. fumigatus*, in this manner reducing the necessity for adding up of costly supplements to the paddy straw for enzyme production. Hence, studies showed that by using better fungal strain and plant-based agricultural biomass, industrially relevant enzyme titers and productivities could be achieved for enhanced saccharification of paddy straw for ethanol production. This can, thus, help to reduce the overall expenditure of ethanol production from paddy straw.

Sherief et al. (2010) studied different fungal species for cellulolytic enzyme production and among these *Emericella niveus*, *Aspergillus fumigatus*, and *A. terreus* showed high yield of carboxymethyl cellulase, exogluconase, and xylanase activities. The enzyme production by *A. fumigatus* was tested on mixed lignocellulosic biomass, i.e., paddy straw and wheat bran added in different ratios (9: 1, 7:3, 1:1, 3:7, and 1:9 ratios). The maximum xylanase, CMCase, and endogluconase activities of 49.30, 14.70, and 0.68 U g^{-1}, respectively, were found in mixed culture of paddy straw and wheat bran in 1:1 ratio, while higher β-glucosidase (8.5 U g^{-1}) and exogluconase (0.93 U g^{-1}) activities were detected in mixed culture of rice straw and wheat bran in the 7:3 ratio. Thus, this study showed that paddy straw mixed with wheat bran can serve as superior substrate for cellulase and xylanase production.

Similarly, Reddy et al. (2015) studied different combinations of natural lignocelluloses for enzyme production by *A. niger*. The combination of wheat bran and rice bran (1:1) served best combination for maximum production of cellulases with filter paper, CMCase, and β-glucosidase activities of 29.81, 25.20, and 32.18 U g^{-1} under solid-state fermentation, respectively.

8.4.1 Biofuel Production from Mixed Biomass

Although literature on mixed biomass use is often inadequate, a significant rise in the publications related to the production of biofuel from MLF was recorded over the past 5 years. Lignocellulosic feedstocks from a diversity of sources have been utilized in mixture with other feedstocks or first-generation residues for ethanol production. Numerous reports have shown that the production of ethanol in mixture of components is superior compared to that found in single lignocellulosic biomass. Where different lignocellulosic feedstock can be utilized in mixture for production of bioethanol, individual substrates possibly will be pretreated first and then hydrolyzed independently or in combination. In separate pretreatment or breakdown, the products of hydrolysis from the single feedstocks combined before fermentation (Imamoglu and Sukan 2014); but for combined pretreatment or hydrolysis, the emerging hydrolysates of the raw combination is utilized directly for fermentation (Lissens et al. 2004; Elliston et al. 2015). In the case of starch-based substrates, hydrolysates of starch can be diluted prior to use or can be directly used with the cellulosic hydrolysate (Brandberg et al. 2007; Erdei et al. 2013). Simultaneous saccharification and fermentation (SSF) and separate hydrolysis and fermentation (SHF) are often reported for the production of ethanol from mixed feedstocks. The implementation of saccharification and simultaneous co-fermentation (SSCF) and consolidated bioprocessing (CBP) is rarely reported. High bioethanol production in the 90–99% range is widely reported with SSF for the combinations of the first- and second-generation feedstocks (Erdei et al. 2013; Ji et al. 2015). Complete lignocellulosic mixtures usually have low yields for SSF in 70–80% range (Lissens et al. 2004; Martín et al. 2008) and SHF (Pereira et al. 2015; Imamoglu and Sukan 2014).

8.4.2 “Mixed Starch-Based Agricultural Waste” (MSBAW) for Integrated Production of Biofuel

“Starch-based agricultural waste” is a prospective component of bio-fuel production as it is cheaper, inexpensive, and less competitive. In addition, they contain a high-strength starch polymer together with usual holocellulose backbone that is common throughout the lignocellulosic biomass. Additionally, the use of such high-energy wastes of the world frees the environment from possible health risks related to their disposal as well as decay (Aruwajoye et al. 2020a). Utilizing biofuel production from these components in commercial quantities is also possible if the common concern of “waste-based biofuel production” is adequately addressed due to the MSBAW route. The drawbacks of commercial waste-based biofuels estimates are mainly based on the high cost of feedstock delivery and the technological complexity associated with low-throughput and advanced processes (Banerjee et al. 2010). Feeding the supply chain arises from the cost related to the collection plus transport of feedstocks to the biorefinery machine. Moreover, the seasonal accessibility of single feedstock from which the wastage is produced disturbs its immediate delivery to the biorefinery. On the other hand, the utilization of MSBAW in equal or varying ratios is a possible way out to the above-mentioned challenges. Even though there is inadequate literature available on bioenergy production from MLF, but they offer numerous benefits as compared to the use of single feedstock (Aruwajoye et al. 2020a). For example, the use of MSBAW in particular has the potential to produce a higher output during pre-processing. In addition, the seasonal feedstock that normally requires wide storage of the single feedstock is avoided owing to the presence of different starchy wastages from different seasons which ultimately lessens the

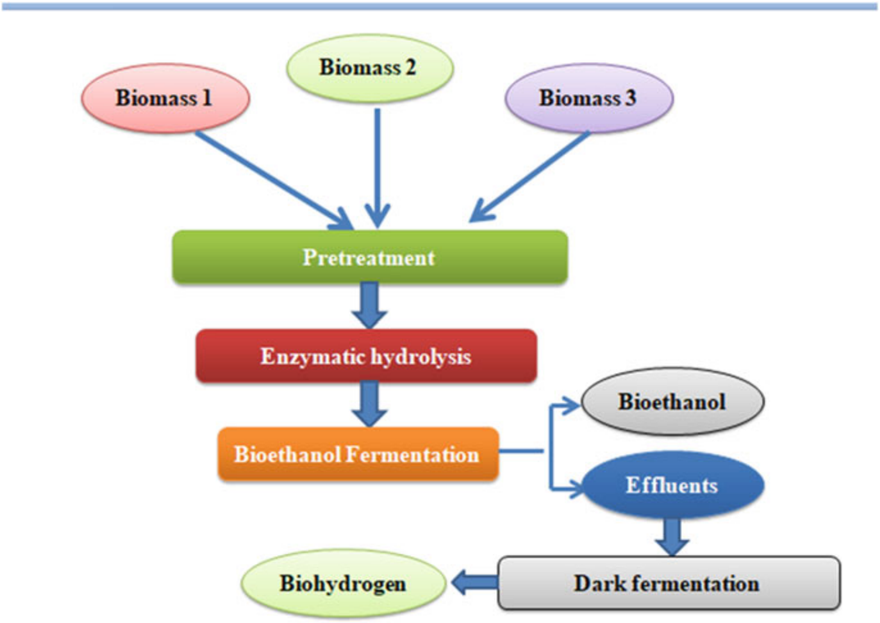

Fig. 8.5 A planned design of integrated biohydrogen and bioethanol production

time frame for the collection of biomass and the apparatus use, workers, and sources required under the strict use of single feedstock (Rentizelas et al. 2009). Furthermore, the utilization of MSBAW for the integrated production of bioethanol and biohydrogen meets the basic criteria for mixed feedstock utilization for biofuel production. These include similar features, given the high yield of sugar that can be fermented (existence of starch), hence bioethanol or biohydrogen (Aruwajoye et al. 2020a), and cheap and abundant. However, after designing an efficient production system from mixed starchy wastage, it is essential to select handling methods that will suit all components of the mixture throughout the main stages of the process. This is important as a result of the existence of different features of mixed starchy wastes such as ash, moisture, and chemical composition. The proposed process for the integrated production of bioethanol plus biohydrogen from mixed starch-based wastages is presented in Fig. 8.5. Modifications related with ethanol from mixed starchy waste biomass followed by biohydrogen should be accompanied by major phases of lignocellulosic biofuel production. The three crucial stages of ethanol generation from waste biomass are pretreatment, saccharification, and fermentation (Aruwajoye et al. 2020b).

In an experiment reported by Fan et al. (2019), the pretreated sugarcane bagasse (SCB), molasses, and DER with various proportions were studied with a low solid load of 12%, with an optimal combination proportion of 1:0.5:0.5 for the pretreated bagasse/molasses/DER was tested for ethanol yield and concentration. However, it has been observed that yield of ethanol declined from 79.19 to 62.31% as the solid loading raised from 12 to 44% in batch modes, except for the fact that three-component fermentation was done under the appropriate conditions described above. Therefore, various fermentation methods like fed-batch and fed-batch with Tween 80 have been developed to promote the improvement of ethanol concentration along with its production at high solid loads between 36 and 44%. A high ethanol concentration rate of 91.82 gram per liter (69.33% of theoretical yield) was achieved with fed-batch with Tween 80 mode during SSF at high solid loading of 44%. Additionally, after the ethanol recovery, the remains were milled for the production of bio-methane and finally produced 320.72 mL per gram of volatile solids.

8.4.3 Advantages of Mixed Approach and Its Different Studies

Many enhancements in feedstock supply chain and conversion technology could be achieved while using mixed feedstocks in a biorefinery machine. In addition, this advancement can have a positive impact on the environment. These improvements could bring about reduction in the cost in the usage of lignocellulosic feedstock as major barriers to its bioprocessing research are linked with logistics and bioconversion methods (Banerjee et al. 2010). In general, there is a need for literature concerning the benefits of cost of the MLF approach. The few that are published are focused solely on the high efficiency of MLF use and in applications other than bioethanol production. Even if the use of MLF for bioethanol production has established on a laboratory scale, still there are presently no strong studies focusing on potential price benefits. Furthermore, since upstream methods like transportation are unusual to most lignocellulosic purposes, its ethanol biorefinery might also find other benefits available in these categories.

First of all, in marking the challenge of waste biomass logistics for the production of biofuels, the selection of feedstocks will be taken into consideration as an important aspect. Non-food resources, for example, agricultural wastes can significantly drive the production of cost-effective biofuel. Several agricultural residues including forest by-products, industrial activities along with municipalities are considered to be rich and renewable biofuel sources owing to the occurrence of energy rich compounds such as polysaccharides with various carbohydrate products. Large amounts of renewable energy thus can be generated from agricultural waste because of its lignocellulosic properties (Li et al. 2014). Agricultural waste residues containing starch, for example, peels of cassava and potato, often produced in large quantities every year worldwide. They are a repository arsenal of essential polysaccharide components that can be bound to bioenergy and biofuels. Starch-based waste biomass can be assessed for ethanol production using appropriate strategies aimed at improving productivity and process efficiency. Waste-based and lignocellulosic feedstock-integrated production of biofuel has been accounted for the production of biodiesel, biohydrogen, bioethanol, and biogas. Such fuel-oils are reportedly produced by a mixture of unadulterated lignocellulosic substrates and starch-free waste biomass (Shamala et al. 2012; Kenney et al. 2013; Sangkharak and Prasertsan 2013) or a mixture of food crops and agricultural waste (Shamala and Sreekantiah 1986). Therefore, the feedstock logistics challenge to biofuel methods can be solved through the utilization of random blends of mixed waste biomass. Further strategies to deal with the present challenges for the production of biofuel are investigating the potential for multiple streams of biofuels from MSBAW in the integrated procedure. Combined production of biofuels permits the production of two or more biofuels from energy-rich waste biomass, thus enhancing the effectiveness of the production method. Agricultural residue-based biofuel processes produce pollution, which is a trouble to ecosystems and microorganisms. Such waste streams include inorganic and organic materials which can be used for further biofuel products, thus rising the productivity of the biorefinery.

8.4.3.1 Associated Reductions in Cost

When several feedstocks are integrated into the existing biorefineries based on single biomass feedstock, there will be an increase in throughput due to additional processing of feedstock. This could translate into a reduction in the cost of a biorefinery machine. This can also increase the level of the biorefinery and fetch the economy with a profitable scale. Presently, no biorefinery functions at a higher capacity than 7000 tons of dry matter per day caused by feedstock problems (Oke et al. 2016). The use of mixed feedstock will make certain nonstop availability thus allowing for the development of the biorefinery capacity. Production costs can be reduced due to the economic optimal size of the biorefinery on a large scale (Sultana and Kumar 2011). In a single biomass method, seasonal allocation requires widespread storage of a large amount of feedstock for large time to attain the year-round operation of the handling facility. As the time framework for collecting this large amount of feedstock is insufficient, so the requirement for sources like apparatus, storage, and personnel also becomes regular, and this leads to increase its cost and lessen its use. But, with multiple feedstocks systems, seasonal accessibility is avoided; hence, an increase in resource costs will also be avoided. Moreover, in the storage case, significant costs can be incurred because the required space will be reduced due to the smooth flow of biomass throughout the year (Rentizelas et al. 2009). The supply of feedstock to biorefinery machine can also be very consistent and reliable as various feedstocks can balance each other as inputs in the biorefinery machine at some point in the short supply time of either of them (Nilsson and Hansson 2001). The biomass feedstock delivery stability will lead to better efficiency which will ultimately reduce labor plus cost of apparatus. In addition, condensed storage necessities and enhanced supply of feedstock will allow for even and continuous operation of the biorefinery throughout the year, thereby increasing the utilization of biomass and processing area scale. The continued operation of machinery may also mean that less expensive alternatives could be used for mixed approach. This is due to the fact that the feedstock would not require being stored for longer periods of time which would require the usage of more exclusive storage services. The utilization of MLF can also bring savings in costs attributable to the combination of integrated lignocellulosic feedstocks.

A powerful simulation report (Nilsson and Hansson 2001), designed at reducing the costs in the feedstock utilization for regional heating purposes, it was estimated that up to 15–20% of the reduced costs could be obtained using wheat straw and reed canary grass (RCG) as a source of fuel rather than using wheat straw only. The authors also point out that the lowest cost can be obtained by combining a mixture of straw of wheat and woodchips with RCG. They say this about the proficient use of equipment, storage space, and the optimum fuel ratios. The corresponding consequence of RCG has also been a major factor in reducing costs by dropping the quantity of costly fuel which is commonly used when straw is the only fuel resource. One more advantage of the MLF method is that it can make sure the efficiency of the feedstock supply. The majority of the biomass as agricultural products are at high risk, for example, weather uncertainty, diseases, insects, floods, hurricanes, etc. The exploitation of different combinations and various biomass varieties will be able to reduce the risk allied with single feedstock by providing a buffering outcome on the delivery of feedstock during disturbances (Vera et al. 2015). The reductions in cost related to the feedstock transport could also be attained when mixed biomass feedstock are utilized in the biorefinery machine. It has been revealed that the supply cost for combinations of agricultural and woody biomass was less than the price of transporting single feedstock varieties (Rentizelas et al. 2009). Such low delivery charges can be obtained if the right types (loose biomass, pellets, barley, chips) for each type of biomass at definite concentrations are used. The investigators found that the supply of a combination of feedstock consisting 30% agricultural waste biomass bales plus 70% woodchips in a biorefinery machine was more reasonable than whole of the either type was supplied (as shown below in Table 8.2).

8.4.3.2 Environmental Advantages

The use of mixture of lignocellulosic biomass feedstocks in biofuel production has some advantages in terms of environmental sustainability. Solid municipal waste collection (MSW) is a major problem in many urban areas around the world. A number of actions taken to dispose of this waste, includes burning, often increase environmental contamination. The waste disposal option is subject to certain restrictions, with the European Union limiting the use of landfill and the amount of decomposing MSW used for this purpose (Li et al. 2007). Besides, the cost of land replenishment has been increasing in recent times (Elliston et al. 2015). Therefore, the conversion of biological components of this waste into biofuel is another effective method for the management of MSW. In Malaysia, free burning of waste is not legally permitted which requires additional control measures (Siddiqui et al. 2009). Earlier studies have shown the possibility of converting mixture of lignocellulosic feedstocks from municipal wastage resources into bioethanol (Oke

Table 8.2 Technological advantages and improvements related with utilization of mixed feedstock

Lignocellulosic biomass feedstocks	Applications	Advantages	Source
Sugarcane residues (straw, bagasse, and hops)	Production of bioethanol	55% high enzymatic conversion plus 25% high bioethanol yield achieved with combination than with only bagasse	Pereira et al. (2015)
Wheat straw and waste paper	Production of bioethanol	Decline in levels of inhibitor in the combination as compared to only one feedstock; declined lag phase in fermentation for combination	Elliston et al. (2015)
Rye grass and clover	Production of bioethanol	Higher cellulose conversion to bioethanol accomplished in the combination without any requirement for the supplementation of urea	Martín et al. (2008)
Clover grass and wheat straw mixture	Production of bioethanol	Higher bioethanol yield obtained in the mixture without extra nitrogen supplementation	Thomsen and Haugaard-Nielsen (2008)
Rice waste residues and palm oil	Production of endoglucanase	Endoglucanase production was 1–7 folds higher on mixture of substrates than on single substrate	Pal et al. (2013)
Hybrid poplar and wheat straw	Production of fermentable sugars	Mixed biomass feedstock gave higher sugar recovery after pretreatment, decreased sugar degradation, and higher yield of sugar after enzymatic hydrolysis than any of the single biomass feedstock	Vera et al. (2015)
Sesame oil cake (SOC) and wheat bran (WB)	Production of phytase	SOC-WB combination gave high yield of phytase than any of the single substrates	Roopesh et al. (2006)

et al. 2016). Additionally, there is a potential for better energy stability when mixed feedstock sources are used for bioethanol than when singles are processed individually. The efficient operation of the process and the efficient use of equipment and resources are likely to produce more energy from the method compared to when processed one by one. This prospect, however, requires testing from intensive experiments and life cycle testing because there is shortage of literature in this view. Since it is one of the objectives of a 2G biofuel to lessen the usage of fossil-derived products, the utilization of lignocellulosic biomass feedstocks can make it feasible. It has shown that mixture of certain types of feedstock reduces the necessity for the adding up of fossil derivative detoxifying substances or supplements of mineral nutrients during fermentation (Erdei et al. 2013; Tang et al. 2011). This is due to the dilution of inhibitors that occur when products of hydrolysis from different feedstocks are combined, resulting in the effect of self-detoxification. In addition, such mixed hydrolysates may have adequate levels of the natural nutrients present in each of the feedstock.

8.4.4 Disadvantages of Mixed Lignocellulosic Feedstock Approach

In addition to biogas production through anaerobic metabolism pathway (Li et al. 2014; Appels et al. 2011), the quantity of literature existing regarding the usage of combined lignocellulosic feedstock resources for bioenergy purposes is very limited when compared to single biomass feedstocks. This may be due to the restrictions and challenges allied with this advancement (Rentizelas et al. 2009). These restrictions are basically associated with logistics and technical concerns which occur from a variety of biomass resources. Since the components of mixtures can have very different features such as moisture content, cellulose, hemicelluloses, lignin, ash, bulk density, particle size, and distribution (Williams et al. 2015), selecting the appropriate method for processing which will be optimum for all the combined components may be complex to formulate as different feedstock has different optimum conditions for pretreatment, saccharification, and fermentation. In addition, mixed lignocellulosic waste residues have a higher level of pollution as compared to single biomass (Faaij et al. 1997). Identifying the best pretreatment and saccharification conditions that will release optimal amounts of fermentable sugar and produce low inhibitors from a mixture of feedstock may need many initial studies that are very time consuming; and in fact, compromise should be made. It is possible to decrease the efficiency and profitability of the method. A list of profitable enzymes that must be well combined with the various and distinct polysaccharide compounds of the combinations must be given to ensure good yield of sugar for them. This may add to higher costs of production. Alternatively, mixed sources of carbon from combined substrates can lead to catabolite repression problems for fermenting organisms particularly when carbon resources are available at higher concentrations. Some of the organisms be likely to use carbon resources merely when the waste biomass are present in limited quantities, but when they are found in high quantities, they use substrates in sequence (Harder et al. 1982), in the literal sense, which can lead to reduced production. This is a daunting challenge to the benefit of the whole process as higher concentration of sugar is required in order to obtain a good yield of ethanol. Similarly, as combined feedstocks may have a different lignin structure, the activity of a fermenting microorganism can be decreased with the lignin of one of the feedstocks despite of whether it works well in another component (parts) of the mixture. The same is true of enzymatic saccharification. Lignin is known to act as barrier for cellulases and microorganisms (Gao et al. 2014; Rahikainen et al. 2013). This crisis can make the procedure less economical as yield and production will be affected. Asset management can be difficult when many feedstock resources are used in the ethanol production process. This is particularly true when feedstocks are acquired in improper forms and in lower bulk density (Sultana and Kumar 2011). Different types of biomass have need of different types of tools for collection, management, loading, and shipping. Where multiple biomass feedstocks are affected, asset management can be a major challenge and the expenditure of this can undermine the possible savings related to the system (Rentizelas et al. 2009). For seasonal waste biomass species, collecting biomass at a different time than its actual harvest day, with the aim of creating different constituents of the mixed biomass feedstock obtainable at the biorefinery at the same time for simultaneously handling can affect the biomass quality for production of ethanol. This is for the reason that harvest time persuades the chemical properties and ethanol possible production of certain biomass varieties (Godin et al. 2013). Adapting to obtainable cellulosic ethanol plants for processing of mixed feedstock can also be hard to attain. This is just because the ethanol plants are often cited near the source of an existing feedstock where its location may be farther away than any other feedstock to be mixed with. This is expected to lead to an increase in shipping costs. Alternatively, existing equipment might be designed to fit only a particular type of feedstock processing and utilizing for any other type of feedstock or combinations of feedstocks can yield unsatisfactory results. Other systemic features such as planning, availability variations, storage, and backup of biomass from time to time are problems that need to be investigated in more detail (Faaij et al. 1997).

8.4.5 Overcoming the Barricades of Mixed Biomass Approach to Biofuel Production

Since literature addressing the approach of mixed biomass is generally limited, studies of effective testing strategies for overcoming the impact of cost of MLF logistics are yet very uncommon. However, laboratory research on the production of ethanol from MLF shows that the expected challenges of MLF usage can be prevail over if strategic measures are taken. While any current approach may seem exploratory, the fact that a number of the actions discussed here have successfully been implemented in the other MLF systems which makes the application of mixed feedstocks for promising ethanol production.

The central behavior for the handling of lignocellulosic biorefineries to manage and process large amounts of biomass in one area is a main challenge in the production of ethanol. In the scenario of mixed feedstock, this difficulty is exacerbated by the variety of feedstocks, supply disruptions, and the cost of the materials involved in each feedstock type. The organization of “regional biomass processing depots” (RBPDs), which procure, pre-process or pretreat, consolidate plus transport feedstock to the biorefinery industry and return products like animal feed to the end users (Eranki and Dale 2011) have been proposed as a way to address the system’s barriers central processing. RBPDs can process several lignocellulosic feedstock streams from each site to have similar features before they are finally transferred to the main biorefinery for pretreatment, saccharification followed by fermentation. The relative life cycle analyzes have revealed that this decentralized scheme can produce the similar energy as the centralized scheme with lower emissions of greenhouse gases.

The expenditure and effectiveness of MLF processing can be enhanced by using suitable technologies which can withstand the different features of feedstock combinations (Morales-Vera et al. 2016). Such technologies are already available for mixed biomass gasification (Faaij et al. 1997). It is likely that these types of technologies were introduced for the production of bioethanol. At present, different pretreatment technologies are appropriate for only certain feedstock types (Alvira et al. 2010). It would be remarkable to have pretreatment methods that can produce optimum sugar yield with a variety of feedstocks for consequent fermentation.

8.5 Conclusion and Future Prospects

The expectation and success of replacement of fossil fuels with lignocellulosic waste biomass for biofuel production is challenged by the high cost of feedstock provide logistics and the complexity of the conversion technology. The utilization of various feedstocks in the biorefinery has potential to significantly reduce costs and thus gain more attention recently. It is thus possible that the use of mixed lignocellulosic feedstock approach may result in significant reductions in operating costs, but further studies are needed to set up this. This approach can also have positive ecological impacts to be demonstrated through life cycle assessments and energy balance explorations. Challenges related to processing technology and the unique features of the mixed lignocellulosic feedstocks (MLF) supply logistics may limit the implementation of this method. However, the adoption of strategies aimed at the supply of feedstock such as delivery of feedstock in suitable forms and ratios, strategic planning, and redistribution of the biorefinery and mixed plantations may alleviate the expected limitations. Similarly, strategies related to technology can facilitate the utilization of MLF in bioethanol production. Such strategies include the special design of feedstock, the use of optimum mixture proportions, the development of flexible technologies that can handle various aspects of the feedstock, etc. The ethanol outlook from MLF is promising. The quick increase in the number of studies in this area is likely to be demonstrated in the upcoming years. Researchers require looking for more innovative measures to ensure the sustainability of the lignocellulosic biofuel sector.

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Chapter 9
Bioenergy: Challenges Ahead and Future

Sandeep Kaur, Loveleen Kaur Sarao, Ankita, and Harmeet Singh

Abstract Increasing population, urbanization, rapid industrialization, fast depleting fossil fuels, environmental degradation, and rising energy demands, have left us with no other means than looking for alternative energy resources. Bioenergy, i.e., energy from renewable resources like biomass, wind, and solar have been looked like promising ventures. Certain crops, resisues from the fields, residues from industries and processing units, algae are some forms of biomass energy which is being explored by the scientists. Biomass energy in the form of crops, residues from industries and fields and processing, algae are explored by scientists. Energy crops can also be a part of highly specialized and diverse agricultural production chains and biorefineries where a variety of bioproducts, in addition to bioenergy can be obtained, which is essential for their economic competitiveness. Land-intensive bioenergy needs too much land and hence cannot be a viable source of energy in future. Hence, we need to look for other options. Solar, wind energy, and bioenergy from algal biomass are the promising ventures. Solar energy and wind energy are not only available in unlimited supply but are also currently the cheapest to harvest, and same scenario is expected to continue in future as well. Algae cultivation can be done on barren lands and hence the competition with food production or occupying of cultivable land for production will be ruled out. The overall cultivation and processing of algae for bioenergy/biofuel is a challenging affair and demands a combination of breakthrough in almost all aspects of cultivation. Bioenergy offers good agricultural market opportunities and has the ability to foster sustainable development of suburban areas, but also has ecological, social, and financial concerns. If not properly developed, bioenergy may have negative effects. There must be adequate environmental and social safeguards to address certain possible negative effects. In order to make available energy which is sustainable and deliver local communities, some finances in addition to GHG emission reductions are important to assess bioenergy on the basis of its overall achievements.

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Keywords Bioenergy · Biomass · Biofuels · Sustainable energy · Aviation biofuels · Algal biofuels · GHG emissions

9.1 Introduction

Increasing population, urbanization, rapid industrialization, and fast depleting of fossil fuels have resulted in an unprecedented rise in energy demands, especially in emerging markets. Almost 80% of world's energy consumed is generated from fossil fuels (International Energy Agency (IEA) 2010). But fossil fuel resources are finite and their use also leads to greenhouse gases (GHG) emissions. And renewable energy resources can be looked upon as solution to the current situation. Being not only environmentally sustainable but also capable of substituting for non-renewable energy resources in all energy requiring markets, biofuels are considered as the most possible replacement of fossil fuels (Bauen et al. 2009). Materials which are inedible and generated from lignocellulosic biomass are gaining popularity as sustainable, cost-effective, and abundant resources for reducing reliance on gasoline and lowering the cost related to its production and feedstock (Iramak 2019). As opposed to the fuels like charcoal, crude oil, and natural gas which are generated from non-renewable resources, these resources make no addition to concentration of carbon dioxide in the environment. Carbon dioxide (CO_2) produced in biomass growth is largely offset by CO_2 released from bioenergy/biofuel production (Fig. 9.1).

Rising global energy demands, the release of emissions from fuels from non-renewable resources and the national security concerns have finally focused attention to sources which are environmental-friendly and are viable replacement too.

Alternative bioenergy not only minimizes reliance on oil trade and decreases uncertainty due to oil price volatility, but it also ensures lower emission levels because of its elevated concentration of oxygen (Huang et al. 2008; Boer et al. 2000). Thus, timber and agricultural energy, the two most available forms of bioenergy, can be the source to fulfill the basic energy requirements as sustainable alternatives.

Agriculture and forestry may be the key sources of feedstock for biofuels like wood pellets, fuelwood, charcoal, bioethanol, and biodiesel in this century, with agriculture and forestry as the main sources of feedstock for biofuels like wood pellets, fuelwood, charcoal, bioethanol, and biodiesel (Agarwal 2007). Energy crops can also be a part of highly specialized and diverse agricultural production chains and biorefineries where a variety of bioproducts, in addition to bioenergy can be obtained, which is essential for their economic competitiveness (United Nations Environment Program 2006). Concerns and questions have been raised on bioenergy as it is energy derived from food (Tilman et al. 2009; Pulighe et al. 2019) and also its effect on GHG emissions (Bosch et al. 2015), this hold true especially when bioenergy will be the main energy supplier as fossil fuels will be depleted. Another issue is the debate of fuel vs food, whether bioenergy resources compete with food

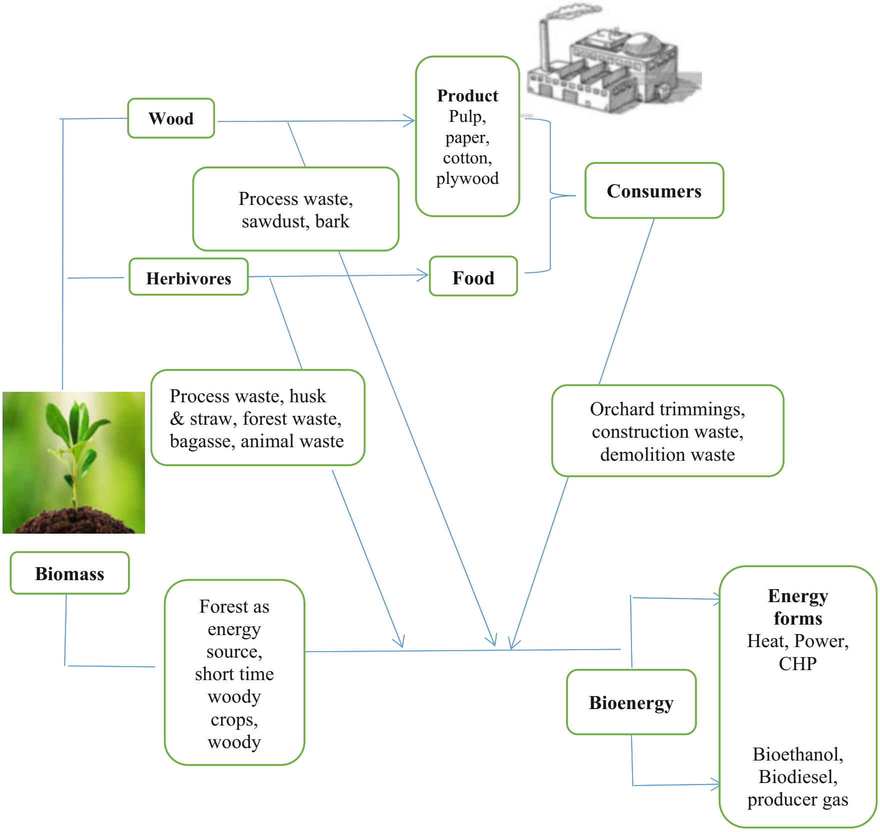

Fig. 9.1 Bioenergy Routes

resources threatening food security and sustainability (Pretty et al. 2010). Noticeable competition has been observed on transformation to bioenergy crops with respect to environmental effects and changes on use of land, water, and ecological preservation (Milner et al. 2015).

One has to find a solution to the problem within the current agricultural scenario and by solving the issues at field scale on which land to use and which to spare (Anderson-Teixeira et al. 2012), and simultaneously conserving and enhancing the ecology in the form of solutions from the nature and based on nature (Nesshöver et al. 2016), so that all challenges are converted to fortuity and answers.

Alternative energy options need to have elevated energy content, thus emitting the minimal GHG possible. Importantly, these fuels' resource extraction and production processes should have no effect on the other parameters as food generation and supply, hydro resources, land use, and climate. These sources, for example, nuclear, solar, geothermal, wind, and biomass are virtually carbon neutral, hence make up as good fuel options (Chung 2013). Also, there has been emphasis from

IEA that infrastructural gains of renewable energy, for example, financial gains, work opportunities along with lesser emissions, and encouraging technology innovation should be kept in mind by the governments while designing plans for the development and use of bioenergy (IEA 2020).

9.2 Bioenergy Current Status

Bioenergy makes up 9.5% of main energy supply and accounts for 70% share in currently used energy from renewable resources (IEA 2017a, 2019). More than 50% of this share comes from conventional use of biomass, i.e., fuel for domestic usage and small ventures such as charcoal and brick kilns. Although, conventional biomass has a lot of room for improvement in terms of sustainability, quality, and health protection (Creutzig et al. 2015), we focus on modern bioenergy and its future in coming decades as it has the prospects of substantial growth. The contribution of modern bioenergy (hereafter "bioenergy"), in 2017 was four times the combined share of solar photovoltaic (PV) and wind, thus contributing 50% to the total consumption of renewable energy (IEA 2018). The majority of bioenergy is used to heat buildings and industries, and it is projected that bioenergy will make up for 3% of electricity generation and 4% of transportation requirements in 2023 (IEA 2018). For transportation, there was an increase in liquid biofuel production before 2010, at the rate of more than 10% per year, falling to 4% annual growth from 2010 to 2016. For bioenergy electricity capacity, the annual average growth rate was 6.5% between 2010 and 2016 (IEA 2017a). Along with liquid biofuels, bioenergy is projected to make 30% increase in its contribution to energy generated from renewable resources between 2018 and 2023 (IEA 2018).

9.2.1 Biomass Potential

Biomass has different types of potentials which include theoretical, technical, environmental, economic, and sustainable, with separate scopes and are based on approaches and methodologies different from each other (BEE 2010; WBGU 2009; Scarlat and Dallemand 2019). The total amount of biomass or biophysical limit that which the current resources (land, water) can possibly generate with no addition to energy production constraints is referred to as theoretical potential. With today's technological standards, technical potential refers to a small fraction of theoretical potential (e.g., structure, framework, approachability, reaping, and processing methods) and the limitations of space (e.g., landscape, height, slant). Environmental potential is the part of theoretical potential which is eco-friendly conserving land, water, and atmosphere. The economic viability of technological potential under specified economic conditions makes up economic potential. Sustainable potential

Table 9.1 Classification of biomass resources

Resource	Category	Source
Energy crops	Traditional crops	Yearly crops, cereals, sugar, and fuel crops
	Perpetual power crops	Short-term crops, grasses, and forests
Principal/ basic waste	Woodland/plantation wastes	Logging residues: branches, twigs, tops; low quality stem wood; landscape care residue
	Farming wastes	Crops (straw and others) Waste from trimming of vineyards/orchards; cattle, manures and slurries, pigs, goats, and sheep residues, poultry leftover
Secondary waste	Timber processing	Sawmill coproducts: wood, shavings, sawdust, bark
	Farming wastes	Food industry waste, processing of farming products Slaughterhouse leftovers
Other waste	Urban wood	Construction and demolition generated; contaminated timber; consumer durables
	Organic leftovers	Paper/cardboard, cooking, garden, clothing, and packaging wastes
	Sewage sludge	Wastewater treatment plants
	Landfill gas	Generated by decomposition of organic waste in waste disposal sites

Adapted from: Scarlat N and Dallemand J-F. 2019. Future role of Bioenergy. In: The Role of Bioenergy in Emerging Bioeconomy. Ed. Lago C., Caldes, N.,Lechon Y. Academic press. pp: 435–547

Table 9.2 Some problems and solutions to biomass usage

Problem	Solution
Although present in sufficient quantity, good quality biomass is in short supply and expensive and not always feasible	Agricultural and timberland residues should be used. They are available in plenty and are sustainable
Farming and timber residues are of poor quality and micro-element (K, Ca, Mg) content is high	Different biomass should be mixed to have required composition
Biomass is available in forests only	Cheaper residues are dispersed around and universally available
Fresh biomass has low energy density and bulk volume, hence adding to storage costs and effecting movement efficiency	To enhance biomass energy density and movement efficiency, chipping should be done at first step
Degradable nature of biomass effects long distance transport and extended storage	Agropellets should be produced. They have less moisture, high energy density, lesser degradation, and transportation issues

Adapted from www.eubia.org

is the one meeting the criteria of sustainability in terms of technological, financial, and ecological constraints (Scarlat and Dallemand 2019) (Tables 9.1 and 9.2).

9.2.2 Limitations of Biomass Potential

Land availability is the primary constraint to land-intensive bioenergy, which will not be a viable power source for prolonged time because of its extensive land requirement. Being limited in amount, it is in short supply and considering the ever-rising human population along with attention towards conservation of natural resources, land will continue to be a scarce commodity in spite of an increase in agricultural yields. Creutzig et al. (2015) estimated that technological potential for bioenergy development is from 1000 EJ/year to tens of thousands of EJ/year. Perspectives and perceptions regarding availability of land, its sustainability, social and economic constraints add to uncertainty in above figures. Committed plantations on marginal and deteriorated lands have been assumed to provide a biomass potential of up to 100 EJ/year, still the amount of land which is not in use or can be usable is debated upon (Creutzig et al. 2015; Field et al. 2008). Even in the absence of bioenergy land demand will continue to rise. Crop and pastureland will still need to grow 10% by 2050, if the rate of increase in agricultural productivity remains the same as half a century in the past with no fresh area allocation to bioenergy production (Searchinger et al. 2018a, b). Ecology has been harmed because land dedicated to ecosystems, natural reserves have been transferred to farming and housing development, leading one million species on the verge of extinction (Díaz et al. 2019; Reid et al. 2005). Conservation of natural habitats and restoration of destroyed ecological reserves on deteriorated lands or lands no more in use for cultivation is required. Conservation and regeneration cannot go hand in hand with extensive growth of land-based bioenergy (Reid et al. 2020). Land conservation will prevent desert formation and degradation of land, but its impact on food security will not be a positive one and at the same time dedication of land for bioenergy generation and conservation and regrowth of forests will lead to GHG reduction and removal of CO_2 from environment (Arneth et al. 2019).

9.3 Why Bioenergy?

9.3.1 Reasons

Despite inefficiently used land and the competition from other processes requiring land, bioenergy has a prominent presence in most energy scenarios for half of the century for three reasons (Reid et al. 2020). First, bioenergy is capable of meeting baseload electric power needs unlike intermittent energy sources. This feature is expected to become increasingly significant as existing non-renewable resource-based thermal capacity moves towards retirement. Secondly, fuels with high energy density are needed for applications in shipping and aviation and biofuels are capable of meeting these criteria at a low cost. Third, Bioenergy with Carbon Capture and Storage (BECCS) can be used to generate carbon-negative energy. The integrated

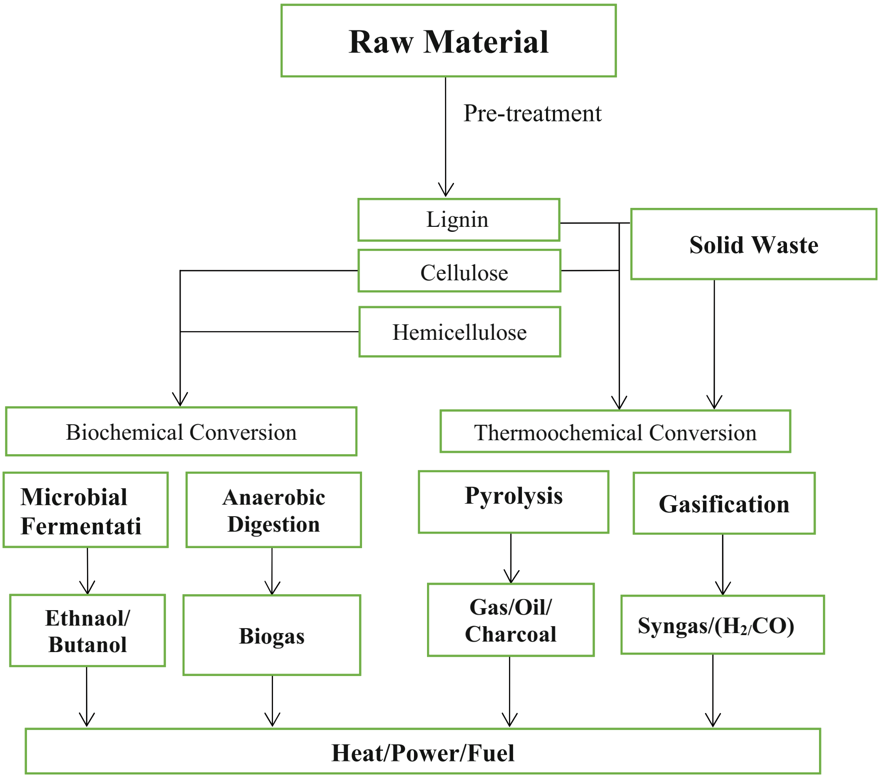

Fig. 9.2 Biomass and solid waste transformation and distribution in different energy pathways (*Source:* Chung, JN. 2013. Grans Challenges in bioenergy and biofuel research:engineering and technology development, environmental impact and sustainability. *Frontiers in Energy Res.* 1: 1–4. https://doi.org/10.3389/fenrg.2013.00004)

assessment models to find negative emission technologies (NETs) are appealing because they are able to effectively delay the much-needed transition from current technologies and also not only offset ceaseless emissions in short term but also removal of GHG in the long run (Field and Mach 2017) (Fig. 9.2).

9.3.2 Effects

The power system planning earlier consisted of economical combination of baseload electrical power (rigid but economical, for example, coal/nuclear), load-following power (adaptable to variations in demand on daily or periodic basis although expensive), and peaking power (flexible with highest cost, for example, gas turbines) (Reid et al. 2020). For baseload electrical energy, bioenergy is a rational substitute in conventional arrangement taking along nuclear, hydro and geothermal resources. In decarbonization framework, biomass is a befitting option for baseload power source, also it is considered a low-carbon, low-cost fuel. Falling of natural gas, solar, and wind energy costs has changed the overall system of power planning. Cost of solar and wind energy is lowest than any energy source in two-third of the world, it is forecasted to be the most pocket-friendly energy source everywhere by 2030 (Bloomberg New Energy Finance 2019).

According to the CEO of NextEra Energy, United States, solar and wind plus storage energy are cost-efficient than charcoal, oil, and nuclear sources and hence will have a detrimental unsettling effect on traditional resources (Roselund 2019). The need for baseload power which is seldom turned off is being replaced by the need for versatile, dispatchable power as intermittent renewables become prevalent.

9.4 Biomass Conversion Technologies: Problems and Solutions

Biomass pre-treatment and fractionation, enzymatic hydrolysis, saccharification, microbial fermentation, and product separation and purification are among the various steps involved in biomass fermentation and conversion processes (Chung 2013) (Fig.9.1). Improvement of each of these intrinsic processes requires further research and analysis. According to Virkajarvi et al. (2009), the problems are related to availability of the raw materials in sufficient quantities and at affordable prices. Processes like pre-treatment, microbial fermentation, and sugar concentration in manufacturing all need to be improved. To constitute, develop, and raise the biochemical conversion system, which includes a fermentor as well as assisting and auxiliary parts, engineering studies are needed. The primary method of conversion of biomass into synthesis gas (Syngas), in thermochemical approach is gasification. Hydrogen, carbon monoxide, carbon dioxide, methane, water vapor, and trace impurities are main components of Syngas (Chun et al. 2013). Thermochemical gasification is among the most economical and reliable processes for energy conversion being gaseous in nature. Syngas finds its use in combustion furnaces, fuel cells, gas turbines, and internal combustion engines. The process of gasification is accomplished with biomass feedstock reacting at a regulated volume of oxygen with or without steam at higher temperature (above 700 °C but without combustion). The requirement of thermal energy for gasification is fulfilled either internally (partially oxidative autothermal process) or an external heat source, for example, electricity (an allothermal process) in the case of plasma gasifiers. The ability of high temperature to act as heat source and promote the conversion of char to hydrogen through water gas change reaction has drawn attention to allothermic/external gasification (Chang et al. 2011; Umeki et al. 2012). Hence, the focus of the problems associated with advancing gasification technology should be on discovering methods which can enhance the thermic and chemical gasification process, for example, development of effective catalysts and additives. For design, optimization and step up of gasification system including the fermentor/reactor along with supporting and auxiliary components requires development of engineering research. Although a functional fuel, conversion of biosyngas to a liquid hydrocarbon fuel will yield a material that is more energy dense than crude oil-derived diesel and petrol. The most significant chemical reaction in the conversion of Syngas to liquid hydrocarbon is the Fischer-Tropsch reaction (Huber 2013). The feedstocks for biomass and petroleum are different from each other (Huber 2013) as high oxygen content of biomass, make it less thermostable and difficulty in functional control. Effective removal of oxygen from molecules generated from biomass and selectively functionalization petroleum compatible target molecules is among the main challenges faced in gas-to-liquid synthesis (Huber 2013). The overall effectiveness of the conversion process of biomass-derived molecules into fuel is dependent on heterogenous catalysis and chemical engineering. Development of clean catalytic technology and processes to understand and monitor the chemical reactions is critical in the advancement of the biomass-to-biofuel conversion. The effective temperature range for gas-to-gas synthesis is a narrow one and the process is an endothermic reaction. Quick pyrolysis, an anaerobic, rapid thermal means of decomposition of organic compounds for the production of oils, char, and gases in small concentrations at 400–500 °C is also an effective thermochemical conversion method (Chun et al. 2013). Pyrolysis derived bio-oil has the ability to make major contribution to the supply of liquid biofuels as well as source of variety of useful chemicals. But there are many issues like plant scaling, economization, improved stability of oil and efficiency producer and consumer norms and standards along with ecological health and safety concerns in operating, moving, and consumption that need to be addressed (Czernik and Bridgwater 2004).

9.5 Environmental Impact: A Reason to Shift

The transition to cleaner and renewable fuel substitutes has been fueled by the energy crisis, air pollution, and greenhouse gas emissions. Biomass has no effect on its resource extraction and processing methods do not alter food supply, water provisions, use of land or climate, besides being carbon neutral, biomass makes a good option for fuel. But better understanding of energy policy, its impact on environment, pollution, and assessment of life cycle with regard to use of biomass for energy should be prioritized for making it a valid candidate. These can be accomplished through (Chun et al. 2013):

- The thermochemical, biological conversion, and aerobic fermentor plants emissions need to be classified on the basis of their effects on change of climate, global warming, and ecosystem.
- Sampling instruments for generated aerosols should be used in conjugation with chromatography (ion), atomic absorption, and carbon analysis to analyze gaseous emissions and classify aerosols for physical and chemical characteristics.

- The emissions generated during working stage of thermal and biological energy production processes along with those generated during extraction, usage, movement, and disposal of waste should be measured by incorporating data into a broader LCA system.
- Resulting environmental effects such as global warming and depletion of ozone layer should be calculated and equated with current systems based on fossil fuels to ensure minimal negative consequences on environment.

9.6 Future

As we talked in Sect. 9.3, the traditional system consisted of mixture of cost-effective baseload electric power, load-following power and peaking power, bioenergy is the most suitable alternative to the traditional arrangement along with nuclear, hydropower, and geothermal energies. It is an attractive alternative power source as it is considered as low-carbon and low-cost fuel hence favoring current decarbonization scenario (Reid et al. 2020) (Table 9.3).

9.6.1 Alternative Fuels

Solar and wind prices are currently among the lowest leveraged energy costs of any energy source and are estimated to be cheapest by 2030 (Bloomberg New Energy Finance 2019). Decarbonized grids require flexible time frames, minutes to seasons, which can be obtained using a number of technologies and strategies for grid management like flexible electricity supply sources (gas and hydro), storage of electricity (batteries, pumped hydro, compressed air), and chemical bonds (hydrogen production, synthetic fuels) (Pierpont et al. 2017), measures in requirement sector

Table 9.3 An estimate of carbon emissions: bioenergy vs fossil fuels—electricity generation

Fuel and technology	Generation efficiency (%)	Grams of CO_2 per kWh
Generator (Diesel)	20	1320
Coal-based power plants	33	1000
Natural gas combined cycle	45	410
Biogas digester and diesel generator (with 15% diesel pilot fuel)	18	220
Biomass steam cycle (BER[a] = 12)	22	100
Biomass gasifier and gas turbine (BER[a] = 12)	35	60

Source: Kartha S. and Larson ED. 2000. Bioenergy Primer: Modernized Biomass Energy for Sustainable Development (New York: United Nations Development Program, 2000)

[a] Biomass energy ratio: Ratio of the energy content of the biomass produced to the energy of the fossil fuel consumed for the production of given biomass

(costs are used to alter the time of customer requirements), and better integration of electric grid areas (Schaber et al. 2012). Short time frame flexibility (minutes to hours), then decreasing battery prices will make battery storage as cheapest energy source by 2030 for intraday energy shifting than the new combined cycle gas turbine (Polymeneas et al. 2018). But there seem no chances of intermittent renewable engines in conjugation with storage to be the most economic means of providing flexibility over longer periods, at least over the coming decades. We need to overbuild the solar system and make it capable of storage for long term owing to its high penetration and storage to substitute for the natural gas or related constant sources of energy generation (Davis et al. 2018). For example, Ming et al. (2019) drew inference from their study of profound decarbonization for California that in 2050, the requirement of natural gas is 17–35 GW capacity, in spite of significant decrease in number of days in which it is used, it will reduce the emissions of the electricity sector by 90–95%. According to some studies, renewable hydrogen (generated from variable renewables via electrolysis) can be a possible and economic supplier of storage for long duration and a means to further decrease the energy demand of firms (Element Energy 2019) although in current scenario this methodology is not considered an economic means of hydrogen production (Davis et al. 2018). That means, in mid-century bioenergy will emerge as a competitor to other power sources for supply of firm energy with interday and seasonal load balancing, and not an alternative for baseload power production. Bioenergy will not be able to make a large part of energy mix for several reasons. Due to low natural gas cost, gas infrastructure in countries like the United States is more prevalent, and the growth rate is higher than bioenergy infrastructure. Existence of such infrastructure uses natural gas plants (at a reduced capacity), a cheapest option rather than sidelining the assets. The emissions are also relatively low because of online nature and availability for limited period of time and projections say that bioenergy without Carbon Capture and Storage (CCS) or hydrogen will be used by these plants by mid-century. Investment in new carbon capture technologies is already being increased in the United States by providing credit on tax for capturing CO_2 and storage power plants (Reid et al. 2020).

When it comes to firm power, land-intensive biofuel may not be the most attractive source of bioenergy, whereas use of biogas, instead, is likely to expand, which is a fuel with low-carbon content and is obtained from cow dung, municipality wastes and water. Biogas provided only slightly less than PVs with 17.2% of the German electricity being generated from renewable fuel in 2016 (Liebetrau et al. 2017). By 2050, the flexibility needs of future energy grids cannot be fulfilled by large baseload power plants which use combustion of wood pellets for fuels, due to difficulty of ramping up energy production. Above all, the financial incitement for modest, transmittable energy will increase substantially as medium renewables saturate the power trade. As discussed earlier in this section, different types of bioenergy will compete with a variety of options such as demand reaction, battery storage, hydro, solar power focus, power gas, hydro energy, and natural gas with CCS, but will also be combined with same demand. The said scenario will be little like the conventional farming of low-emission fuel that replaced the baseload coal power for baseload energy (Reid et al. 2020).

9.6.2 Bioenergy Future Vs Current Scenario

According to IEA (2019), even though bioenergy will make a small part of the power mixture of 2100, conventional and contemporary bioenergy represent 9.5% of main energy supplies and the quantity and the contribution of bioenergy are likely to increase. With coal-powered infrastructure being transitioned between government and power sector owners, the requirement for timber biomass is expected to rise. Between 2006 and 2015, the timber pellets production for biomass energy increased four times to 26 million tonnes (MT) (Thrän et al. 2017). Solid biomass makes up for 44.7% of all renewable energy in the EU, where wood pellet is the main import. East Asia is expanding its biomass merchandise and are expected to compete with European requirements in coming times. For example, the biomass power projects of 11.5 GW were approved by Japanese government with palm oil filling 40% of the total (Obayashi 2017; Watanabe 2017). A major factor in this expansion is that under systems of carbon pricing and for coping up to environmental targets of both national and corporate levels, the legislation of many takes the carbon content of biomass as nil. From climate point of view, this assumption encourages use of bioenergy, as only a segment of obtainable biomass in a 10-year span of time can achieve climate gains (European Academies Science Advisory Council 2019). A decade time period is considered as most applicable to environmental effects, as with the regeneration of fuel source, initial increase in CO_2 with use of bioenergy in a 10-year period will be eventually removed. There is a possibility of creation of a unique "double climate problem" because of an increase in use of forest biomass, as short time emissions are higher than majority of non-renewable fuels with long-carbon return tenures of a decade to longer than a 100 years and hence, degrading, forests' efficiency to settle carbon (Brack 2017; Buchholz et al. 2016; Cornwall 2017; Sterman et al. 2018). Biofuel generation has risen 82 MT of oil equivalent (MTOE) in world and the estimated growth is up to 142 MTOE by 2040 (BP 2019). It is estimated that an increase in demand for palm biodiesel in Indonesia could increase the demand of palm oil by 18.6 MT by 2030, as Indonesia has expanded its biofuel mandate from 5% in 2006 to 30% by 2020 (Malins 2017). Currently, mere 35% of available palm biodiesel oil refinery is in use in Indonesia, it is yet to achieve its blending targets for biodiesel, and it can be taken that they can achieve their targets without any significant additional investment (Wright and Rahmanulloh 2017). There are chances of increased forest degradation as well as destruction of some of the unchanged ecosystems in the world and also an increase in level of carbon generated from transport sector due to the conjugated requirement of biofuels from these young and up-coming markets (Malins 2018; Meijaard et al. 2018). A number of unique challenges are put forward with the hope of reduced requirement in further times with awkward proximity of near term growth in bioenergy. There are

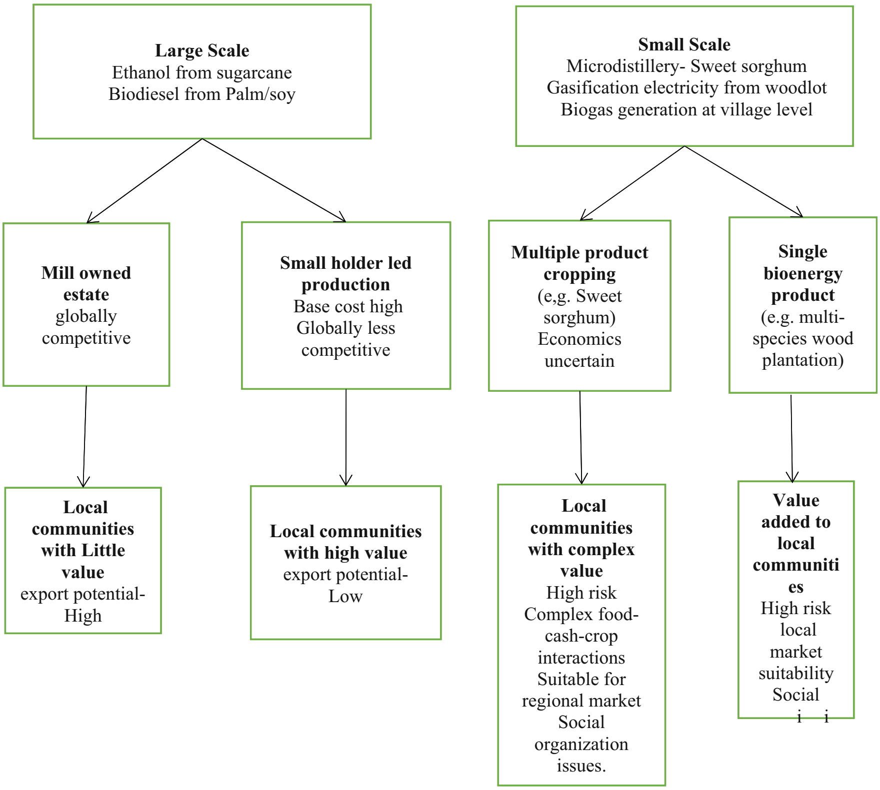

Fig. 9.3 Alternative bioenergy development options (*Source*: Woods, J. 2006. Science and Technology Options for Harnessing Bioenergy. In. Bioenergy and Agriculture: Promises and Challenges. Ed. Hazel LP. and Pachauri RK.)

three different biomass delivery categories, each of which has origin in different ecosystems with different capabilities and schedules for carbon storage, both onsite and offsite. Generation of biomass can be the result of waste produced during activities like timber generation or farming or cooking oil use. With the aim of expanding carbon storage or enhancing the living space, biomass can be removed from the ecosystem, for example, cutting of trees to decrease the wildfire possibility, afforestation, or increase the wood fiber usage in long-term products can all enhance storage of carbon while simultaneously providing a source of bioenergy. Thirdly, biomass can be produced from energy-specific ecosystems. The desirability, sustainability, and prospects for each of these categories are significantly different (Reid et al. 2020) (Fig. 9.3).

9.6.3 Dedicated Biomass for Energy

For herbal crops, forest plantations and naturally regenerating forests, sustainability, and perspectives for energy managed ecosystems are very different (Reid et al. 2020). To work in a system that will actually benefit the climate across all of these ecosystems will be difficult, especially over a decade or less. The "carbon opportunity cost" of land diverted to biomass manufacture along with the possibility of extending the age of provisions that consume both non-renewable and renewable resources is loads worse or in line with that of fossil fuels in a time period of 10 years, after adjustment to emissions linked to transport or processing, indirect usage of land, carbon debt, etc. (European Academies Science Advisory Council 2019; Searchinger et al. 2018a, b; Sterman et al. 2018; Zanchi et al. 2012). Land-intensive bioenergy can not only add pressure on food generation (Frank et al. 2017) and preservation of biological diversity (Smith and Torn 2013), it also tips the scale in opposition of the resources which are marginally climate profitable. In the three types of bioenergy ecosystems, the estimates vary widely on how sustainable land-intensive bioenergy can be produced. According to Creutzig et al. (2015), sustainable technology potential of 100 EJ/year was agreed upon by many in literature although the scope covered 1000 EJ/year. Considering the scarcity of land, the requirement of how the ecosystem protects are restores is of utmost requirement. Reid et al. (2020) considered conservative estimates to be more important. Field et al. (2008) estimated that around equivalent of 27 EJ/year could be land which is not competitive to food production (especially the abandoned agricultural land, which is neither converted to forests nor urban areas). Similar bioenergy production estimates have been developed by Canadell and Schulze (2014) from abandoned agricultural lands with high degree of environmental sustainability and concluded that bioenergy production would reach 3–8% of total primary energy by 2050 from 26 to 64 EJ/year, which is 20–40% of mean bioenergy estimates by 2050 (Rogelj et al. 2018) (Fig. 9.4).

9.7 Prevention of Locking-in of Bioenergy

In the history, complete disappearance of primary resources of raw materials were the only reason of closing down of resource-intensive industries, for example, whale hunting and Bison hunting in North America. But there has been unsustainable management of fisheries, forests, and agriculture in many places (Reid et al. 2020). Until recently, the potential to transform the planet in twenty-first century was unimaginable. As the land is fully quantitative, land-intensive bioenergy may transform lands to an essentially unacceptable scales when protections were missing. With assumptions of dissipation of bioenergy demands during this century, types of protections to trust to build a sustainable future is a valid question to ask. There are very few examples of governments or societies in history that have been able to have

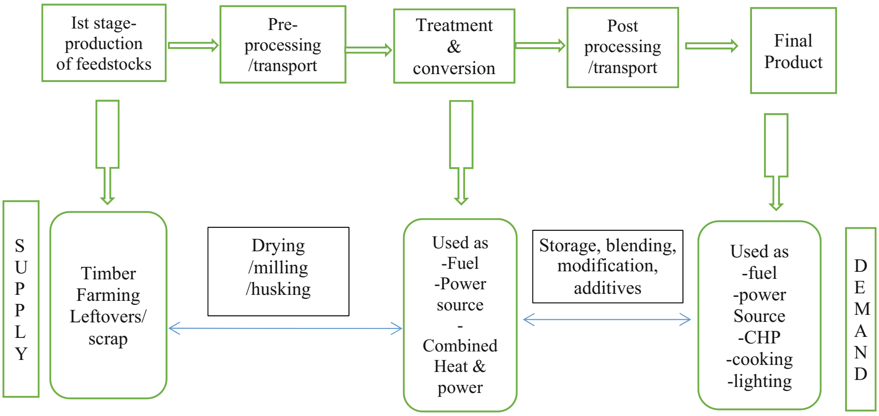

Fig. 9.4 Bioenergy- demand and supply

a successful transition which was trouble free and financially sustainable, in any system or industry on a grand level, not to mention energy system. In general, such systems develop inertial resistance (path dependency) to major systemic changes, which are driven by social and economic initial conditions, along with increased rate of returns (Seto et al. 2016). There are three contributing factors to energy system lock-in: (Seto et al. 2016):

1. An energy system would remain in order for an extended duration than optimum by the lock-ins of physical infrastructures such as power plants of longer duration, pipes, processing plants, establishments, and communication systems.
2. Infrastructure lock-in can be straightened by institutional lock-in, which means financial, political, and social factors seeking to strengthen a trajectory of status quo, favoring their own interests. Industry obtains financial and political weight as it evolves and continues to retain status quo in spite of transition being good for society.
3. Status quo can be further strengthened through lock-in behavior with societal rules and traditional values.

When it comes to bioenergy risks of physical, institutional, and behavioral lock-in are not difficult to recognize. It takes centuries to restore a natural ecosystem if it has been converted because of expansion of energy crop production. Wood pellets have been used in Europe through combined combustion (cofiring) or total switchover to biomass fuel to increase the life of power stations using coal. In Japan, South Korea and the UK-dedicated biomass power plants are under construction, which once complete will slow the transition to more cost-efficient or cost-effective energy systems. Maize ethanol industry in the United States has acquired political power sufficient to promote the growth if ethanol and gasoline mix, even though the benefits of corn ethanol to the climate are questionable, when it comes to liquid biofuels. Talking about financial inferences of lock-in of electricity sector, Kalkuhl et al. (2012) concluded that lock-in of a lower mechanics can remain for several decades, unless specific policies have been applied. To counter lock-in the grants for new techniques, feed-in tariffs and legacy technology quotas were found to be effective. Policies are needed to limit infrastructural, institutional, and behavioral interference ensuring that bioenergy meets short tenure requirements of carbon emission reductions and transformation to energy resources which use land effectively and give better cost. Still, the dependence on path is inevitable. We need effective policies that will not only help industry/large-scale manufacturing level in coming few decades but also help to maintain industry or raising it market contribution beyond that. The appropriate short-term expansion of bioenergy can be facilitated by a number of specific policies, certifications, and standards, while discouraging long-term inefficiencies. There are four broad categories of potentially effective policies: (Scarlat and Dallemand 2019). While some focus on taking proper account of gains and price of bioenergy along with the acknowledgment of the complete restriction on availability of land and possibility of restoration. Others emphasize on feedstocks' features and circumventing those which are endangering the climate in coming times and some encourage the biomass industry to avoid long-term reimbursement infrastructure commitments. And the rest are still promoting substitute technology.

Several attempts have been made to design a future picture of global energy system capable of reducing the carbon emissions required to attain the continuing objective of climate change. A Bioenergy Roadmap was prepared by IEA based on Energy Technology Perspectives modeling framework for supply of energy, structures/establishments, industry, and means of movement perspectives (IEA 2017a). This Roadmap covers three scenarios in a low-carbon energy system with various energy technologies. In each scenario, the Roadmap (IEA 2017b) recognized the part of technology profile in future sustainable global energy systems to control the rise in temperature as accomplishment of the long-term goal. The following scenarios have been analyzed: (Scarlat and Dallemand 2019).

- **Reference Technology Scenario (RTS)—**The basic framework, in line with the global climate deal reached by the 21st COP (CoP21) of the United Nations Framework Convention (UNFCCC) on climate change, which considers both—current and planned climate and energy commitments.
- **2DS—**A power system scenario that allows average global temperature to be limited to 2C by 2100.
- **B2DS scenario—**Speeding up the deployment of clean energy technology to more ambitious climate goal by 2100 by reducing the average global temperature to 1.75 °C.

Based on the assumption if Nationally Determined Contributions (NDCs) are implemented as proposed by Paris Agreement signatories, it will require a change in systems and policies (Scarlat and Dallemand 2019) and owing to this a mean temperature rise of 2.7 °C will take place by 2060. With widespread use of renewable energies, 2DS call for significant energy efficiency improvements across all sectors. Whereas based on an important bioenergy contribution and a greater CCS role to deliver further reductions in emissions, the B2DS scenario examines an ambitious decarbonization pathway. Thus, there is a requirement of a difficult and ambitious energy sector transformation, with B2DS scenario facing more technical and political challenges. There were approximately 34.3 Gt CO_2 emissions globally in 2014, including emissions from industrial processes. It is expected that CO_2 will reduce by 70% from current levels by 2060, in 2DS scenario, with almost 1170 Gt release of CO_2 between 2015 and 2100 which counts emissions from industry as well.

In 2DS, CO_2 emissions will decrease further after 2060 in the energy system to reach CO_2 neutrality by 2100. A cumulative carbon budget lower by 40% is expected by 2060 in 2Ds when compared with RTS, which requires and additional 760Gt CO_2 reduction during the period. Most technologies based on renewable energy are motivated by the need of speedy decarbonization in the 2DS and with use of biofuels in transportation, building heating and industry are being deployed in the energy sector. Between 2015 and 2100, the B2DS results in the energy industry emissions of about 750 Gt CO_2 cumulatively and the CCS energy system's carbon neutrality in 2060, backed up by negative emissions using CCS bioenergy. In order to reach net null emissions in 2060, in B2DS the deployment of bioenergy with Carbon Capture and Storage (CCS) is necessary. The negative emissions compensate for very difficult to abate or very expensive emissions in industry and transport (IEA 2017a). It is expected that during 2015–2060 period, the B2DS scenario will control the CO_2 emissions from energy sector to almost 750 Gt, requiring cumulative emission reduction by nearly 60% by 2060 as compared to RTS or about 1000 Gt $CO_{2.}$ It is expected that B2DS will practically decarbonize the power sector by 2060 (IEA 2017a). The B2DS is considered to decrease CO_2 emissions to nil by 2060, where the decarbonization pathway is much faster than 2DS. For energy sector transition, energy efficiency is crucial, accounting for 40% cumulative reductions required to move from RTS to 2DS and additional 34% emission reduction required to move from 2DS to B2DS (IEA 2017a). The expectation of growth in global primary energy is from 576 EJ in 2015 to 843 EJ in 2060 under the RTS scenario. The fossil fuels are still dominating the primary energy supplies although there will be a fall from 82% in 2014 to 67% in 2060, with the hope that biomass and waste, other renewables and nuclear will make up 12%, 14%, and 7% of the remaining share, respectively. It is expected that fossil fuel share will decline from 82% in 2014 to just 35% in 2060 in energy mix and other renewables will make up as primary source contributing 52% (348 EJ) in energy mix. The biomass and waste share will double to 144 EJ by 2060 and will represent 22% of the energy mix. It can be said that the energy industry is approaching carbon neutrality by 2100.

9.8 Biofuels in Aviation Market

Although the aviation industry contributes very little to the global anthropogenic CO_2 emissions (approx. 2.6% per year), commercial aviation growth rate is expected at 5%/year in the next few decades (Scarlat and Dallemand 2019). Thus, by the mid-century, the air traffic share to global CO_2 emissions will increase from 4.6 to 20.2%. To cope with impact of aviation on climate, measures are being taken by states, industry, and international organizations. Ten years after the first commercial flight in 2008 between London and Amsterdam, several airlines were operating commercial flights using aviation biofuels in the beginning of 2018 (Scarlat and Dallemand 2019). In order to comply with jet fuel specifications fit for aircraft that are currently in use, the international standard of ASTM d7566 has been there since 2009. According to Kostova (2017), five conservation processes with different blending levels of 10–50% were approved for March 2018 and number of others were in progress. Aviation biofuels are defined as the fuels with the ability to produce lesser GHG emissions in a life cycle than traditional petroleum-derived jet fuel (Scarlat and Dallemand 2019). Drop-in aviation biofuels are the fuels which are completely replaceable and suitable substitutes of petroleum jet fuels, i.e., it can be used in aircraft in current use, and there is no need for the adaptation of the jet aircraft/engine to the biofuel. GHG emissions in aviation can be reduced by savings during the production of renewable, biological material which will be subsequently converted to biofuels. There is no reduction in emissions in actual combustion stage of drop-in mix of biofuels with conventional petroleum. Hence, although the potential savings in aviation industry can be as high as 80%, but it is dependent of the path taken, i.e., the collaboration of variety and the transformation processes of the feedstock. The possible straight and indirect effects, counting the transformation and use of cultivable land are of crucial significance for biofuels generated from farm crops, similar to situation of road transportation. As bioenergy comes in competition with other possible uses of biomass (food, feed, fiber, biomaterials, and green chemistry) along with feasible waste disposal loads, the scope of producing alternative air fuels from waste are of particular attention. The commercial production of biofuels still remains an unsatisfactory task even though the aviation biofuels are technically operational. There are big expectations from the possibility of aviation biofuels to decrease GHG emissions from aviation industry of Europe and around the world and hence with the aim of enhancing the generation and use of biofuels, numerous initiatives have been introduced. For example, European Advanced Biofuels Flight Path aimed at attaining two million tonnes of aerospace fuel per year by 2020 and US initiative “Farm to Fly” targets to produce one billion gallons of sustainable jet fuel by the end of 2018 (Scarlat and Dallemand 2019). One should not miss that in EU and US regulatory frameworks definitions of sustainable biofuels are different. The EU directive 2009a,b/28/EC (RED) with the aim of supporting development of aviation biofuels in Europe had the target of having 10% share of bioenergy in transport by 2020. In comparison to 2010, the EU Fuel Quality Directive 98/70/EC (FQD) set a mark of decrease in GHG emission from all transport energy by 6% by 2020. Both RED and FQD have harmonized, sustainability requirements acting as exclusion criteria to meet the regulatory objective (Figs. 9.5 and 9.6).

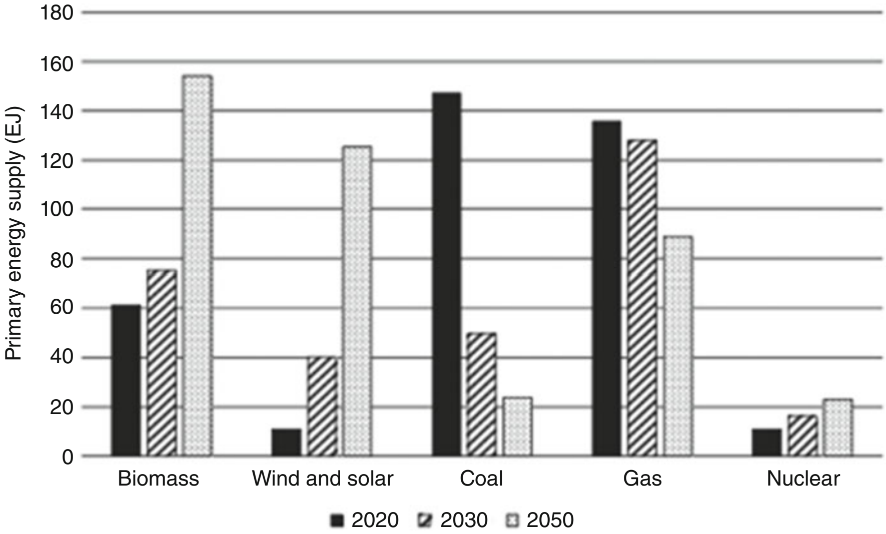

Fig. 9.5 Mean supply of global primary energy based on 85 1.5 °C pathways including all low- and high-energy pathways. The expected CO_2 emissions under these pathways are 38.5 Gt CO_2/year (2010), 29.1 Gt CO_2/year (2030) and 1.0 Gt CO_2/year (2050). (Source: Rogelj et al. 2018)

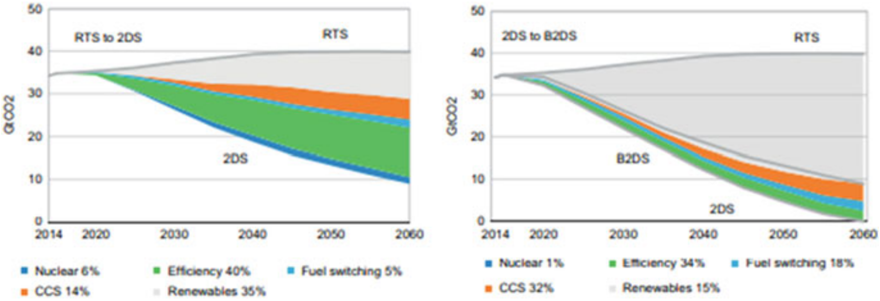

Fig. 9.6 Cumulative global CO_2 reductions in different scenarios until 2060. (*Source*: IEA 2017a. Technology Roadmap. Delivering Suitable Bioenergy. International Bioenergy Agency)

9.9 Algal Systems as Perspectives for Bioenergy

As a potential resource of biomass for multiple uses, algae have been of interest to scientists (Scarlat and Dallemand 2019). So far, around 40,000 to 100,000 algal species with varying morphological, structural, and chemical features besides different lipid, protein, and carbohydrate content have been identified. Almost one and half decade ago, algal biofuel was dubbed as third-generation biofuel, which was supposed to hold several key advantages over previous feedstock-based plant crops of first and vegetable and animal waste of second generation of biofuels (Lo 2020).

Algal biofuels are advantageous with higher biofuel yields against previous systems and the option of providing a variety of biofuels as biodiesel, butanol, and jet fuelPlus that fact that land unsuitable for food crops can be easily utilized for algal cultivation and hence removing the major concern of competition of biofuel feedstock crops with food producer crops. There are different types of algae with photoautotrophs fixing atmospheric inorganic carbon through photosynthesis and heterotrophs using organic carbon substrate as carbon source are the main types (Rocca et al. 2015). Algae are of two types—microalgae and macroalgae on the basis of their size. Algal biomass has high photosynthesis efficiency and is high yielding and also possesses the ability to grow in non-fertile soils in a variety of aquatic habitats (saline, fresh, brackish), plus the advantage of additional CO_2 capturing. Thus, using algae as an energy source is advantageous as compared to biomass crops cultivated on land. Within a biorefinery concept, algae offers extraction of variety of marketable coproducts, for example, chemicals and nutrients besides biofuel production (FAO 2009; van der Velde et al. 2017). Macroalgae, for example, green (Chlorophyta), red (Rhodophyta), and brown (Ochrophyta), depending on the species have various lipid, protein, and carbohydrate proportions and using microbiological conversion processes that can be used to produce biomethane, biobutanol, and bioethanol (Jiang et al. 2016). Asia accounts for 99% of world seaweed production of about 28 million tonnes, but that is mainly for food and food additives, pharmaceuticals, cosmetics, and the chemical industry. Algae industry is in initial growth stages in Europe and seaweed for industry use is supplied almost exclusively from harvesting (FAO 2016). Marine waters offshore are used to cultivate macroalgae, attached to specific growth structures, such as anchored networks and for onshore farming land-based farm systems have been used. Land-based farms can achieve higher productivity (up to 50 tonnes of dry matter per year) either in single cultivation farms or combined crop and aquaculture farming (FAO 2009; van der Velde et al. 2017). Algae harvesting needs various steps, including drainage and drying, in order to reduce water levels in algae from 80 to 20% and from 85 to 30%. Microalgae cultivation is mainly for food, pharmacy, cosmetics, and chemical products additives and large open ponds or lagoons are used for the process in Asia (Vigani et al. 2015; Scarlat et al. (2015)). Commercial cultures of microalgae having high-value, low-volume foods, feed and nutraceuticals are cultivated in Asia, the United States, Israel, and Australia since 1980s. These mainly include green algae (chlorophyte), blue-green algae or cyanobacteria (cyanophyta), golden brown algae (chrysophyta), and diatoms (bacillariophyta) (Rocca et al. 2015; Scarlat et al. (2015)) (Table 9.4).

9.9.1 Biology and Adaptation

Microalgae are quick growers and the oil content is high in comparison to land crops, having a maximum of 5% dry weight of soil (Chisti 2007). Microalgae gets doubled

Table 9.4 Minimum fuel selling price: Technical and economic analysis

Transformation system	Feedstock	MFSP bio-jet produced in multiple plants EUR per tonne
Hydroprocessed Easters and Fatty Acids (HEFA)	UCO	1350 (USD 1518)
Gasification through Fischer-Tropsch (FT)	Timber waste/ wheat straw	1800–2650 (USD 2204-2098)
Hydrothermal Liquefaction (HTL)	Timber waste/ wheat straw	900–1300 (USD 1460-2080)
Pyrolysis	Timber waste/ wheat straw	1300–1850 (USD 1460-2080)
Alcohol to Jet (ATJ)	Timber waste/ wheat straw	2400–3500 (USD 2700-3935)
Direct Sugars to Hydrocarbon (DSHC)	Timber waste/ wheat straw	4,80–6400 (USD 5397-7196)

Source: De Jong, S., R. Hoefnagels, A. Faaij, R. Slade, R. Mawhood, M. Junginger 2015. “The feasibility of short-term production strategies for renewable jet fuels – a comprehensive techno-economic comparison.” Biofuels, Bioproducts and Biorefining, 9: 778–800

Table 9.5 Technologies: Status and estimated capital costs as aviation biofuels

Transformation system	Standing	Financial inputs-M EUR$_{2013}$
HEFA	Commercial	200–644 (USD 265–855)
Gasification—FT	Demonstration	327–1186 (USD 434–1575)
Pyrolysis and upgrading	Pilot/demo	156–482 (USD 207–640)
ATJ (from ethanol; excluding ethanol production)	Demo	68–72 (USD 90–96)
Advanced fermentation of sugars to hydrocarbons (farnesene)	Small commercial	292 (USD 388)
Alcoholic fermentation from farming waste (including pre-treatment, enzymatic hydrolysis)	Commercial	215–426 (USD 285–566)
Sugar extraction from farming residues (includes pre-treatment and enzymatic hydrolysis)	Commercial	206 (USD 274)

Source: De Jong, S., R. Hoefnagels, A. Faaij, R. Slade, R. Mawhood, M. Junginger 2015. “The feasibility of short-term production strategies for renewable jet fuels – a comprehensive techno-economic comparison.” Biofuels, Bioproducts and Biorefining, 9: 778–800

[a] Values are based on normalized reported values from literature for 500 t of fuel/day with figures based on 2013 values

in magnitude every 24 h. This time period can decrease to three and half hours during peak growth phase (Chisti 2007). Microalgae oil content is between 20 and 50% dry weight (Table 9.5), which can reach 80% in some strains (Metting 1996; Spolaore et al. 2006).

9.9.2 Cultivation

Mostly microalgae are photoautotrophic, i.e., light and CO_2 are used as energy and carbon sources. To make minimum investment, biofuel production from algae normally uses photoautotrophic cultures. Besides photoautotrophs, algae can be heterotrophs (use organic substrates) and mixotrophs (extracting energy for growth from phototrophic and heterotrophic processes) (Mehrabadi et al. 2015; Judd et al. 2015). Mixotrophic algae are useful in low light and low nutrient environment. Heterotrophs although rich in lipids and biomass productivity, need organic carbon feed and energy, besides which they are at high risk of contagion by other organisms (Mehrabadi et al. 2015; Judd et al. 2015).

As said earlier photoautotrophic system is the preferred system of cultivation, many photoautotrophic algal systems are available (Zhiyou 2019). Suspension based open ponds and closed photo-bioreactors have been in use for the production of biofuel from algae presently. An open pond is a series of ponds in open, whereas a photo-bioreactor is an advanced reactor, adaptable to both indoor and outdoor conditions. Although inexpensive and giving the ease to operate Open Racing Ponds (ORP) have several disadvantages of low potency, below power usage of light, high water evaporation losses and excessive contagion. In comparison PBRs giving high productivity and low contamination potential are closed and controlled systems, but their dependence on complex designs and requirement of high investment and maintenance costs add to disadvantages (Scarlat and Dallemand 2019). Harvesting of microalgae also requires a series of steps like thickening (flocculation), removal, and dewatering to increase algal mass concentration from 0.1 to 1025% and drying after that. The current ORP and PBR plans are small-scale experiments and their production on large scale and commercialization are quite far away (FAO 2009; Vigani et al. 2015; Milledge and Heaven 2013; Rocca et al. 2015) (Table 9.6).

Table 9.6 Microalgae oil content

Microalga	Oil content (% dry weight)
Botryococcus braunii	25–75
Chlorella spp.	28–32
Crypthecodinium spp.	20
Cylindrotheca spp.	16–37
Nitzschia spp.	45–47
Phaeodactylum spp.	20–30
Tetraselmis suecica	15–23

Source: https://farm-energy.extension.org/algae-for-biofuel-production/

9.9.3 Future

Bioenergy, biofuel production from algal biomass faces many challenges in the form of identification of best suited species, conditions of growth, output, and chemical configurations, identifying and developing energy efficient and cost-efficient biofuel pathways to name a few (IEA 2017c). Besides this, many parameters like methods of reaping, ensiling suitability of algae spp. used, carbon balance along with cost of the seaweed and finished product price-bioenergy/biofuel need to be adequately assessed (IEA 2017c). The overall cultivation and processing of algae for bioenergy/biofuel is a challenging affair and demands a combination of breakthrough in almost all aspects of cultivation. In particular, developing collection and dewatering technology is a prime question and a crucial point in terms of energy demands and price given the microscopic dimension and characteristics of microalgae strains. Production of bioenergy from algae is not expected to be financially possible in coming future as algal biomass production costs are still the most important obstacle to trade viability in algal-focused production (IEA 2017c). The complete working demonstration of pre-treatment/hydrolysis processes (e.g., ultrasound and enzyme utilization), extraction of oil, biological, chemical (anaerobic, fermenting), and thermochemical conversion technologies (Pyrolysis, HTL) are also required (Rocca et al. 2015; Scarlat et al. (2015)).

Current requirement is the development of harvesting and conversion of large-scale growing systems, along with developing economic methods for offshore and farm/land pond farming, improving yields, and proving economic output. Proper marine farming technologies and infrastructure for macroalgae cultivation should be developed on the basis of existing macroalgae cultivation experience in food, drug, cosmetics, and chemical additives. There have been insufficient evaluations of the available algae potential for energy production. The quantity of natural harvestable algae is still not quantified although the combination of nutrients and light for the offshore algae system can measure the ecosystems' capacity to guarantee algal growth. There is a need to understand and properly address the ecological impact of harvesting natural resources (Scarlat and Dallemand 2019). It is also doubted if it is possible to harvest algae to a scale required to produce significant amounts of bioenergy.

After fading in 2005, there is a fresh interest developed in algal biofuel in recent years (Zhiyou 2019). With a target of being able to get a commercial algal biofuel production research is being done by both educational and entrepreneurs to develop new methods for improving the overall efficiency of algal biofuel production process. These efforts can be classified as: (Zhiyou 2019).

1. Methods to increase oil concentration of current strains or looking for new options having high oil content.
2. Increased algal growth rate.
3. Development of a strong growth system for algae in any of the environments—open or enclosed.
4. Development of side products along with oil.

5. Use of algae in bioremediation.
6. Development of an efficient oil extraction method.

Genetic and metabolic engineering of algal species is one way to achieve these goals, or we can look towards developing new or improved growth technologies. Besides being used for bioenergy/biofuel production, use of algae as fertilizer and in pollution control can also be explored. Many species can be used as organic fertilizer either in raw or semi-decomposed forms (Thomas 2002). Algae can help reduce CO_2 emissions from power plants, as through photosynthetic metabolism, microalgae can purify air with efficiency.

9.10 Sustainability of Bioenergy

9.10.1 Sustainability Directives

New EU sustainability criteria for bioenergy are included in the proposal for a new directive on the promotion of renewable energy sources ([(COM (2016a, b, c) 767 final)], extends their area to include all bioenergy resources and forms for cooling, heating, and electricity generation. The criteria of sustainability for farm biomass is being organized to decrease the bureaucratic constraints; as already discussed under the CAP, the criterion of cross-compliance is removed. There is a new requirement for ensuring that the timber used in power production is adequately carbonized according to LULUCF sector rules. Forest biomass sustainability criteria aims at minimizing the possibility of unendurable logging, requiring that timber biomass both domestic and imported be subject to the following minimum requirements: (1) legitimacy of harvests, (2) afforestation, (3) security of high-value regions counting wetlands and peatlands, (4) reduce the impact of harvesting on soil and biodiversity, (5) harvest is within the capacity of forests to manufacture long-term (Scarlat and Dallemand 2019). Forest biomass must meet the following LULUCF requirements with the aim of limiting the chance of negative impacts on timberland carbon stocks (Scarlat and Dallemand 2019).

1. Country/place of biomass origin (1) is a member of Paris convention (2) submitted an NDC to the UNFCCC on agricultural, forestry, and land use (LUCF) emissions and disposal accounts (3) have a national reporting system.
2. Woodland administrative frameworks are put in to ensure the retention of stock and sink of forest carbon (Table 9.7).

Table 9.7 Policy changes by countries effecting bioenergy after 2021

Nation	Change in policy	Year of impact
Brazil	2020 electricity auctions have been postponed indefinitely	2023–2025
Chile	Auctions delayed from June 2020 to December, 2020	2024–2026
China	Subsidy free project application postponed from Feb 2020 to April 2020	2022–2023
France	Few solar PV auctions delayed by half year	2021–2022
Germany	Selection of bidders in previous auctions delayed	2022–2023
Portugal	700 MW solar PV auction delayed	2022

Adapted from: IEA (2020), Renewable energy market update, IEA, Paris https://www.iea.org/reports/renewable-energy-market-update

9.10.2 Beyond 2021

All biofuel/bioliquid and biogas plants which have fuel capacity same as or more than 0.5 MW shall be subject to sustainability and GHG criteria and to solid biomass facilities with fuel capacity equivalent to or above 20 MW. The processing of waste/leftovers as soot, wood chips, dung, black liquor, etc. is helpful in saving GHGs. For plants which have been operational since October 2015, the performance of GHG in respect of biofuels was raised to 60% and to 70% for plants which started working after January 1, 2021. Biomass-based heating/cooling and electricity (plants operational since Jan 1, 2021) are subject to an 80% saving requirement, while those plant start-ups after January 1, 2026 receive 85% saving requirement. Electricity generation in big extensive plants of equal to or more than 20 MW capacity should be through the use of highly efficient co-generation technology from biomass and must meet the criteria of longevity (sustainability) and GHG. The draught RED sets out a European Union obligation for providers of fuel to make available 6.8% share of low-emission and renewable fuels in 2030 (including renewable electricity and advanced biofuels). For iLUC issues, 7% of total energy consumed in transport by road and railways is to be limited by biofuels and bioliquids obtained from the farming (both food and feed); by 2030, this will be limited to 3.8%. For advanced biofuels, a specific, increasing submandate is introduced, which by 2030 should reach 3.6% or higher. An important step forward are the new legal sustainability requirements for all bioenergy routes. On a larger scale of an economy based on biofuels, ensuring biomass sustainability is a key issue. Energy biomass can be produced in different categories of feedstock, which can be used also for foodstuffs, feed fibers, and biomaterials. Only in respect of the use of biofuels and bioenergy have sustainability requirements been established. Similar commodities do not need to comply with those requirements with other applications that have similar environmental, social, and GHG impacts. A dual-standard policy is most likely to result in indirect movement effects between the production of biomass for bioenergy generation and food, forage, fiber, or materials of biological origin since biomass providers need to ensure sustainable production of the portion of biomass required for bioenergy (Scarlat and Dallemand 2011). It has been observed from experience that voluntary certification, aimed exclusively at forest certification, will unlikely end unsustainable timber production and use and avoid LUCs and deforestation. Consequently, sustainable biomass production and non-biomass use of GHG emission requirements should be addressed in order to prevent leakage. Further points like resources efficiency for differentiation between pathways for a variety of biomass could also be included in sustainability criteria. Global sustainability concerns, either direct or indirect can be addressed through certificates provision for the production of biomass and hence capable of achieving more efficiency (with a constant land administration standards or rules applicable to timber and farming governance practices, directives for protection of nature and environment and planning and use of land). The labeling of biobased products can play a major role by making clear information about product features and environmental effects available to customers. We need a world-wide initiative with determined participation from nations to construct a world-wide governing infrastructure based on universal accord on sustainability (Scarlat and Dallemand 2011; Pelkmans et al. 2014).

9.11 Conclusion

The problems of decreasing fossil fuels reserves and energy security, the negative effects of fossil fuel consumption and change in climate have created a modern bioenergy. Besides, climate and energy targets, bioenergy generation opens notable options for a range of social, ecological, and financial benefits (IEA 2016). Bioenergy offers good agricultural market opportunities and has the ability to foster sustainable rural development. At the same time, usage of biomass for bioenergy has environmental, social, and economic concerns. If not properly developed, bioenergy may have negative effects. The real emissions of GHGs from certain bioenergy routes, food safety, LUCs and ecological diversity, and higher contention for resources are key issues (food, forage, fiber, or materials). The discussion of biofuel longevity, food against fuel, and LUC has many times ignored possible useful results as sustainable development of suburban areas. The gains and effects of biofuels or the generation of bioenergy relies heavily on this particular context. Bioenergy alliance can generate several gains, if properly worked out and administered, with farming, hydro systems, ecological systems, well-being, and security. There must be adequate environmental and social safeguards to address certain possible negative effects. In order to make sustainable energy available and contribute to residential populations' prosperity plus GHG emission reductions, it is important to assess bioenergy on the basis of its overall achievements (Osseweijer et al. 2015; Fritsche et al. 2017).

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Chapter 10
Production of Bioethanol from Mixed Lignocellulosic Biomass: Future Prospects and Challenges

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Abstract The demand for alternative fuels like biofuels, which are produced from lignocellulosic biomass, is increasing day by day due to the depletion of natural resources continuously and rapidly, which is a major cause of global warming. So, cheaper and more sustainable biofuel production, especially bioethanol, which can be used as a substitute, forest materials, energy crops, agricultural residues, and municipal solid waste are used as raw materials for bioethanol production. While biochemical conversion of raw material into bioethanol involves the process of pretreatment followed by hydrolysis and fermentation, most of the work has been done on the second generation of bioethanol, and this chapter also elaborates on lignocellulosic biomass as having a key role in producing second-generation bioethanol (second-generation bioethanol). In the future, research is being conducted to produce third-and fourth-generation bioethanol from algae and genetically engineered plants, respectively. This chapter demonstrates and highlights the key role of lignocellulosic material in producing ethanol and its importance in the future.

10.1 Introduction

Natural fossil fuels hold the world's economy. But recently, diesel and petrol-like energy sources are going to be depleted due to an increase in population, technological devices, and transportation. This could lead to an increase in fossil fuel demand and its price (Haq et al. 2016). Thus, there is a dire need for non-conventional alternate bioresources to meet the energy demand and reduce the depletion of fossil fuels and global warming (Demain et al. 2005; Hill et al. 2006; Lin and Tanaka 2006; Ragauskas et al. 2006). Therefore, fuel produced from other sources, like plant biomass, is termed "biofuel" (Chiaramonti 2007). Bioethanol, bio-methanol, bio-hydrogen, biodiesel, and biogas come under biofuels (Balat 2008). Bioethanol is the most sustainable, renewable, and easily producible fuel

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among all of these, which is considered a substitute for gasoline (Tamburini et al. 2011).

10.2 Generations of Biofuel

There are three types of raw materials that are used to produce bioethanol. These include sugar/starch, lignocellulose-based materials, and algae. Based on raw materials, bioethanol is classified. Bioethanol is referred to as “first generation” if sugar and starch are used as raw materials for fermentation. “Second-generation” bioethanol is referred to as the one that is produced from lignocellulose-based material. “Third-generation” bioethanol is produced using corn cobs as a raw material. It is an emerging one (Nigam and Singh 2011; Sahoo 2016). Biofuel has been produced by various technologies or methods like thermal processes, biochemical and chemical processes of the fourth, third, second, and first generations.

10.2.1 First-Generation Biofuels

The bioconversion of sucrose and vegetable oils into bioethanol and biodiesel and crop plants containing energy-rich molecules like sugars, oils, and cellulose is called the first-generation biofuel (McAloon et al. 2000). It has a bad impact on food and fuel yields. Besides this, there was a need to introduce non-food feedstock to overcome all types of crises; including food, cost, and energy quality for the transport sector as well (Chiong et al. 2018).

10.2.2 Second Generation Biofuels

Second-generation biofuels are being produced from lignocellulosic material and residuals, and thermal processes like hydrotreating are being used for synthetic fuel production. The product of second-generation biofuel is under development and varies with the first-generation fuel product. It requires pretreatment as well as hydrolysis steps (Maeda et al. 2013*). The study has shown that developing the efficient hydrolysis process and the efficient enzymes for this purpose is the key step for second-generation bioethanol (Scordia et al. 2010*).

10.2.3 Third-Generation Biofuels

The third generation of biofuels is the production of fuel from algal biomass (Mielenz 2001). Currently, researchers are focused on the improvement of the metabolic production (Brennan and Owende 2010) of fuels and the process of separation in bio-oil production to remove non-fuel components and minimize the costs (Sun and Cheng 2002).

10.2.4 Fourth-Generation Biofuels

The fourth generation of biofuels is based on photobiological solar fuels and electrofuels, which are expected to cause changes in biofuels. Through emerging technology, this solar biofuel could be a wonder (Scaife et al. 2015) by which solar energy is directly converted into biofuel using cheap, inexhaustible, and easily available raw materials. For such advanced technology, synthetic biology is considered to be the best (Cameron et al. 2014*). Solar biofuel production from cyanobacteria has also been possible (Scaife et al. 2015).

Sugar and starch-based raw materials-based bioethanol increases food scarcity and food prices. So, the renewable nature of lignocellulosic biomass is widely used for the production of bioethanol (Asgher et al. 2013; Asgher et al. 2011). Globally, 10–50 billion tonnes of lignocellulosic biomass are produced each year (Srivastava et al. 2015). Pretreatment, hydrolysis, fermentation, and distillation are the four steps in the production of bioethanol from lignocellulosic material (Srivastava et al. 2015; Xiao et al. 2012). The quality of bioethanol produced depends upon the type of sugar source and also the method of pretreatment.

Similarly, acid pretreatment yields more glucose as compared to xylose (Demirbaş 2005; Mood et al. 2013).

10.3 History

The production of bioethanol has exponentially increased from 200 million gallons (1982) to 2.9 billion gallons (2003). Then, in 2009, production was extended to 11 billion gallons. The US became the world's leader in biofuel production in 2010, by producing approximately 13.5 billion gallons (Renewable Fuels Association 2010). In 2014, 24.5 billion gallons of bioethanol were produced globally, and this amount increased from the 23.4 billion gallons of bioethanol produced in 2013 (Demirbas and Balat 2006).

10.3.1 Lignocellulosic Biomass

Lignocellulosic biomass available for bioethanol production is categorized into three types:

- Primary sources (crops or key products)
- Secondary sources (residues from production processes)
- Tertiary sources (municipal solid waste)

10.3.2 Energy Crops

It includes crops such as perennial grasses and other delicate crops or key products like short-rotation energy plantations and sugarcane.

10.3.3 Forest Materials

It includes forest products like hard and softwood, bark thinning residues, pruning, and sawdust. Softwood originates from pines, firs, and spruces.

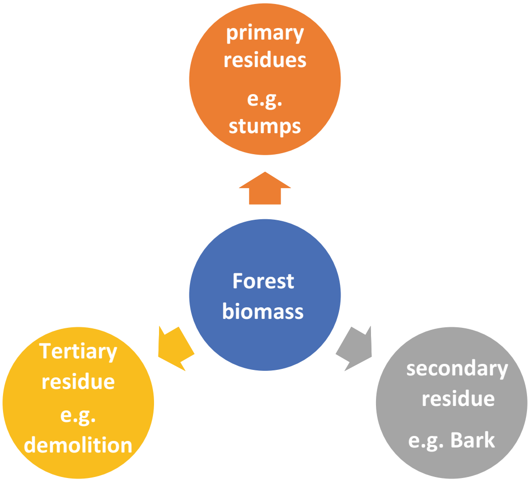
They are gymnosperms, while hardwoods originate from maples, oaks, and birches, and they are angiosperms (Bond 2002). A large amount of bioethanol is produced from forest materials. Approximately 370 million tonnes of woody biofuel are mass-produced in the USA annually (Perlack 2005). Sawdust, branches, wood chips, bark, and stumps are used for ethanol production (Amarasekara 2014).

10.3.4 Agricultural Residues

It is the most common way of producing bioethanol in many countries. It includes agricultural residues such as corn stover, rice husk, straw, wheat straws, and sugarcane bagasse [24]. Approximately 25–35% more hemicellulose content is available in agro-waste as compared to crop biomass (Demirbaş 2005).

10.3.5 Organic Portion of Municipal Solid Wastes

Bioethanol can be produced from industrial and municipal waste. It is an effective and inexpensive method of bioethanol production (Shi et al. 2009). On the other hand, household by-products and organic waste can be easily utilized before disposal in the environment (Khanna 2011).



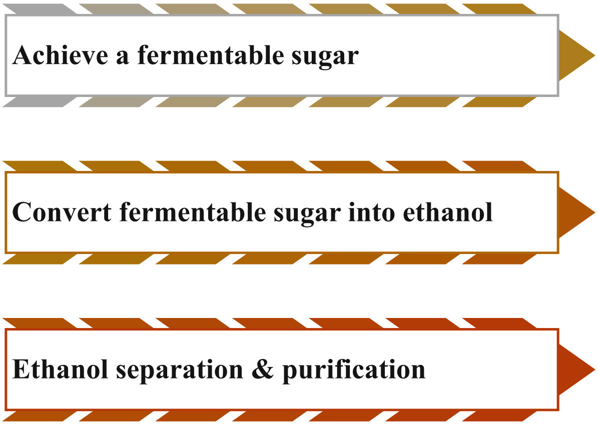
10.3.6 Marine Algae

It is used to produce third-generation bioethanol. Refinery expansion also helped to produce biofuels, mostly bioethanol. It is an effective and suitable raw material [28]. According to a study, it is estimated that approximately ten times more ethanol is produced per corn growing area (Ferrell and Sarisky-Reed 2010).

10.4 Lignocellulosic Molecular Component

Lignocellulosic biomass is composed of cellulose, hemicellulose, and lignin. In addition to these, lignocellulosic biomass consists of water, protein, and lipids (Edye and Doherty 2008).

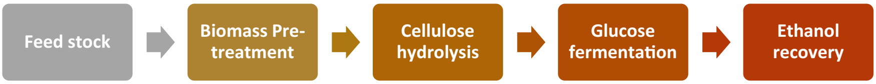
About 70% of the whole biomass is composed of cellulose and hemicellulose. They are resistant to chemical or physical treatment due to their connection with lignin through covalent bonds (Balat et al. 2008; Edye and Doherty 2008).



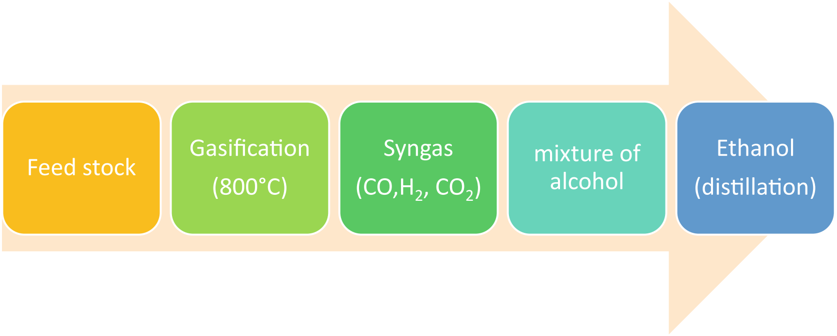
Steps involved in ethanol production from biomass

10.4.1 Routes of Bioethanol Production

Bioethanol can be produced from lignocellulosic biomass in two ways. Thermochemical conversion and biochemical conversion (Demirbas 2007).



Biochemical conversion



Thermochemical conversion

Biochemical route is most widely used today for ethanol production.

10.5 Pretreatment

Pretreatment is the first step in the conversion of lignocellulose-based materials to ethanol. This step helps to remove the hemicellulose and lignin so that the cellulose content is available for enzymatic hydrolysis. Pretreatment steps help to increase the yields of fermentable sugar. Pretreatment is furthermore categorized into different broad groups:

- Physical method
- Chemical method
- Biological method

10.5.1 Physical Method

The physical method involves pyrolysis, mechanical methods, thermolysis, milling, and irradiation. Generally, all physical methods work by decreasing the degree of polymerization of cellulose by increasing the surface area and pore volume of biomass (Szczodrak and Fiedurek 1996).

- **Extrusion Method**

  It is a physical method that involves the subsequent heating, mixing, and shearing of biomass when it passes through the extruder. To increase the availability of carbohydrates to enzyme action, barrel temperature and screw speed help to disrupt the structure of biomass and result in short fibers (Kang et al. 2013).
- **Freeze Pretreatment**

  It is a unique physical approach that helps improve the enzyme digestibility of feedstocks like rice husk. The advantage of this method is that it has less impact on the environment. But this technique is not widely used due to its cost.
- **Microwave Pretreatment**

  It is an easy to implement and effective physical method. This method helps to change the structure of the feedstock and degrade hemicellulose and lignin so that cellulose is available for further processing (Chang et al. 2011).

10.5.2 Chemical Methods

Chemical pretreatment involves various methods like acid pretreatment, alkaline pretreatment, organosolv pretreatment, and ozonolysis.

- **Acid Pretreatment**

  The conditions under which acid pretreatment is used depend upon the type of substrate (Dagnino et al. 2013). This method is used to remove lignin and solubilize hemicellulose content in lignocellulosic biomass. For this, various acids like sulfuric acid (H_2SO4), hydrochloric acid (HCl), nitric acid (HNO_3), and phosphoric acid (H_3PO_4) were used in varying concentrations. They can be used either in concentrated or in diluted form, but the diluted form is preferable.

10.5.2.1 Dilute Acid Hydrolysis

Hydrolysis by dilute acid is an old technique, and it is done at high temperatures and pressures. Temperature ranges exist from 200 to 400 °C. Sulfuric acid is mostly used for this purpose. 0.73% sulfuric acid is used for this purpose. This method has an advantage over concentrated acid hydrolysis, as it does not corrode equipment as acid hydrolysis does (Gírio et al. 2010). However, there is a disadvantage to using this method in that it produces cell wall inhibitors.

10.5.2.2 Concentrated Acid Hydrolysis

It is an effective method of hydrolysis because it produces 80% of free sugar. And it also produces a lower number of cell wall inhibitors. This method was performed at moderate temperatures (Zhang et al. 2007). But despite the major advantage of this method, there is a drawback that a large amount of acid is required to perform this method, so it is not cost-effective (Hamelinck et al. 2005).

- **Alkaline Pretreatment**

  The most widely used alkalis are sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide (Ca(OH_2), and ammonium hydroxide (NH_4OH). This method of chemical pretreatment takes place at room temperature and ranges from a few seconds to days. To improve yield for the next step, calcium and sodium hydroxide are mostly preferable.
- **Organosolv Pretreatment**

  Simultaneous delignification and pre-hydrolysis are involved in this type of chemical pretreatment. This method uses a mixture of organic solvents, for example, ethanol, methanol, ethylene glycol, and acetone. Some catalysts like H_2SO_4, HCl, and salicylic acid are also used along with these solvents (Sahoo 2016).
- **Ozonolysis**

  In this method, ozone gas is used to remove the lignin and hemicellulose to improve the digestibility of the cellulose. The advantage of this method is that it can be performed at room temperature without the formation of toxic compounds (Travaini et al. 2013). However, there is a disadvantage to acquiring a large amount of ozone.

10.5.2.3 Physico-chemical Pretreatment

Physico-chemicalpretreatment method involves various methods like steam explosion, CO_2 explosion, wet explosion, ammonium fiber explosion (AFEX), and the liquid hot water method.

- **Steam Explosion Method**

  It is a thermo-mechanical-chemical process that helps to break down the lignocellulosic biomass by steam heating and shearing force (Jacquet et al. 2010). It is a widely used physico-chemical pretreatment method for the breakdown of lignocellulosic biomass and is highly cost-effective (Yang et al. 2017; Zhang and Chen 2012).
- **Ammonia Fiber Explosion (AFEX) Pretreatment**

  In this method, concentrated high-temperature and high-pressure ammonium gas is exposed to the lignocellulosic biomass, then the pressure is reduced abruptly. The main advantage of this method is that biomass is digested to a higher extent (Liu et al. 2013), and this could lead to higher production of bioethanol. It significantly improves the hydrolysis and fermentation processes by removing the lignin, resins, and latex (Chundawat et al. 2012). The cost of this process mainly depends on the ammonium price and the consumption of energy.

  Therefore, to make this process more economical, we have to recover the ammonia.
- **CO_2 Explosion Pretreatment**

  CO_2 is used as an effective solvent to digest the lignocellulosic biomass because it provides many advantages, such as being low cost, non-flammable, non-toxic, environmentally friendly, and easy to recover. Along these lines, the biggest advantage is that the process is carried out at low temperatures.

10.5.2.4 Biological Pretreatment

This method is used to digest the lignocellulosic biomass with the help of microorganisms.Among the microorganisms, white-rot fungi, soft-rot fungi, and brown-rot fungi are commonly used for this purpose, while white-rot fungi are widely used (Sarkar et al. 2012). Lignin and hemicellulose are targeted by white-rot and soft-rot fungi, while brown-rot fungi attack cellulose. For the bioconversion of lignocellulosic biomass, this method is preferable. but it has a serious disadvantage, i.e., it provides lower hydrolysis rates as compared to the other pretreatment methods. This method requires more incubation time.

10.6 Hydrolysis

- Pretreatment of lignocellulosics is followed by hydrolysis. Cellulose and hemicellulose are broken down, for further analysis, into their monomeric soluble compounds.

10.6.1 Enzymatic Hydrolysis

The enzymes used in this step can break down the glycosidic bond between cellulose and hemicellulose. After the enzymatic reaction, biomass is converted into glucose and xylose. This reaction takes place at an optimum temperature of 45–55 °C and an optimum pH of 4–5. The advantage of this method is that it produces fewer cell wall inhibitors.

Cellulase and hemicellulase enzymes are used for enzymatic hydrolysis. **Cellulase** is composed of **endoglucanase, exoglucanase,** and **cellobiohydrolase**. While hemicellulase is a complex enzyme composed of **exo-xylanase, endo-xylanase, β-xylosidase**, **ferulic acid esterase, acetyl xylan esterase**, **α–arabinofuranosidase,** and **α–glucoronisidase**. These ligninolytic enzymes are produced by microorganisms like bacteria and fungi. Bacteria like Bacillus and Clostridium and fungi like Penicillin, Aspergillus, and Trichoderma produce these types of enzymes.

10.6.2 Fermentation of Sugar

Hydrolysis is followed by the fermentation process to produce ethanol from biomass. This process needs microorganisms that produce alcohol from sugar. For this conversion of sugar, mostly bacteria and fungi are used in the absence of oxygen (anaerobically) to convert the monosaccharide and disaccharide into ethanol and by-products like CO_2 (Sarris and Papanikolaou 2016). Bacteria like ***Zymomonas mobilis*** are used to ferment sugar. Mostly, the microorganism used for fermentation is **yeast**, which is known as ***S. cerevisiae***. This yeast ferments the sugar in the absence of oxygen at 30 °C and converts it into alcohol. This is known as **separate hydrolysis and fermentation (SHF)**. Because of this process, hydrolysis and fermentation take place in different steps separately.

But ***S. cerevisiae*** is not able to ferment all sugar. They can only ferment hexoses. Therefore, we need other methods that can ferment all types of sugar. According to the latest research, **simultaneous saccharification and fermentation (SSF)** is used for hydrolysis and fermentation takes place simultaneously.

One of the various advantages of using this method is the low cost of the process and avoiding the production of various inhibitory compounds. Fermentation can be done in one of its three modes:

- Batch fermentation
- Fed batch fermentation
- Continuous fermentation (Oliveira et al. 2016)

Which mode of fermentation is selected depends upon the type of microorganism used for fermentation and the type of substrate.

10.7 Distillation

After fermentation, the resulting product is a mixture of alcohol and water. To separate these compounds, **distillation** processes were used. Mostly, fractional distillation has been performed for the separation of ethanol from water depending upon the different volatilities. For this purpose, a column is used, known as a **distillation column**, which is heated, and then the mixture can be poured onto the top of the column. Ethanol is collected first at the lower boiling temperature of 78.3 °C. While water is separated at its boiling temperature of 100 °C, 92% of ethanol can be recovered in this process. To obtain 99% ethanol, further, dehydration is required (Cardona and Sánchez 2007). Some other techniques can be used for the recovery of ethanol. It includes gas stripping, pervaporation, gas stripping, liquid-liquid extraction, and steam extraction.

10.8 Factors Affecting the Bioethanol Production

- Temperature
- pH
- Incubation time
- Initial substrate concentration
- Microbial load
- Accumulation of by-products

10.9 Conclusion: Future Perspective

For energy, bioethanol is one of the most promising renewable sources, which can be produced from several sources. Currently, on a commercial scale, a large amount of bioethanol is produced from sugarcane and corn biomass. But the energy requirements are very high, so we need other sources to produce bioethanol. For this purpose, lignocellulosic biomass is used. There are several different lignocellulosic biomasses available to produce bioethanol. Therefore, much effort has been put into using lignocellulosic biomass to produce bioethanol. But still, some challenges are faced by scientists. The major problem is the energy consumption in the pretreatment step, and sugar degradation is the main concern, which increases the cost of the product. It is trying to improve the technologies and optimize the different factors used in the processing of bioethanol from lignocellulosic biomass. Efforts have been made to produce bioethanol that is low in cost. For these new enzymes, improved techniques and the production of new systems are required. Therefore, according to current trends, genetic engineering, biotechnology is being directed to improve processes and products. Therefore, research is being directed toward third- and fourth-generation bioethanol.

In the third generation, algae can be used as raw material, while in the fourth generation of bioethanol, there is a concept that we can use specially engineered plants to produce hydrocarbons. This could help us to preserve our natural resources and also fulfill the demand for bioenergy. The concept of fourth-generation bioethanol in the future could lead to significant changes (Niphadkar et al. 2018).

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