Biomass to Energy — an Analysis of Current Technologies, Prospects, and Challenges

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Abstract

With the ever-increasing environmental concerns and the rush to meet the United Nations' sustainable development goals, it is an uphill task to find a single source of energy that may completely replace fossil fuels. Energy derived from biomass is an attractive alternative to transportation fuel along with electricity and heat generation. The bioenergy from agricultural biomass, food crops, forest residue, algae, and municipal waste can also allow sustainable waste management. However, most bioenergy conversion facilities are still in the research or pilot stage and have many technological and economical limitations. This critical review provides an insight into different recourses of biomass, bioenergy conversion routes, and other challenges to biofuel production. An attempt has been made to elucidate the novel technological advancements made in these processes like bio-chemical looping combustion, torrefaction, and photo- and dark fermentation. The integration of these systems with artificial intelligence and machine learning-based modeling and optimization is also discussed to bring insight to alternate advancement routes. A comparison of the conversion methods is attempted to bring insight into the feasibility, sustainability, and advancement of bioenergy production and its commercialization.

Abbreviations

1G	First generation
2G	Second generation
3G	Third generation
4G	Fourth generation
AI	Artificial intelligence
ANN	Artificial neural network
ATP	Adenosine triphosphate
BIG/CC	Biomass integrated gasification with combined cycle
CLC	Chemical looping combustion
CLG	Chemical loop biomass gasification
CSIR	Council of Scientific & Industrial Research
EDP	Entner-Doudoroff pathway
EMP	Embden-Meyerhof pathway
FT	Fischer-Tropsch
GHG	Greenhouse gas
IEA	International Energy Agency
LFG	Landfill gas
LHV	Lowest heating value
MMT	Million metric ton
ML	Machine learning
PPP	Pentose-phosphate pathway
SCWG	Supercritical water gasification
SSCF	Simultaneous saccharification and co-fermentation
SSF	Simultaneous saccharification and fermentation

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Introduction

Coal, natural gas, petroleum products, and petrochemicals have been an ingrained part of human existence for over two centuries, driving the industrial revolution and all other subsequent technological innovations. However, concerns over the environment and climate changes have forced humankind to look for alternate energy resources. The Paris Energy Agreement in 2015, and the Sustainable Development Goals implemented by the United Nations General Assembly in 2015, established a framework for global cooperation in identifying and implementing a reliable, economical, and sustainable renewable energy source by 2030 [1]. With this

framework, the uphill task is to identify energy sources to meet the household, industry, and transportation energy requirements of the world at an affordable price. Table 1 provides a glimpse of the total primary energy supply in 2017 globally and by the top five major energy-supplying countries as reported by the International Energy Agency (IEA) [2, 3].

It is quite interesting to note that in the current race to identify the most economical and efficient renewable energy resources, biofuels and biomass waste are one of the front-runners, with a ~ 11% contribution, along with solar, wind, and hydropower as can be seen from Table 1. Also, interestingly, India contributes around 21% of the total energy supply from biomass and waste. It is not a surprising figure as India generates 960 million tonnes of solid waste every year and 680 million people in India rely on biomass waste for traditional cooking [3, 4]. However, currently, a negligible amount of the biomass waste produced in India contributes to electricity generation or as a transportation fuel [3]. In China, currently, 3.7% of energy from biomass and waste comes from 650 million tonnes of coal equivalent of biomass waste being produced every year which contributes to 13% of electricity generation [5]. It is quite apparent that with the new energy policies and mandates in place, renewable energy is slowly picking up the pace; however, the major chunk of the total world's energy supply (~ 81%) is still being provided by fossil fuel.

Biomass as a potential energy source has its major advantages in its global availability and ease of storage. It can also contribute toward all the commercial energy requirements like heat, electricity, and transportation fuel [6–12]. Nevertheless, traditional biomass has some major challenges which require immediate attention for it to become commercially viable. There is a lack of global standards, monitoring, and regulation for biofuel production with a certification of biomass origin and sources [8, 13, 14]. Due to multiple sources, there is always variability in biomass quality, composition, and properties, leading to variable product quality.

The biomass (both agricultural and waste) collection, segregation, and transportation are a huge problem leading to uneven supply [8, 15, 16]. Furthermore, most of the bioenergy conversion technologies being developed are still in their nascent stage. Major technological interventions toward pre-treatment of lignocellulosic biomass, improving energy efficiency, and reducing the cost of production are required [17, 18].

Biomass to bioenergy conversion is a well-reviewed topic. Numerous reviews and journal articles have been published to elucidate the technologies and their limitations; however, most of these papers are specific to a type of conversion technologies. Also, very few review articles include more novel technologies like dark and photo-fermentation, bio-CLC, and torrefaction along with the traditional methods and analyze their feasibilities and challenges. Furthermore, an attempt has been made to understand the applicability of AI/ML-based modeling, simulation, and optimization to these processes to improve process design, productivity predictions, and biomass supply chain. The paper also strives to understand the feasibility of these processes based on economy, ease of operation, and scale-up and provide possible solutions to some of the existing challenges. This review is an attempt to bring the entire biomass to bioenergy conversion technologies, their prospects, challenges, and feasibility from feed to product in one framework.

Biomass as Feedstock and Classification of Biofuels

Biomass as a feedstock is as varied as its source. Biomass derived from agriculture or plant residues is rich in cellulose, hemicellulose, and lignin with varying percentages, whereas animal residues are mostly comprised of proteins, and cereals are composed of starch [19]. The biomass source from plants contains primary metabolites and secondary metabolites. The primary metabolites are lignin

Table 1 The total primary energy supply by fuel in the world and the top five countries based on total primary energy supply in 2017 [2, 3]

	Oil	Natural gas	Coal	Nuclear	Hydropower	Biofuels and waste	Wind/solar	Total (Mtoe)[1]
World[2]	31%	22%	37%	5%	2%	11%	2%	13972
China[2]	18.7%	6.5%	64.0%	2.1%	3.2%	3.7%	2.3%	3063 (22%)
USA[2]	37.4%	32.7%	14.7%	10.2%	1.2%	5.0%	2.1%	2155 (16%)
India[3]	25.3%	5.8%	44.3%	1.1%	1.4%	21.2%	0.8%	882 (6%)
Russian Federation[2]	21.0%	53.1%	15.5%	7.3%	2.2%	10.7%	0.02%	732 (5%)
Japan[2]	38.7%	22.5%	26.6%	3.9%	1.7%	3.3%	2.1%	432 (3%)

[1]*Mtoe*, million tonne equivalent of oil

[2]World Energy Balances Overview (2019)

[3]India 2020 Energy Review Policy (2020) by International Energy Agency

and carbohydrates (cellulose, hemicellulose, starch, etc.), which form the base of biofuels and the secondary metabolites are gums, resins, rubber, terpenoids, steroids, triglycerides, etc. that can be used to produce value-added chemicals like food flavors and pharmaceuticals [8, 20–23]. The physicochemical properties of the biomass like cellulose/lignin ratio, ash content, moisture content, calorific value, fixed carbon to volatile matter ratio, alkali metal content, and bulk density play key roles in identifying the biomass feedstock to be used for a certain form of bioenergy [17, 19, 24–26]. Each of these properties provides information about the quality of the fuel produced. If ash content in biomass is high, it means that the proportionate fuel produced will be low. A high calorific value indicates high heat release from fuel burning [17, 24]. High cellulose to lignin content indicates reduced pretreatment requirement for lignin removal and ease of conversion processes [24, 27]. Low carbon to volatile matter ratio means more ease of burning and high alkali metal content leads to processing problems [17, 24]. These properties also decide which technology will be employed for the conversion of biomass to fuel. For example, for high-moisture content, biomass like sugarcane is a better fit for aqueous conversion like fermentation into bioethanol, whereas dry biomass like wood is better suited for gasification or thermal conversion into bio-methanol. Similarly, if the cellulose to lignin ratio in biomass is low, then they are less suited for biochemical processes as the biodegradability of lignin is low compared to cellulose [17, 24]. Table 2 describes the chemical compositions of distinct groups of biomass feedstocks.

To better understand the source, composition, and application of the biomass, it can be classified into distinct groups based on (a) source of the feedstock, (b) vegetation type and (c) use and application. However, Tursi in his paper accepted that "there is no definite way of categorizing the biomass so they can be classified differently depending on the purpose and scope" [19]. The details of each of the below classifications are shown in Fig. 1a, b, and c.

Woody biomass is currently the most used source of energy (~ 30 EJ) as traditional wood burning for cooking and space heating is prevalent [19, 28, 30]. This mode of energy extraction is also leading to major environmental challenges globally [3, 31]. The agricultural residues are a reliable source of energy; however, their availability is varied across regions and is not well monitored and controlled. Aquatic biomass like algae on the other hand is an ideal source of biomass for biodiesel production as their productivity is higher compared to terrestrial crops and they do not compete with food crops [19, 28, 32–37].

Biofuels from biomass can be categorized into primary and secondary biofuels. The primary biofuels are used unprocessed for cooking and heating like firewood, wood chips, and pellets [20, 38, 39]. The secondary biofuels are further classified into (i) first-generation biofuels (1G), (ii) second-generation biofuels (2G), (iii) third-generation biofuels (3G), and (iv) fourth-generation biofuels (4G), based on the type of raw materials used and the techniques employed for their production. The classification of biofuels and details can be seen in Fig. 2. The first-generation biofuels are established processes, produced from starch, and sugar-based food crops by the process of fermentation or transesterification of vegetable oils, residue oils, and fats. However, they compete for land and water with food and have high production and processing cost [20, 40]. Around 2% of the agricultural land is used for biofuel edible feedstock which can feed half the current population of the world. This competition with the source as food and biofuel is predicted to increase the market price of these feedstocks and thus the need for second-generation biomass [41–43]. A comparison of all four generations of secondary biofuels is given in Table 3.

The second-generation biofuels are lignocellulosic, which are derived from dry products of agricultural wastes, and industrial and forest residues [20, 29, 40, 47]. Annually

Table 2 Chemical compositions of different biomass feedstocks [19, 28]

	Wood and woody biomass	Herbaceous biomass	Aquatic biomass	Animal and human residue	Mixed biomass
Fixed carbon (%)	6–25	9–35	22–33	12–13	1–15
Volatile matter (%)	30–80	41–77	42–53	43–62	41–79
Moisture content (%)	5–63	4–48	8–14	3–9	3–38
Ash content (%)	1–8	1–19	11–38	23–34	3–43
Carbon (%)	49–57	42–58	27–43	56–61	45–71
Oxygen (%)	32–45	34–49	34–46	21–25	16–46
Hydrogen (%)	5–10	3–9	4–6	7–8	6–11
Sulfur (%)	< 1	< 1	1–3	1–2	< 1–2
Nitrogen (%)	< 1	< 1–3	1–3	6–12	1–6

Fig. 1 **a** The classification of biomass feedstock based on the source of feedstock [20, 29]. **b** Classification of biomass feedstock based on vegetation type [19]. **c** Classification of biomass feedstock based on use and application [8]
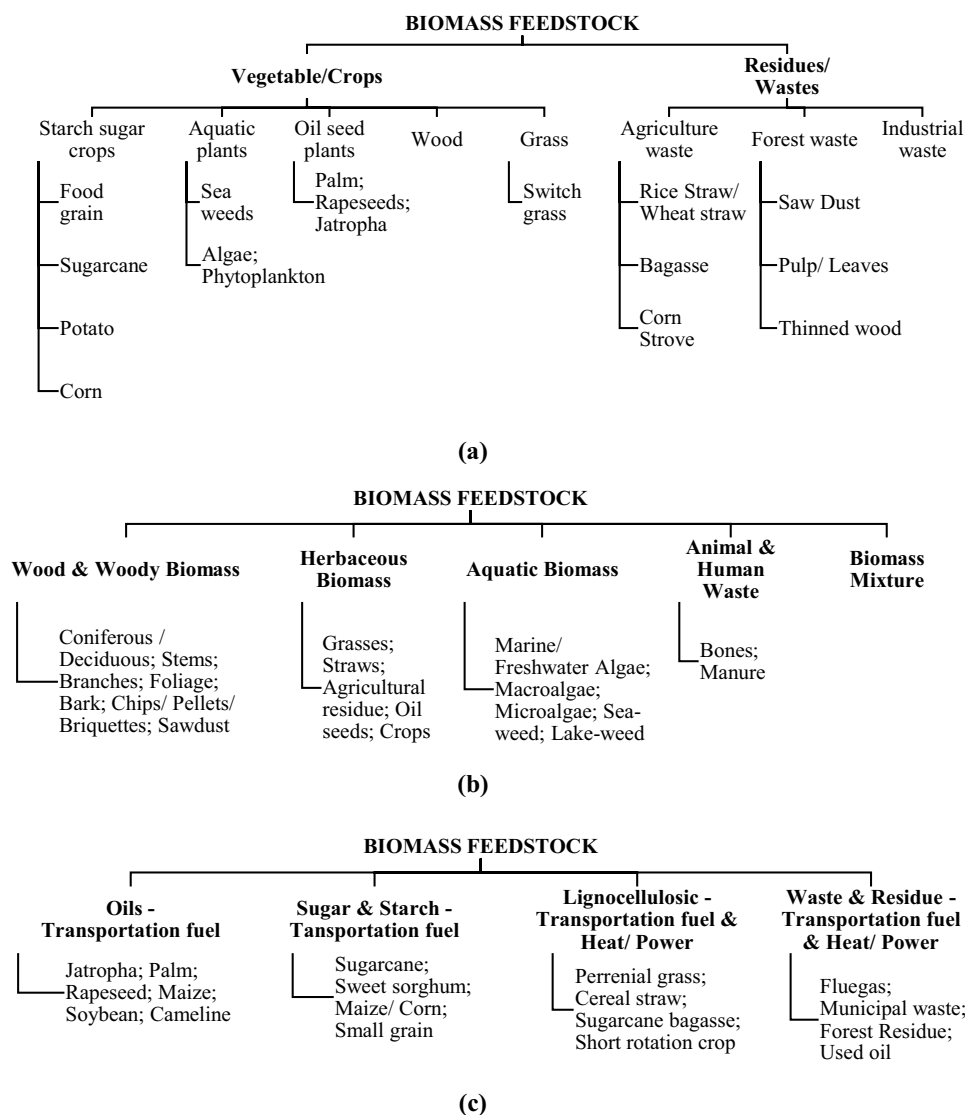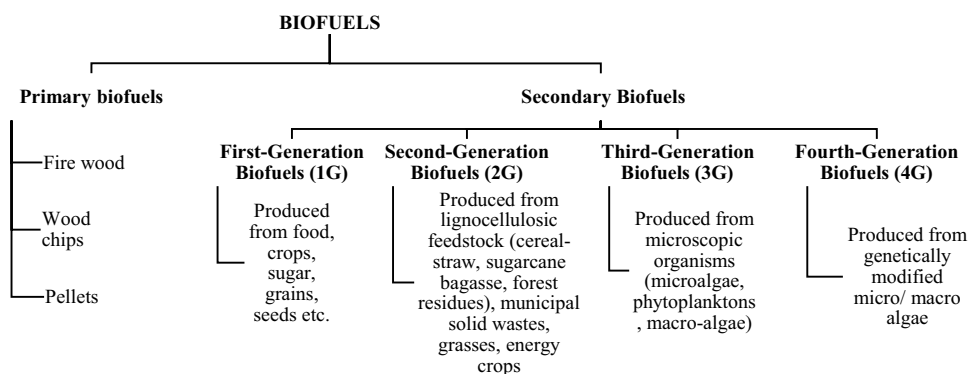
BIOMASS FEEDSTOCK

Vegetable/Crops

- **Starch sugar crops**
  - Food grain
  - Sugarcane
  - Potato
  - Corn
- **Aquatic plants**
  - Sea weeds
  - Algae; Phytoplankton
- **Oil seed plants**
  - Palm; Rapeseeds; Jatropha
- **Wood**
- **Grass**
  - Switch grass

Residues/ Wastes

- **Agriculture waste**
  - Rice Straw/ Wheat straw
  - Bagasse
  - Corn Strove
- **Forest waste**
  - Saw Dust
  - Pulp/ Leaves
  - Thinned wood
- **Industrial waste**

(a)

BIOMASS FEEDSTOCK

- **Wood & Woody Biomass**
  - Coniferous / Deciduous; Stems; Branches; Foliage; Bark; Chips/ Pellets/ Briquettes; Sawdust
- **Herbaceous Biomass**
  - Grasses; Straws; Agricultural residue; Oil seeds; Crops
- **Aquatic Biomass**
  - Marine/ Freshwater Algae; Macroalgae; Microalgae; Sea-weed; Lake-weed
- **Animal & Human Waste**
  - Bones; Manure
- **Biomass Mixture**

(b)

BIOMASS FEEDSTOCK

- **Oils - Transportation fuel**
  - Jatropha; Palm; Rapeseed; Maize; Soybean; Cameline
- **Sugar & Starch - Tansportation fuel**
  - Sugarcane; Sweet sorghum; Maize/ Corn; Small grain
- **Lignocellulosic - Transportation fuel & Heat/ Power**
  - Perrenial grass; Cereal straw; Sugarcane bagasse; Short rotation crop
- **Waste & Residue - Transportation fuel & Heat/ Power**
  - Fluegas; Municipal waste; Forest Residue; Used oil

(c)

Fig. 2 Classification of biofuels based on the source of biomass and process of production [19, 20, 29]

BIOFUELS

Primary biofuels
- Fire wood
- Wood chips
- Pellets

Secondary Biofuels

- **First-Generation Biofuels (1G)**
  - Produced from food, crops, sugar, grains, seeds etc.
- **Second-Generation Biofuels (2G)**
  - Produced from lignocellulosic feedstock (cereal-straw, sugarcane bagasse, forest residues), municipal solid wastes, grasses, energy crops
- **Third-Generation Biofuels (3G)**
  - Produced from microscopic organisms (microalgae, phytoplanktons, macro-algae)
- **Fourth-Generation Biofuels (4G)**
  - Produced from genetically modified micro/ macro algae

approximately, 5 to 8 million tons/year of lignocellulosic biomass get generated as forest and agricultural residue. Thus, their abundant availability makes them an attractive feedstock for bioenergy production [40, 59–61]. The USA and European Union have proposed many projects for lignocellulosic-based biofuels as an initiative to move from a fossil fuel-based economy to a more sustainable one [62]. The lignocellulosic biomass consists of cellulose (~ 40–50%), hemicellulose (~ 25–30%), and lignin (~ 15–25%) [63]. Because of the presence of lignin, the

Table 3 Prospects and shortcomings of different generations of secondary biofuels

Prospects	Shortcomings
First-generation biofuels	
• The process is widely commercialized [41]	• Competition with food for land and water
• Contributes to about 50 billion liters of the total biofuels production per year [44]	• The threat to food security problems may lead to an increased market price [41]
• Reduced greenhouse gas (GHG) emissions by 45–65% [45]	• Excessive usage of fertilizers may cause land pollution [46]
• Comparatively less expensive [40]	
Second-generation biofuels	
• No competition with food for land and water and no harmful effect on food security [47]	• High cost of the biofuel conversion process and expensive biofuel [49, 50]
• Waste biomass is used for bioenergy thus better waste management	• Pre-processing of lignocellulosic biomass is expensive and difficult to *scale up* [50, 51]
• Reduces GHG emissions by 50–70% [48]	• High energy consumption during processing
	• Commercialization of the process is a challenge [52]
Third-generation biofuels	
• No competition with food and animal fodder for land and water [40]	• Biomass cultivation and oil production is yet not commercialized [32]
• Micro-/macroalgae can grow in arid land and wastewater [53]	• Standalone algal biorefinery may not be sustainable
• Higher productivity and increased CO_2 sequestration rate [32]	• The processing cost of lipid extraction is high [55]
• High lipid/oil content [53, 54]	• The cost of the biofuel derived from microalgae is high [56]
Fourth-generation biofuels	
• Genetically modified algal species with improved lipid content, growth rate, adaptability to the poor environment, and higher CO_2 sequestration ability [57]	• The process is still being researched [57]
	• The environmental effects of the genetical modifications in micro-/macroalgae are yet to be understood [40]
	• The cost of processing and production may be high [58]

lignocellulosic biomass requires extensive pre-treatment before it can be processed into biofuels [64–67]. Biochemical, thermochemical, and hybrid processes like pyrolysis, thermochemical liquefaction, and torrefaction are a few conversion technologies employed to convert the lignin-cellulose-based biomass to biofuels [68, 69]. These methodologies are also known to have a higher yield compared to simple fermentation but at a higher cost due to the pre-treatment required for the feedstocks [49, 66]. Moreover, second-generation biofuels also require extremely high consumption of energy for the entire conversion process [66, 70, 71].

The limitations of the 1G and 2G biofuels led to the exploration of the third-generation biofuel feedstocks like microalgae, macroalgae, and phytoplankton [20, 40, 72–74]. Algae as a fuel source have proven to be lucrative due to its high cultivation rate, productivity, and ability to sequester carbon dioxide faster [32]. Also, they can be cultivated in moist land or wastewater [75]. Few microalgae species like *Botryococcus braunii*, *Dunaliella salina*, and *Chlorella* spp. contain 70–80% lipid (dry weight basis) which can be easily converted into useable biofuels using biochemical or thermo-chemical processes [32, 73, 74]. However, the lipid produced is sometimes highly volatile which affects the stability of the oil [76–78]. Also, the processing of the algal biomass requires a large input of energy, for drying of the algae as well as for the oil extraction and processing which leads to negative energy gain [44, 77, 79–81].

The fourth-generation biofuels concentrate on genetically modifying the microalgae to better sequester carbon dioxide and produce more lipid and oil [82, 83]. These biofuels also enable the integration of the algal generation process with wastewater treatment or flue gas utilization [84]. Both the 3G and 4G biomass feedstocks provide a sustainable source for biochemicals that can be converted into high-value food products, biochemicals, and biofuels [85, 86]. However, scientists are also skeptical regarding the environmental repercussions of genetically modified algal productions [58, 84, 87]. Table 5 provides a comparison of biofuel productivity/yield from different generations of biomass. It is evident from Tables 3 and 4 that second, third-, and fourth-generation biofuels provide better possibilities of being developed into a sustainable source for bioenergy and other value-added bioproducts compared to first-generation biofuels.

Energy from Biomass — Conversion Technologies

The process of conversion of biomass to biofuel, heat, chemicals, and electricity depends vastly on the origin of the biomass feedstock. A biorefinery is a facility that integrates all these processes to produce value-added products from biomass feedstock and wastes [19, 20, 65, 86, 97–101]. The biorefineries can be three types, based on the type of

Table 4 Biofuel/bioethanol/lipid production/yield from different generation biomass

Biomass feedstock	Biofuel yield	Reference(s)
First-generation biofuels		
Biofuel yield (L/kg)		
Corn	0.4–0.6	[88]
Barley	0.41	[76]
Rice	0.48	[40]
Sugarcane	0.25–0.5	[88]
Oats	0.41	[76]
Second-generation biofuels		
Bioethanol yield (L/kg dw biomass)		
Corn stove	5.85	[89]
Barley straw	0.054	[90]
Eucalyptus	0.612	[91]
Rice straw	116.65	[92]
Palm oil residue	1,09,600–1,72,100	[93]
Third-generation biofuels		
Lipid productivity (mg/L d)		
Chlorella spp.	290	[94]
Nannochloropsis	290–321	[95]
Ankistrodesmus	459	[94]
Chlorella vulgaris	200–1100	[96]
Chlorella protothecoides	1209–3701	[57]

feedstock as well as the flexibility or ease of operation [86, 102, 103].

1. The first kind utilizes dry grain as feedstock to produce bioethanol, dried distiller grain, and carbon dioxide in a fixed processing capacity [86, 102, 103].
2. The second type of biorefinery produces starch, high fructose syrup, ethanol, carbon dioxide, etc., using dry grain feedstock but with a much more flexible processing capacity [86, 102, 103].
3. The third type of biorefinery is advanced and uses mixed feedstock [97, 102]. They are based on high-value low volume and low-value high volume output principles and produce various fuels and value-added products by using a combination of technologies [97, 98, 102]. Lignocellulosic biomass refineries, algal-based biorefineries, waste biomass-based refineries, green biorefineries, intergraded biorefineries, etc. are a few examples of this type. The pre-treatment required for the processing of these biomasses and their conversion methodologies are complex and expensive but hold immense potential for sustainable bioenergy generation and bioeconomy [86, 99, 102–106].

Green biorefineries use natural wet feedstocks like grass, green plants, or green crops [97, 102]. These refineries are primarily treating the first-generation biomass for bioethanol production via fermentation, digestion, or esterification processes [97, 98, 102].

The lignocellulosic biorefineries can be developed into a sustainable production route for bioproducts as well as biofuels by process integration of various technologies [86, 101, 107–111]. Processes like extractive distillation with ionic liquids, adsorption with molecular sieve and biobased adsorbents, nanofiltration, extractive fermentation, and vacuum membrane distillation are a few advanced technologies that hold huge potential for the future of lignocellulosic biorefineries [102, 107, 108, 110, 112]. Critical analysis of lignocellulosic refineries shows that though they provide clean energy with sustainable agricultural development, they require high capital investments with an equally high operating cost [110].

Algal biorefineries which are based on third and advanced fourth-generation biomass require lower land and have higher productivity compared to lignocellulosic biorefineries [86, 89, 113–116]. However, very few biorefineries have been established with just algal biomass as the primary feedstock and are limited to extracting primary bioproducts [80, 86, 115, 116]. Nonetheless, research shows that more suitable technological developments and process integrations (like with wastewater treatment) will allow sustainable development in algal biorefineries [34, 80, 116–120].

The waste biorefineries use non-edible biomass and biogenic waste as the feedstock to sustainably convert them into biochemical, biopolymers, and biofuels [86, 104, 121]. This allows recycling and reusing of the waste as well as better waste management which is slowly becoming a global problem [86, 104, 122, 123]. To allow better conversion of waste to value-added bioproducts, proper characterization of the waste is required in synergy with the process of conversion [86, 124, 125]. Several types of waste like food waste, municipal solid waste, lignocellulosic waste, paper waste, and manure are being researched as a possible feedstock for waste refineries [64, 86, 104, 123, 126–131].

The biomass to biofuel conversion technologies employed for different generations of biomass and their products for several types of biorefineries are given in Fig. 3. The conversion technologies require an in-depth understanding of chemistry, pre-processing technologies, production technologies, conversion processes, economics, scale-up, and environmental effects, and policies to be developed into a large-scale commercialized biorefinery process [97, 98, 108, 112].

Biochemical Conversion Methods

The biochemical conversion methods are used to convert sugar, starch-based, and sometimes lignocellulosic-based biomass into grain-ethanol or bioethanol [19, 20].

Fig. 3 Biomass to biofuel conversion technologies for different generations of biomass and their final energy products [19, 20, 86, 102, 132–134]
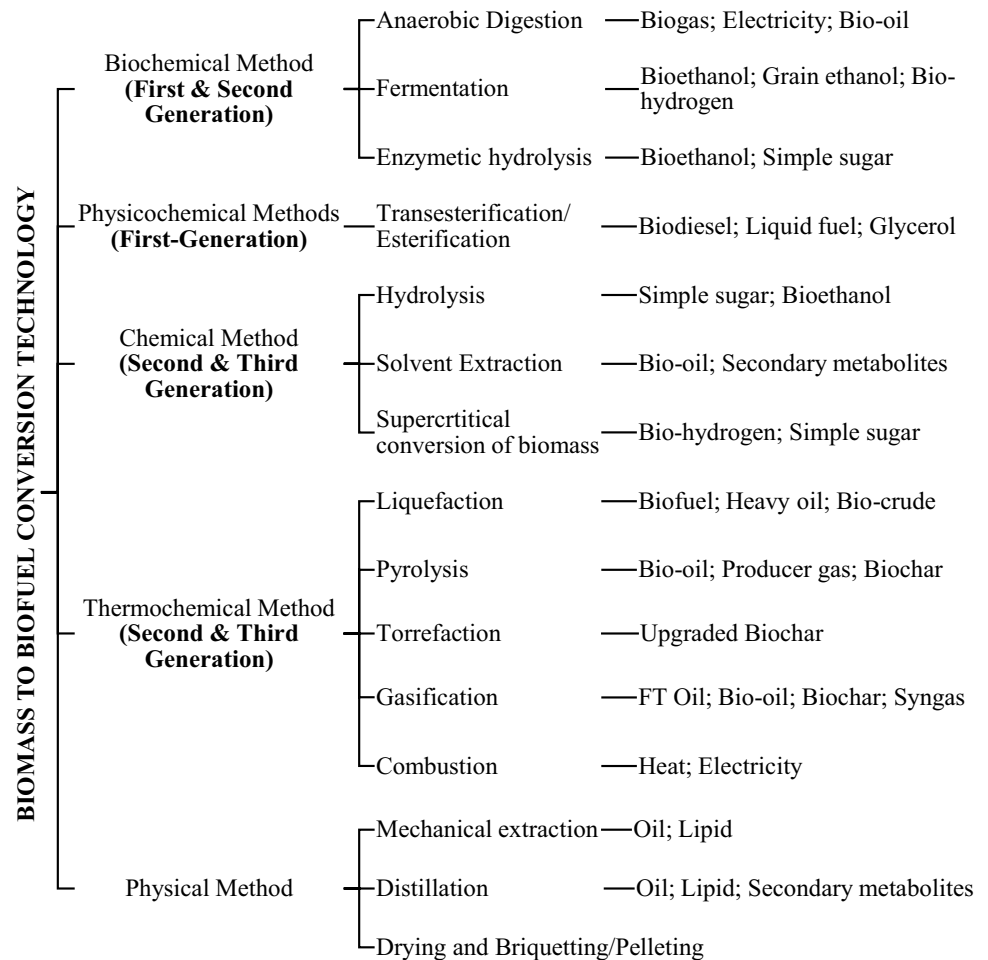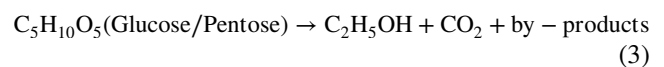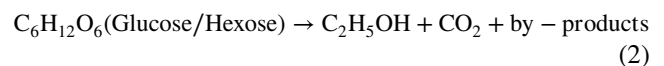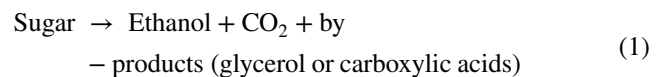

Fermentation, anaerobic digestion, and enzymatic hydrolysis are a few conventional, well-established, and cost-effective processes that produce bioethanol, grain-ethanol, biogas, bio-oil, and electricity as fuel products with other value-added biochemicals [19, 20, 133, 135]. These processes allow chemical decomposition of the biomass into carbohydrates which then convert into liquid fuel or biogas [19, 136].

Fermentation

The fermentation is a chemical conversion process where simple sugars like hexoses (glucose/fructose) and pentoses (ribose) are converted into ethanol and CO_2 under anaerobic conditions using microorganisms like yeast (*Saccharomyces cerevisiae*), bacteria (*Zymomonas mobilis*), and fungi (*Fusarium avenaceum*) [19, 102, 137–140]. The feedstock used for the process can be sugar or starch like corn and wheat producing grain-ethanol and lignocellulosic substrates producing 2G bioethanol [19, 41, 139]. Sugar feedstocks are simple to ferment and convert into ethanol; however, starch is a complex branched glucose polymer comprising amylose

and amylopectin [140, 141]. These macromolecules need to be hydrolyzed into simple fermentable sugar like hexoses (glucose/fructose) and pentoses (ribose) by a process called mashing which typically contains 15–20% starch [44, 140, 141]. The simple sugars are then converted into ethanol using microorganisms under anaerobic conditions [137, 140, 141]. The reactions 1–3 below show the conversion stoichiometry for sugar to ethanol [19]. Theoretically, the conversion of sugar to ethanol is 51%; however, as the microorganisms utilize a part of the sugar for their metabolic activities, the fermentation efficiency is between 40 and 48% [19, 102]. The quality and productivity of the process depend upon feedstock, pH, agitation time, temperature, microorganism used, inoculum, and fermentation time [140].

$$\text{Sugar} \rightarrow \text{Ethanol} + CO_2 + \text{by} - \text{products (glycerol or carboxylic acids)} \tag{1}$$

$$C_6H_{12}O_6(\text{Glucose/Hexose}) \rightarrow C_2H_5OH + CO_2 + \text{by} - \text{products} \tag{2}$$

$$C_5H_{10}O_5(\text{Glucose/Pentose}) \rightarrow C_2H_5OH + CO_2 + \text{by} - \text{products} \tag{3}$$

The conversion of simple sugar to ethanol can take place via two different pathways depending upon the initial substrate. The pentose sugar follows the pentose-phosphate-pathway (PPP), whereas the hexose converts into ethanol via glycolysis or the Embden-Meyerhof pathway (EMP) [19, 142]. Microorganisms like *Saccharomyces cerevisiae* follow the EMP pathway and produce an ethanol concentration of 18% of the fermentation broth [137]. Few bacteria like the *Zymomonas* follow the Entner-Doudoroff pathway (EDP) as an additional metabolic pathway that adds more carbon to the fermentation process and yields half as much ATP per mole of glucose as the EMP [137]. The ethanol yield widely varies with the type of feedstock used and the fermenter parameters. Also, genetically modified microorganisms produce better yields compared to un-engineered species [41].

The processing of lignocellulosic biomass via fermentation is more complex compared to sugar- or starch-based feedstock because of the presence of carbohydrates like cellulose and hemicellulose, and lignin. Through the biological conversion process, the biomass is first delignified where the cellulose and hemicellulose bonds with lignin are broken. Then, the carbohydrates (cellulose and hemicellulose) are broken down into simple sugars (glucose, xylose, etc.) by hydrolysis. In this entire pre-treatment process, the delignification of biomass is the most complex, expensive, and rate-limiting in nature [137, 142–144]. A list of different pretreatment techniques for lignocellulosic biomass is given in Table 5. Recently, micro- and macroalgae are also being researched as feedstock for the

fermentation process [34]. Different algal biomass consists of several types of polysaccharides (glucans) like green algae containing cellulose and starch and red algae containing cellulose and cellulose and Floridean starch. Along with glucans, some non-glucans are also present like agar, carrageenan, and alginate. For improved ethanol productivity, hydrolysis of both glucans and non-glucans is essential [34].

The fermentation process for biomass to bioethanol conversion follows the schematic given in Fig. 4. The size reduction and milling are the first unit operations where the biomass is ground and milled. The milling can be (i) dry milling and (ii) wet milling [142, 144]. Dry milling is when the biomass is milled into flour without separating the nutritional components and sent for processing as a whole crop. Wet milling is when the biomass is treated with water to separate starch and fiber, and only starch is further processed. The advantage of wet milling is the separation of different value-added products from the biomass before processing and has a higher production capacity [44, 142, 144]. Dry milling produces distillers' dried grains which is an excellent animal fodder rich in proteins, fats, and carbohydrates [44]. Once, milling is done, then the processed biomass is sent to the pre-treatment chamber, where, based on the biomass type (sugar-based, starch-based, or lignocellulose-based), it is processed into simple sugar by hydrolysis. The simple sugar or saccharine is then sent for fermentation to be converted into grain/bioethanol [19, 137, 142, 144]. Typically, fermentation of sugar or starch-based feedstocks is done at

Table 5 Pre-treatment methodologies for lignocellulosic biomass [19, 51, 109, 145]

Pre-treatment	Mechanism/principle
Mechanical pre-treatment	
Grinding/milling/chipping	Mechanical breakdown of the lignin, cellulose, and hemicellulose bonds; decrystallization of cellulose
Screw press	Mechanical breakdown by shear and pressure forces
Thermal drying	Desiccation of the biomass
Thermal pre-treatment	
Hydrothermal pre-treatment	Solubilize hemicellulose at elevated temperature and pressure; increased surface area
Steam explosion	Solubilize hemicellulose; change in lignin structure
Chemical pre-treatment	
Acidic pre-treatment	Dissolution of hemicellulose and removal of lignin in acids like H_2SO_4 and HCl
Alkali pre-treatment	Solubilize lignin levels and eliminate acetyl groups using bases like CaO and NaOH
AFEX	Liquid ammonia at high temperature and pressure conditions decrystallizes cellulose and breaks lignin and hemicellulose bonds
H_2O_2	Change in lignin structure and dissolution of lignin
CO_2	High-pressure CO_2 is used to break bonds
Ionic liquids	Destroy cellulose crystallinity
Organosolv	Use of organic solvents like ethanol, tetrahydrofuran, etc., at high pressure and temperature
Organocat	A two-phase water-organic solvent system with oxalic acid
Biological pre-treatment	
Fungal/microbial pre-treatment	Solubilize cellulose and hemicellulose, change lignin structure

Fig. 4 Schematic for the fermentation process [19, 41, 137, 138, 144, 146]
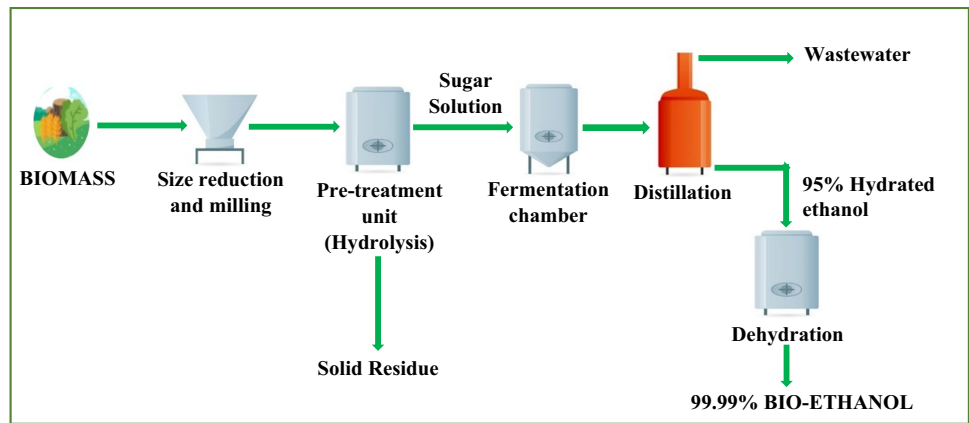
30–40 °C with 3.7–5.5 pH and under continuous stirring of 150–300 rpm [41].

In the case of lignocellulose-based biomass, sometimes, saccharification and fermentation are combined into the simultaneous saccharification and fermentation (SSF) process. This is done because, when cellulose is hydrolyzed using cellulase enzyme, glucose inhibits its activity. SSF process keeps the concentration of glucose low allowing low inhibition and better ethanol conversion [137, 143, 147]. Compared to the two-staged process, SSF yields higher ethanol concentration (~40%) with a shorter fermentation time and less contamination [137, 147]. Also, to effectively increase the production of 2G ethanol using lignocellulosic feedstock, it is advisable to maximize the conversion of xylose sugar present in hemicellulose using engineered *Saccharomyces cerevisiae*. The process where saccharification and co-fermentation of xylose to 2G ethanol occurs is called the saccharification and co-fermentation process (SSCF) by co-culture of two recombinant yeasts [76, 148–150]. Furthermore, research shows that efficient removal of lignin, increase in the cellulose porosity, and reduction of cellulose crystallinity during pre-treatment improve the efficiency of hydrolysis by many folds [76, 102, 151]. The fermented product thus obtained is sent for distillation where 90–95% hydrated bioethanol is obtained, which is then dehydrated to obtain 99.99% pure bioethanol [41, 138, 146].

Recently, the solid-state or solid substrate fermentation process is also employed on agricultural and industrial waste which occurs in the absence or near absence of water. The process is known to enhance the production of various value-added products and biofuels at a lower cost of operation [152]. Photo-fermentation and dark fermentation are the other two novel fermentation techniques being researched to convert biomass into bio-hydrogen. Dark fermentation is an anaerobic fermentation process occurring in the absence of light at temperatures between 25 and 80 °C. Photo-fermentation is a catalytic conversion of biomass into hydrogen by nitrogenase bacteria using solar energy under a nitrogen-deficient medium. These conversion processes have several constraints like time-consuming, expensive, and high-energy demand, which limits their applicability [153].

The fermentation as a process is commercially well established and can yield high productivity with high purity when first-generation biomass is used (~450 l of grain-ethanol can be produced per ton of dry corn) [17]. However, pre-treatment of lignocellulosic biomass and hydrolysis becomes a problem when fermentation is employed for second-generation biomass [41, 146]. The lignocellulosic biomass processing techniques are not well developed and still at the laboratory or pilot plant scale [131]. Also, fermentation being a biochemical process requires numerous chemical and biological parameters to be controlled and optimized to be sustainable.

Anaerobic Digestion

Anaerobic digestion is a multi-staged biochemical process that is commercially established for high-moisture content waste (~80–90% moisture) treatment as well as for bioenergy generation [17, 102, 154]. Agricultural residue, municipal solid waste, sewage sludge, etc. are a few feedstocks commonly used for the anaerobic digestion process. The process can directly convert biomass to biogas (60–70% methane and ~30% CO_2 with small quantities of other gases like H_2S) and digestate [155, 156]. The conversion occurs through a series of biochemical reactions occurring via metabolic pathways of bacteria under anaerobic conditions which breaks down the macromolecules into simpler molecules that converts into biogas [17, 19, 102, 155].

The schematic for the anaerobic digestion process is given in Fig. 5. The biomass feedstock is first made into a slurry, before feeding into a digester. In the digester, the biomass converts into biogas and is digested in the following four steps [157, 158]

Fig. 5 Schematic for the anaerobic digestion process [17, 19]
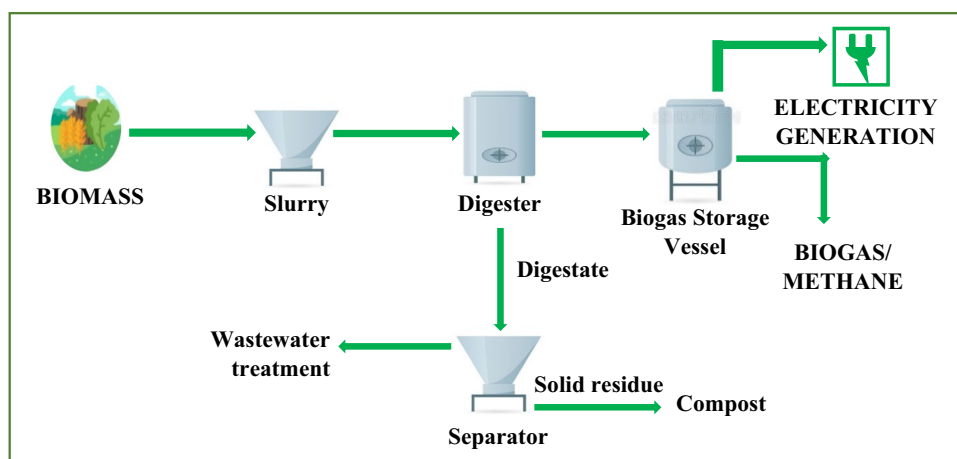
i. *Hydrolysis*: Biomass is consisting of macromolecules like fats, carbohydrates, and proteins. In the first step of conversion, these large organic polymers are hydrolyzed into smaller compounds like fatty acids, monosaccharides, amino acids, and peptides using fermentative bacteria. Hydrogen and acetate are some by-products resulting from this rate-limiting stage. The hydrolysis occurs at a temperature between 30 and 50 °C and an optimum pH of 5–7.

ii. *Acidogenesis*: In the second step of anaerobic digestion, the products of hydrolysis are picked up by acidogenic microorganisms and converted into lighter volatile fatty acids, H_2, NH_3, CO_2, H_2S, carbonic acids, and alcohols. The more is the lighter volatile fatty acids formed in this stage, the more will be the formation of acetic acid in the next stage.

iii. *Acetogenesis*: Acetogenesis is the third phase of digestion, where acetogenic microorganisms catabolize the products from the acidogenesis stage into acetic acid, carbon dioxide, and H_2. This step facilitates the methanogenesis process to produce the final product as methane.

iv. *Methanogenesis*: In the last step of the digestion process, methane is produced by *hydrogenotrophic methanogens* and *acetotrophic methanogens* from acetic acid, carbon dioxide, and H_2 via two reaction mechanisms, (a) acetoclastic methanogenesis and (b) hydrogenotrophic methanogenesis, as shown in reactions 4 and 5 [154]. The methanogens need to be maintained under anaerobic conditions with a pH between 6.5 and 7.5 to enable proper conversion.

$$\textit{Acetoclastic methanogenesis} : CH_3COOH \rightarrow CH_4 + CO_2 \tag{4}$$

$$\textit{Hydrogenotrophic methanogenesis} :$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{5}$$
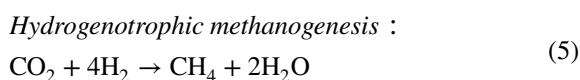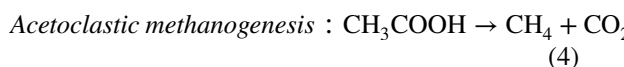
After digestion, two products are formed: (a) biogas and (b) digestate. The biogas is sent to a collection tank, where it may be further distributed for electricity production or other household usage. The digestate is sent to a separator, where the wastewater is sent for treatment and the solid residue may be used as compost or biofertilizers [17, 19, 102, 159]. Feedstock composition and size, inoculum to substrate ratio, liquid recirculation, rate, bed compaction, and use of bulking agents are some of the parameters that affect the performance of the digester [158, 160].

Different technological advancements are being made to improve the anaerobic digestion process to enhance methane formation. Electrical treatments, biological pre-treatment of the substrate, thermal hydrolysis, etc. are a few methodologies employed to enhance the rate-limiting hydrolysis process. Improved hydrolysis allows the better formation of micro-molecules which further enhances the acidogenesis and acetogenesis steps and the products [161]. For lignocellulosic biomass, pre-treatment and removal of lignin again become important as lignin adversely affects the hydrolysis stage of the digestion process [162, 163]. The choice of enhancement and pre-treatment methodologies is influenced by economic and energy efficiency analysis [145]. Many new reactor designs have also been proposed which improve the efficiency of the process. Zhang et al. have developed a three-staged digester with each step of digestion, hydrolysis, acidification, and methanogenic, occurring in three independent chambers. This design improves the yield by 24–54% over a single-phase or two-phase single-chamber process [164]. Digesters with high-pressure biological membrane systems also show a significant effect on methane yield during the methanogenesis step [157]. Integration of the fermentation process and anaerobic digestion of fermentation residue to produce ethanol and methane is also found to increase the decomposition rate of food waste by 27% and reduce the energy requirement by 52% [157]. Nowadays, a lot of research is being done to study anaerobic

digestion with microalgal biomass as a feedstock or as a co-substrate [143, 165].

One of the major advantages of this process is that biogas produced can be directly used for electricity generation with overall biomass to electricity conversion efficiency which is about 10–16%. It can also be upgraded to higher quality natural gas by removing carbon dioxide from the mixture [17]. The application of anaerobic digestion in landfills to process municipal solid wastes generates an equal amount of methane (CH_4) and carbon dioxide (CO_2). These gases along with trace amounts of nitrogen, oxygen, and other volatile organic contaminants like hydrogen sulfide (H_2S) and vinyl chloride (C_2H_3Cl) are known as landfill gas (LFG) [157]. The usage of LFG for electricity generation and other applications requires efficient treatment of the LFG to remove the containments and carbon dioxide [166]. Lately, a lot of effort is being made to produce liquid fuel in the form of methanol instead of gaseous fuel using anaerobic digestion as a treatment of biogas/methane and its storage is expensive [157, 166]. The liquid fuel is easy to manage, store, and distribute. Also, it has low ash and sulfur content compared to biogas [166].

Enzymatic Hydrolysis

The enzymatic hydrolysis process is normally always combined with fermentation for the conversion of biomass into bioenergy. As the name suggests, the hydrolysis stage of converting carbohydrates into simple sugar is facilitated by enzymatic activities. Enzymatic hydrolysis is very often preferred for starch-based and lignocellulosic biomass feedstock and has recently been researched on algal biomass hydrolysis [34, 167]. For starch enzymatic hydrolysis, amylase is the first enzyme that decomposes the starch macromolecules into short chains of glucose. The *amylase* enzyme liberates "maltodextrin" oligosaccharides which are then further hydrolyzed by enzymes like *pullulanase* and *glucoamylase* in a process called saccharification. During saccharification, all the dextrin is converted into glucose and maltose which are then fermented to produce ethanol using microorganisms [102]. In lignocellulosic biomass, the cellulose consists of glucose, and hemicellulose is made up of pentoses (D-xylose in abundance and D-arabinose) and hexoses (D-mannose, D-glucose, and D-galactose) [63]. Lignin is composed of three aromatic alcohols, p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [63]. Pre-treatment allows the cellulose and the hemicellulose to be available for easy hydrolysis. During the enzymatic hydrolysis process, *cellulolytic* (*cellulase*) enzyme hydrolyzes the cellulose into glucose and *xylanases* break down hemicellulose into xylose which can be then co-fermented to produce 2G ethanol [63, 168].

A novel approach to improve the economic viability of the process is to increase the solid loading of the process called "high-solids" enzymatic hydrolysis. The process can be considered high solids when the solid content is more than 15% (w/w) dry matter and there is no free water present at the onset of the hydrolysis process. This methodology improves the energy conversion at lower capital and operating cost and reduces the energy input requirement [51]. As, with other biochemical processes, the abundance of lignocellulosic biomass and its usability has made it a preferred feedstock choice for enzymatic hydrolysis. However, the scale-up of the lignocellulose pre-treatment processes and the cost of enzymes are the major limitations to its commercial success [51]. Many new techniques for lignin pre-treatment like benzenesulfonic acid-induced hydrotropic fractionation [169] and supercritical carbon dioxide pre-treatment [170] are also employed in integration with enzymatic hydrolysis to improve energy yield.
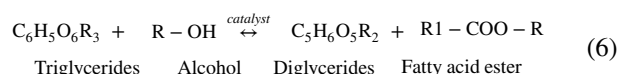
Physicochemical Conversion Processes

The physicochemical conversion process like transesterification leads to high-density biofuels like biodiesel [19]. Biodiesel is an attractive substitute for diesel as it is non-toxic, has high oxygen content, and has better lubrication properties which allow efficient combustion in diesel engines [19, 29, 102].
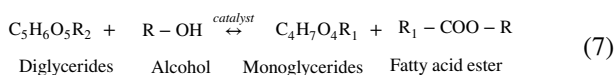
Transesterification/Esterification Process

The oil-containing first-generation crops like *Jatropha*, palm, rapeseed, and sunflower oil, waste vegetable oil, and microalgae, can be used as the feedstock for the conversion of oil to biodiesel (fatty acid alkyl esters) by the transesterification process [19, 29, 171]. Currently, 80–85% and 10–15% of the total biodiesel production in the world are produced from rapeseeds and sunflower seeds respectively [19]. The oil extracted from crops, algae, and the waste vegetable oil is composed of triglycerides, which, when burned as fuel, lead to incomplete combustion and deposition inside the combustion engine [29]. Thus, conversion of triglycerides into biodiesel is a required step. The reversible chemical reaction of triglycerides with alkyl alcohol to form fatty acids alkyl esters and glycerol in the presence of a catalyst is called transesterification [171]. The process occurs at atmospheric pressure and 50–70 °C temperature, in the presence of excess methyl or ethyl alcohol to increase the forward reaction rate as shown in reactions 6–8 [171].
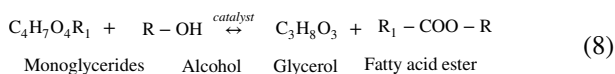
Step 1: Conversion of triglycerides into diglycerides

$$C_6H_5O_6R_3 \;+\; R-OH \;\overset{catalyst}{\leftrightarrow}\; C_5H_6O_5R_2 \;+\; R1-COO-R \tag{6}$$

Triglycerides Alcohol Diglycerides Fatty acid ester

Step 2: Conversion of diglycerides into monoglycerides

$$C_5H_6O_5R_2 \quad + \quad R-OH \overset{catalyst}{\leftrightarrow} \quad C_4H_7O_4R_1 \quad + \quad R_1-COO-R \qquad (7)$$

Diglycerides　　Alcohol　　Monoglycerides　　Fatty acid ester

Step 3: Conversion of monoglycerides into glycerol and fatty acids alkyl esters

$$C_4H_7O_4R_1 \quad + \quad R-OH \overset{catalyst}{\leftrightarrow} \quad C_3H_8O_3 \quad + \quad R_1-COO-R \qquad (8)$$

Monoglycerides　　Alcohol　　Glycerol　　Fatty acid ester

Homogeneous catalysts like liquid acids (HCl, H_2SO_4, etc.) or liquid bases (NaOH, KOH, etc.) can be used for the conversion; however, their activity reduces in the presence of excessive free fatty acids. Moreover, transesterification reaction with homogeneous catalysts produces a huge amount of wastewater and the catalysts are corrosive and non-eco-friendly [172]. Heterogeneous catalysts on the other hand are preferred as they can simultaneously esterify fatty acids and transesterify triglycerides [173]. Heterogeneous catalysts can be solid acids or solid bases and have immense potential as they are easy to separate and have fewer environmental repercussions [173, 174]. Also, the reusability of the catalyst and less consumption make biodiesel production more economical compared to the homogeneous catalyzed process. In the case of the vegetable oil transesterification process, solid acid catalysts are preferred because the base catalysts are known to cause saponification of the free fatty acids, which reduces biodiesel formation and increases the cost of production [171, 173].

The process of transesterification starts with the extraction of oil from the biomass feedstock as shown in the schematic in Fig. 6. The extraction of the oil can be done using various methods like solvent extraction, supercritical fluid extraction, ultrasonic extraction, microwave extraction, osmotic shock, and enzymatic extraction [78, 171]. The oil extracted is then sent for transesterification. The glycerol formed as the by-product of transesterification is a much denser compound compared to fatty acid esters and can be easily separated. The fatty acid esters once separated are sent for distillation, where the excess alcohol is removed. The distilled biodiesel is sent for a final water washing where the residual catalyst and soap are removed [19, 174].

Integration of different processes together to enhance the production and treat mixed biomass feedstock has also been researched. Karpagam et al. observe that integration of transesterification with biochemical processes enhances bioethanol and biodiesel production for algal biomass [175]. Similar observations have also been made by Jung et al. and Sundaramahalingam et al. when they combined transesterification with thermal enhancement and ultrasound effects and reported a biodiesel yield of 59.3% and 94.7% respectively [172, 176]. A considerable amount of research is needed to identify reusable catalysts and economical downstream purification processes. It is also evident that single process conversion of vegetable/crop oil to biodiesel is not economical and proper integration of processes is advisable [174].

Chemical Conversion Methods

Hydrolysis

The chemical hydrolysis process is the pre-fermentation step of converting long-chain carbohydrates into simple sugars. Acid hydrolysis or acidolysis can be employed for starch-based, lignocellulosic, and microalgal biomass [177–179]. Inorganic acids like HCl, H_2SO_4, nitric acid, and phosphoric acid and organic acids like citric acid, oxalic acid, and acetic acid can be used for the process [178]. Acid concentration, temperature, time, and surface-to-volume ratios are important parameters that affect the hydrolysis process [177, 178, 180]. Hong and Wu reviewed that when microalgae *G. verrucose* is treated with 0.1 M HCl at 121 °C, it yields 34.9% of hydrolysate, whereas when it is treated with 0.1 M citric acid using 10% biomass at 150 °C for 60 min, it yields 57.8%

Fig. 6 Schematic for transesterification process to produce biodiesel [17, 19]
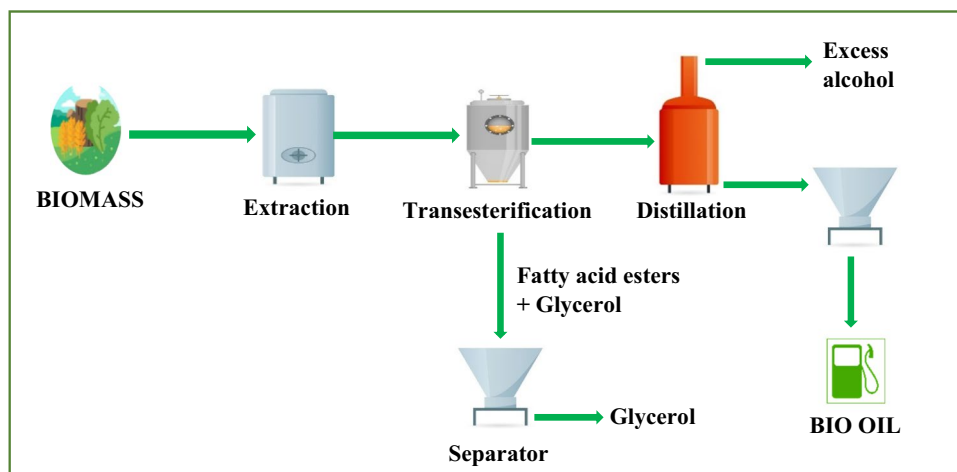
hydrolysate [178]. Thus, the feasibility of acidolysis using organic acids is economical and environmentally friendly [178]. Integration of acid hydrolysis with ultrasound and microwave is currently being researched to improve the yield of the process [178, 181]. Ultrasound causes shearing of the cell wall of biomass due to cavitation which enhances the release of low-molecular-weight sugars from polysaccharides [181]. Microwave-assisted hydrolysis on the other hand improves hydrolytic efficiencies by enabling better temperature and heating control [178]. Though the processes are well tested, their commercial applications are still at their initial stages [178].

Solvent Extraction

Solvent extraction of oil or lipid from oil-containing biomass like rapeseeds, palm seeds, corn, soybean, *Jatropha*, micro-, and macroalgae is a conventional method being commercially used over the last 50 years [182]. Solvent extraction is also extensively employed to extract secondary metabolites from biomass like terpenoids, waxes, resins, sterols, and alkaloids [182]. Extraction is a chemical process in which the solute (oil or lipid) is separated from the carrier (biomass) by allowing the solute to selectively dissolve in the solvent. For efficient extraction, the solvent needs to penetrate the biomass and match the polarity of the solute (lipid/oil). The choice of solvent is essential in this process as extraction and further separation of solvent from the extracted oil are both required [102]. Also, for the process to be cost-effective, the solvent must be inexpensive and easily available. Organic solvents like benzene, hexane, cyclohexane, acetone, and chloroform are effective in extracting oil from the plant and algal biomass by degrading the cell wall [183]. Microalgal species like *Botryococcus braunii* actively secrete oil, which can be then recovered without damaging the cell wall using solvents like decane [183].

The process of solvent extraction follows the schematic given in Fig. 7. The biomass is initially dried and then sent for extraction using a choice of solvent. The extracted oil and solvent mixture is then sent for separation and the de-oil

biomass meal is sent for toasting [102]. Integration of solvent extraction with processes like hydrolysis, fermentation, and transesterification is also being applied in biorefineries. The solvent extraction removes the secondary metabolites from the biomass, and hydrolysis and fermentation of the remaining biomass meal lead to bio-oil production. Frequently, mechanical extraction is combined with solvent extraction to enhance the oil extraction process. The mechanical extraction processes like bead milling or wet milling allow the plant cell wall to be disrupted and ease the solvent extraction process. Mercer and Armenta report an increase in oil extraction from 5.6 to 18.8% when bead milling is combined with extraction from *Chlorella protothecoides* using hexane solvent [183].

Microwave-assisted, ultrasound-assisted, and high-shear-assisted extraction processes are a few advanced processes that enhance the overall yield of bio-oil [184–186]. Supercritical extraction using supercritical CO_2 is another alternative to improve the yield of oil [183]. This method of extraction is completely free of solvent and thus yields pure products. Solvent extraction efficiencies can also be improved by a process called "Accelerated solvent extraction," where the organic solvent is used at temperature and pressure above its boiling point [182, 186]. The increase in extraction temperature and improved contact between the solvent and biomass shortens the time required for extraction. However, thermal degradability and oxidation of lipids are a few critical shortcomings of the process. Also, the conventional solvent extraction method may not be efficient in removing lipid from plant cells. Furthermore, parameters like solvent-to-sample ratios, sample sizes, extraction temperatures, and extraction cycles need to be optimized to make the process commercially viable [182].

Supercritical Conversion of Biomass

Supercritical conversion of biomass is an efficient alternative to the chemical or enzymatic hydrolysis process. Chemical hydrolysis is expensive and enzymatic hydrolysis requires pre-treatment of the lignocellulosic biomass [187]. Contrary to these, supercritical water or CO_2 can easily convert

Fig. 7 Schematic for the solvent extraction process [19]

BIOMASS → Drying → Solvent extraction → Distillation → Solvent / BIO OIL

De-oiled biomass meal
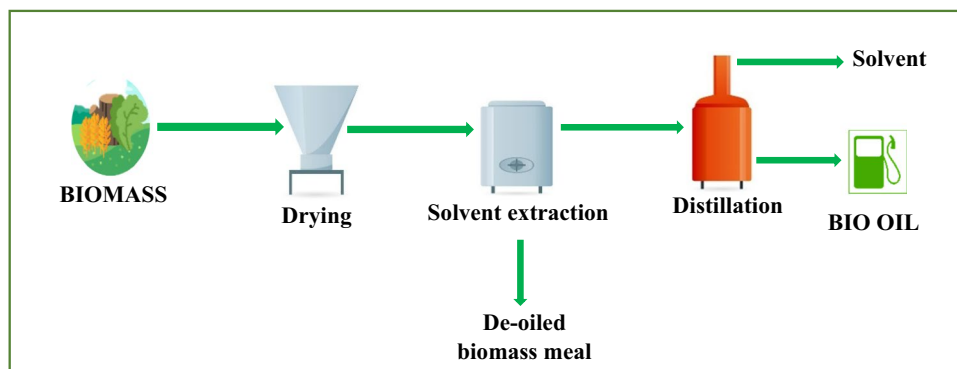
biomass into a mixture of oils, alcohol, organic acids, and methane and cellulose into sugar [187]. A supercritical fluid is a state of matter that is at a temperature and pressure condition above the critical point. At the supercritical state (water, 644 K and 22 MPa; and CO_2, 304 K and 7.4 MPa), the fluid is neither liquid nor gas [102, 115, 188]. Water under supercritical conditions is present in its ionic H^+ and OH^- form and dissolves separately in the lignocellulosic biomass enabling faster rupture of the bonds and formation of simple sugars. The simple sugars (glucose and xylose) get converted into bioethanol and the lignin into bio-oil [102, 115, 188].

Supercritical water gasification technology can convert cellulose into glucose in 10–20 s and produces bio-hydrogen [189]. When the temperature of the supercritical water is increased up to 873 K, the water acts as a strong oxidant leading to the complete decomposition of biomass. The oxygen atom from water reacts with the biomass carbon atom, allowing the free hydrogen atom to form bio-hydrogen. This method is effective for biomass with moisture content and does not require any drying pre-treatment [189]. Also, the reaction medium being water allows better mass transfer and reduced coke formation. This method produces high energy-dense renewable hydrogen gas at low purification and downstream separation cost. However, due to the requirement of elevated temperature and pressure requirement, the process is not yet industrially established [189].

Thermochemical Conversion Methods

The thermochemical processes of converting biomass to energy apply thermal and chemical decomposition methodologies under varied oxygen supply and temperature conditions. Some of the methods like liquefaction, pyrolysis, and torrefaction are modern technologies with numerous benefits like small carbon footprint, short reaction time, and capability of handling several types of biomass feedstocks [105]. However, most of these methods are still in the pilot or research stages of development.

Liquefaction

The liquefaction or hydrothermal liquefaction process converts biomass into stable liquid hydrocarbons with a high *H/C* ratio under moderate-temperature (~280–370 °C) and high-pressure (10–25 MPa) conditions [19, 190–192]. The fuel obtained has a high heating value and low oxygen content making it a stable energy source. Lignocellulosic biomass (dry biomass) and algal biomass (wet biomass) are the preferable feedstocks for the process with an adequate pre-treatment [190, 193, 194]. Prestigiacomo et al. have recently studied hydrothermal liquefaction of municipal sludge as a feedstock in a stirred reactor [195]. The process

of liquefaction is either direct or indirect in the presence of alkalis, glycerine, and propanol or butanol [196]. In direct liquefaction, fast pyrolysis of biomass occurs producing liquid tar/oil and condensable gases, whereas indirect pyrolysis requires catalysts to convert the non-condensable gaseous products into liquid fuel [196]. The biofuel produced is highly viscous and water-insoluble and requires solvents, reducing gases like CO and H_2 and the presence of a catalyst to upgrade its properties. Alkali salts like sodium carbonate and potassium carbonate can act as a catalyst for the lignocellulose liquefaction process, which converts cellulose and hemicellulose into simple compounds by depolymerization and deoxygenation [196]. Nagappan et al. have reported that usage of heterogenous catalysts like Ni/Al_2O_3 or Mo/Al_2O_3 improves selectivity and thus improves yield [197]. Ni/Al_2O_3 is known to be more selective toward lipid for deoxygenation and Mo/Al_2O_3 facilitates the deoxygenation of carbohydrates. Also, heterogeneous catalysts are easy to recover and are less corrosive [197].

The presence of water, alkalis, glycerol, and propanol/butanol during indirect liquefaction facilitates different degradation processes [198]. In the presence of glycerol and alkali salts, glycerol enables a reduction in surface tension of the solvent at a higher temperature, thus allowing the alkali salts to penetrate the lignocellulosic biomass and break the lignin bonds [102, 196]. In the aqueous liquefaction of lignocellulosic biomass, the water molecules cause desegregation of the wood structure followed by partial depolymerization of the compounds. It is observed that the bio-crude yield from aqueous liquefaction is higher in the presence of a catalyst (~63%) compared to its absence (~31%) [102].

The process of liquefaction, in general, follows three major steps: (i) depolymerization, (ii) decomposition, and (iii) recombination. Initially, the biomass depolymerizes and decomposes into smaller compounds. However, the presence of free radicals causes these simple compounds to repolymerize and recombine into bio-crude and solid residues. In depolymerization, long chains of hydrocarbons break down into smaller chains under high pressure and temperature conditions, mimicking the natural process of fossil fuel production. The decomposition step involves the removal of water molecules (dehydration), removal of amino acids (deamination), and loss of CO_2 molecules (carboxylation). The dehydration and decarboxylation processes facilitate the removal of oxygen from the biomass. The recombination or repolymerization of molecules occurs post decomposition due to the presence of excessive free radicals and the absence of hydrogen molecules. If hydrogen molecules are freely present during the liquefaction process, then it reduces the free radical activities enabling more stable molecular weight species yield [190]. The complete absence of free hydrogen leads to more coke formation. Parameters like temperature, pressure, residence time, and biomass type

significantly affect the process kinetics and product composition [190, 199, 200]. It is observed that elevated temperature (> 350 °C) yields gaseous products whereas low temperature (150–200 °C) favors solid formation, with bio-oil production maximized at moderate temperature (250–300 °C) [199].

The lignocellulosic biomass is liquefied at 350 °C and 150 bar pressure for 15 min in a liquefaction unit in either a batch or continuous manner [190]. Elliot et al. have studied hydrothermal liquefaction of algal biomass in batch and continuous systems at 523–653 K and 1.0 MPa with a residence time of 3–5 min [201]. A spontaneous phase change of biomass occurs under these process conditions producing CO_2, bio-crude, water, and solid residues [202]. It is observed that the more the lignin content in the biomass, the more will be solid residue production. The solid residues formed can be used as biofertilizers or biofuels. The bio-crude produced is sent for further processing and upgrading as can be seen in Fig. 8 [190, 202]. The upgrading of the bio-oil obtained can be done by esterification, catalytic cracking, hydrogenation, molecular distillation, and catalytic pyrolysis [199]. Lignocellulosic biomass can also be directly converted to liquid hydrocarbons or bio-crude by reacting it with syngas in the presence of a catalyst [196]. The use of subcritical and supercritical solvents and water for direct liquefaction of lignocellulosic biomass is also known to yield fuel with 80% energy efficiency [203, 204].

Microwave-assisted liquefaction for algal biomass, simultaneous hydrothermal liquefaction, esterification for sugarcane bagasse, and liquefaction by plasma electrolysis are a few technical integrations currently being researched [205–207]. Araujo et al. show that the integration of simultaneous liquefaction with esterification of sugarcane bagasse biomass yields 91% bio-oil and 9% biochar [207]. One of the major benefits of the liquefaction process is the generation of bio-crude which can be upgraded to replace fossil fuel. Also, the process has an energy efficiency of 85–90% and can recover 70% of the carbon content of the feedstock [190]. Furthermore, the bio-crude generated does not require extensive treatment or upgrading for commercial utilization [190]. However, the economics and scale-up of the process become an issue due to the high-pressure and high energy input requirements [190, 203, 204, 208]. The process is still at the lab-scale research stage and requires further understanding of chemistry, kinetics, catalysts, hydrodynamics, and economics before it can be made commercially viable [190].

Pyrolysis

Pyrolysis is the process of thermal degradation of biomass in the absence of oxygen to produce bio-oil, biochar, and gaseous fuel [209]. The fuel obtained has a medium–low calorific value [210]. The high temperature of ~ 500 °C facilitates breakage of the bonds and the release of volatile substances which are condensed into liquid fuel [19, 209]. The pyrolysis oil obtained can be utilized as transportation fuel, electricity generation, and heating [211]. Algal biomass, forest residue, municipal sludge, agricultural residue, waste cooking oil, and lignocellulosic biomass are the possible feedstock for the pyrolysis process [212–214].

The process of pyrolysis occurs in stages, where primary phase decomposition at ~ 450–550 °C releases all the volatile matters present in the woody biomass and forms non-condensable gases like CO, CO_2, and CH_4. The secondary decomposition occurs at temperatures ~ 400–500 °C, causing cracking of the bonds and releasing vapors that can be condensed to form bio-oil. Finally, some extent of repolymerization of the small chain hydrocarbon occurs to form char, bio-oil, and gaseous products [215]. For lignocellulosic biomass, lignin is known to decompose over a larger range of temperature (~ 550–770 K) compared to cellulose (~ 510–620 K) and hemicellulose (~ 470–530 K) which decomposes over shorter temperature ranges [210]. The kinetics, temperature for decomposition, the extent of decomposition, and product composition vastly vary with biomass feedstock, reactor type, temperature, heating rates, and pressure [210].

Fig. 8 Schematic for hydrothermal liquefaction process [196, 202]
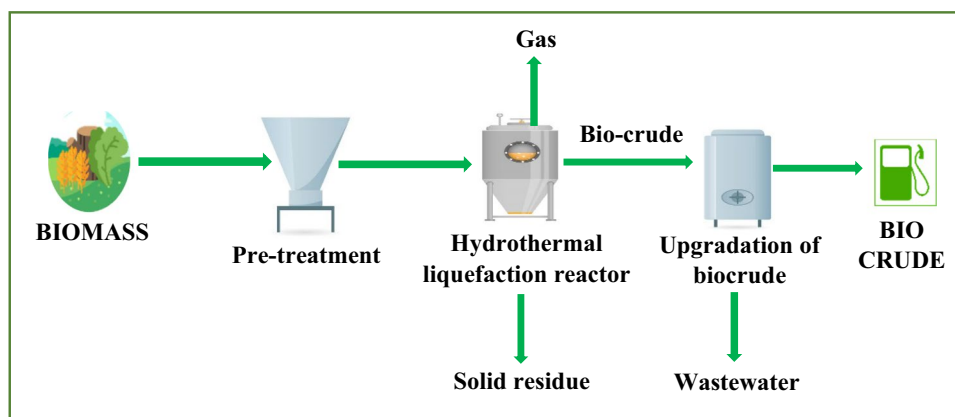
Extensive research is being done to understand the correlations between biomass type, pyrolysis pathways, and kinetics, and the suitable reactor designs to improve pyrolysis conversion [216]. Based on the operating conditions, the pyrolysis process can be categorized into five types [209].

i. *Slow or conventional pyrolysis*: The pyrolysis occurs at a low heating rate (~ 0.1–1 °C/s) with a vapor residence time of 10–60 min [209]. In slow pyrolysis, the first stage of decomposition, called pre-pyrolysis, leads to the internal arrangement and breakage of bonds, the release of water molecules, and the formation of free radicals, carbonyl, and carboxyl groups. In the second stage, fast decomposition of the solid state occurs forming the pyrolysis products. In the third stage, the char decomposes at a slow rate forming carbon-rich solid residue [210]. This process is ideal for producing biochar. Studies show that yield of bio-oil is maximum (~ 24–43 wt%) at an optimum temperature of 500 °C with 34 to 63 wt% of biochar formation [209]. The major disadvantage of this process is excessive cracking of the primary feedstock leading to low-quality bio-oil production [215].

ii. *Fast pyrolysis*: Fast pyrolysis occurs under rapid heating rate (1000 °C/s), higher temperature (500–650 °C), low residence time (0.5–10 s), and using fine particle (< 1 mm) [19, 102, 209, 215]. This process is recommended for producing bio-oil [17]. In fast pyrolysis, the biomass rapidly decomposes to form vapors, aerosols, and a small amount of char. The vapor and aerosols can then be condensed to form bio-oil with a heating value of about half of the conventional fuels [102, 215]. Fast pyrolysis yields a product with 60–75% bio-oil, 15–25% biochar, and 10–20% non-condensed gases depending upon feedstocks [211].

iii. *Flash pyrolysis*: Flash pyrolysis occurs at an extremely high temperature (450–1000 °C), short residence time (< 0.5 s), and very high heating rate with very fine biomass particle size (< 0.2 mm) [102, 215]. Flash pyrolysis can produce bio-oil fractions up to 75% with 80% efficiency [17, 211]. Fluidized bed reactors are preferred for both fast and flash pyrolysis processes [209].

iv. *Catalytic pyrolysis*: Catalytic pyrolysis is done to enhance the bio-oil quality and reduce the oxygen content of the bio-oil. The catalyst also alters the pyrolysis pathway and allows the process to occur at a lower temperature (300–600 °C). Acid and base catalysts are used for the process, with acid catalysts facilitating the production of more biochar, and base catalysts producing more bio-oil [209, 217]. Among all the catalysts, nickel catalysts are found to be better as they activate decarboxylation and decarbonylation reactions during the hydrodeoxygenation process [209].

v. *Hydro-pyrolysis*: This is a novel pyrolysis process that occurs in high-pressure hydrogen conditions with nitrogen used as the carrier gas. Compared to other pyrolysis processes, this method produces hydrocarbon with better structural stability and less oxygen content. The optimum condition for maximized bio-oil and biogas production is 310 °C, 3 MPa, and 60 min. The addition of catalysts and conversion of the process to fast hydro-pyrolysis have been shown to improve the overall bio-oil productivity [209].

Figure 9 shows the schematic for the pyrolysis process. Microwave-assisted pyrolysis is an advancement made in the conversion methodology [209, 218, 219]. This process is slowly gaining importance because of its ability for mass conversion, uniform heating, and easy controllability. However, the process is expensive and is still in the lab scale of operation [209, 219]. Solar pyrolysis is another advancement that has gained importance in recent times due to its usage of solar as the source of energy [220, 221]. The bio-oil obtained from pyrolysis can be used as a feedstock for biorefineries and can also be used in engines and turbines.

Fig. 9 Schematic for the pyrolysis conversion process [19]
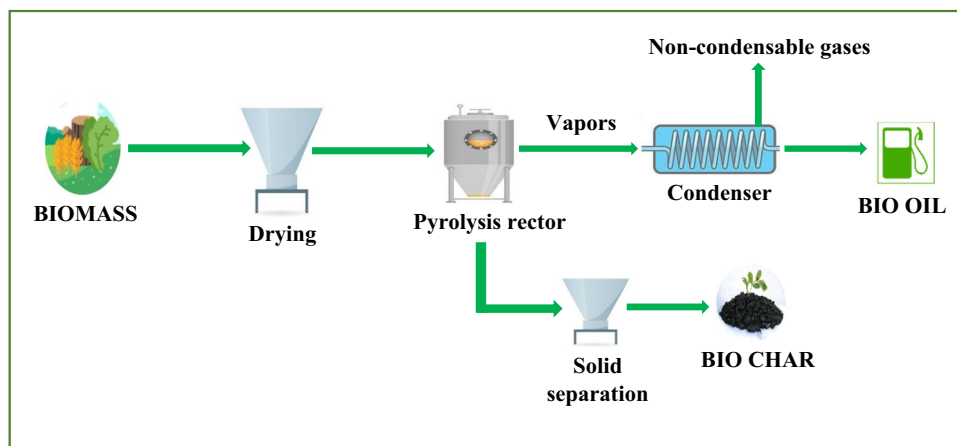
However, poor thermal stability, corrosive nature, and extensive upgradation requirements function as major roadblocks in its commercial application [222]. Oxygen content reduction and alkali removal by dehydrogenation and catalytic cracking are a few treatments needed for the fuel produced to be commercially applicable [223]. Hydrotreating of pyrolysis oil or catalytic cracking can produce naphtha, high octane gasoline, and fuel oil [223, 224].

Torrefaction

Solid biomass has low energy density, high moisture content, low bulk density, low compositional homogeneity, and low shelf life (easily biodegradable) which are hurdles in its applicability as an efficient fuel in the industry [105]. Torrefaction is a thermochemical conversion technology that is applied to upgrade biomass and improve biochar quality as an alternative to coal [225]. Like liquefaction and pyrolysis, torrefaction also occurs in the absence of oxygen-producing solid biomass like biochar or coke as the primary product. The torrefaction of biomass (lignocellulosic, algal, municipal waste, etc.) may occur via (i) wet torrefaction, (ii) dry torrefaction, and (iii) steam torrefaction [226]. The upgraded biomass from the torrefaction process may be commercially used for cofiring or combustion, as a feed for pyrolysis or gasification, as adsorbents for pollution, etc. [105, 227, 228].

Dry torrefaction occurs at 200–300 °C under either oxidative or non-oxidative conditions. In non-oxidative states, nitrogen and CO_2 act as the carrier gas to sweep the biomass during the thermal degradation process [105, 229]. In oxidative torrefaction, air or flue gas may be used as a carrier. The presence of oxygen enables oxidative torrefaction to have a higher reaction rate compared to non-oxidative torrefaction, thus reducing the time for degradation [230]. However, oxidative torrefaction yields lower biochar compared to non-oxidative torrefaction. It is also found that biomass torrefied with higher oxygen concentration and temperature below 300 °C displays a lower heating value. Non-oxidative torrefaction requires high energy input and nitrogen separation from air compared to oxidative state processing [105, 230, 231].

Torrefaction of biomass occurring in the presence of water or dilute acid at 180–260 °C and reaction time of 5–240 min is called wet torrefaction. The solid generated as the product of wet torrefaction is called "hydro-char" [105, 229, 232]. The properties of water like density, viscosity, diffusivity, and dielectric constant change drastically with an increase in temperature which affects the biochar quality during the torrefaction process. Therefore, wet torrefaction is preferably operated under conditions near the subcritical state [233]. It is observed that when biomass is treated with hot compressed water at 180 °C, volatile acids like aldehydes and furfural derivatives get generated which enhances the torrefaction process [105, 234]. The addition of acids like sulfuric acid and acetic acid, to water, is also known to improve the process [235]. A major advantage of wet torrefaction is the non-requirement of any drying pre-processing. Thus, wet biomass feed like sludge, manure, and sewage can be considered for this process. Furthermore, with wet torrefaction, one can obtain a product with higher energy density and mass yield compared to dry torrefaction [236]. Another difference between wet and dry torrefaction is the ash content of the biochar. Ash is inert and its composition in the upgraded biochar increases proportionally after dry torrefaction. However, with wet torrefaction due to the dissolution of minerals in ash into the aqueous phase, the final ash content in the biochar is hugely reduced. The reduction in ash content prevents agglomeration, corrosion, fouling, and slagging during the hydro-char conversion processes [105, 225, 237].

Steam torrefaction is a process where high-temperature and high-pressure steam explosion is used to torrefy the biomass. In this process, the lignocellulosic biomass is treated in a chamber at 200–260 °C using high-pressure and high-temperature steam [105, 238]. The pressure inside the chamber is slowly increased which caused the biomass to swell and disintegrate into separate components. The volatile matter present in the biomass also gets removed by a steam explosion which increases the carbon content and calorific value of the biochar and decreases its mean particle size and bulk density [227, 231, 232, 239]. Furthermore, the biochar derived from steam torrefaction has higher elasticity and mechanical strength compared to wet and dry torrefaction. However, steam torrefaction requires a high energy supply and is expensive [105, 232, 239].

The commercial development of the torrefaction process is still at its initial stages. Various technical aspects like high ash content in the biochar, emission of dibenzofurans and polychlorinated dibenzo-p-dioxins during torrefaction, formation of tar as a by-product (~2000–8000 tons/year of tar gets generated during torrefaction), and scale-up are a few roadblocks in the commercial feasibility of the process [105, 240].

Hydrothermal carbonization (HTC) is a thermochemical conversion process similar to wet torrefaction technology. Many studies have discussed "wet torrefaction" under the terminology of "hydrothermal carbonization" [192, 229, 241, 242]. However, the products formed at the end of both these processes are different in characteristics and usability. The wet torrefaction produces upgraded solid fuels, whereas the hydrothermal carbonization produces charcoal with high carbon content, which can be used as activated charcoal, fertilizers, catalysts, biosensing, supercapacitors, and fuel [192, 229, 243]. The HTC is a process of removing oxygen from biomass via dehydration and decarboxylation reactions (reducing the molar ratios of O/C and H/C), producing a

more coal-like product [192, 242, 244–246]. Analysis of the various process parameters shows that increasing the residence time and operating the reactor under optimum temperature (180–260 °C) and pressure (< 300 bar) conditions can improve the "hydro char" characteristics [192]. A lot of the current research is focused on integrating HTC with wastewater treatment and municipal solid waste treatment to improve energy production and recovery. Industries and researchers are working on developing portable and flexible HTC processes for these integrated systems [242]. However, the treatment and processing of the contaminated water received from HTC as a by-product remains a major challenge for this process [192, 242].

Combustion

Combustion is an exothermic reaction process where the biomass reacts with oxygen (air) at high temperatures to form carbon dioxide, water vapor, and chemical heat. This process accounts for 90% of the total renewable energy generated from biomass [19, 102]. The heat produced from combustion can be converted into useful mechanical and electrical energy [228]. Dry wood, dry leaves, hard vegetable shells, agricultural residues (rice/wheat straws), etc. are some of the feedstocks that are used for the process to produce around 20 MJ/kg biomass of thermal energy [247]. The combustion is carried out inside a combustion chamber at 800–1000 °C for biomass with moisture content less than 50% as shown in Fig. 10 [19]. High moisture content biomass is better suited for biochemical conversions. The generated heat from combustion is used to produce steam which is fed to a turbine to generate electricity.

The current biomass combustion plants generate 20–50 MW of electricity with electrical conversion efficiencies of 25–30%. With the incorporation of processing techniques like fluidized bed systems and improved gas processing, the production can be upgraded to 100–3000 MW with conversion efficiencies up to 30–40% [17, 19, 248, 249].

Integration of biomass combustion with coal-fired power generation is also attractive as it improves the conversion efficiencies [105, 250, 251]. The process of converting biomass to energy by combustion is a conventional route that is widely implemented both at the commercial and household level. However, the emissions of particulate matter and CO_2 are the major concerns with the process [247, 252]. Chemical looping combustion (CLC) integrated with biomass feedstock (bio-CLC) which combines bioenergy with CO_2 sequestration is a novel technique to reduce CO_2 emissions [253]. The CLC consists of air and a fuel reactor. Oxygen carriers in the form of metal oxides carry oxygen from the air reactor to that of the fuel reactor, where it reacts with the fuel to produce H_2O and CO_2. This process enables pure CO_2 generation which can be easily sequestered without any further processing [253, 254].

Gasification

Gasification is the conventional process of converting biomass into the combustible gas mixture (CO, H_2, CO_2, CH_4, and N_2) called syngas or synthesis gas and biochar by partial oxidation at a high temperature of around 800–1100 °C [255]. Syngas, which normally have the lowest heating value (LHV) of 4–13 MJ/N m^3, can be used to generate electricity, petrochemical products, methanol, and hydrogen [255]. The char produced contains carbon, unconverted organic residue, and ash and has an average LHV of 25–30 MJ/N m^3 [255]. The composition of the char majorly depends upon the gasification methodology and biomass type and quality. Lignocellulosic biomass, forest residues, agricultural residue, etc. can be as feedstock for gasification [256, 257]. Pre-treatment and drying of the biomass are required before it can be converted. It is observed that the initial moisture content of the biomass adversely affects the LHV of the biofuel produced [255].

Gasification is an endothermic process and is conducted in an air-tight chamber under air suction or low air pressure

Fig. 10 Schematic for the combustion process [19]
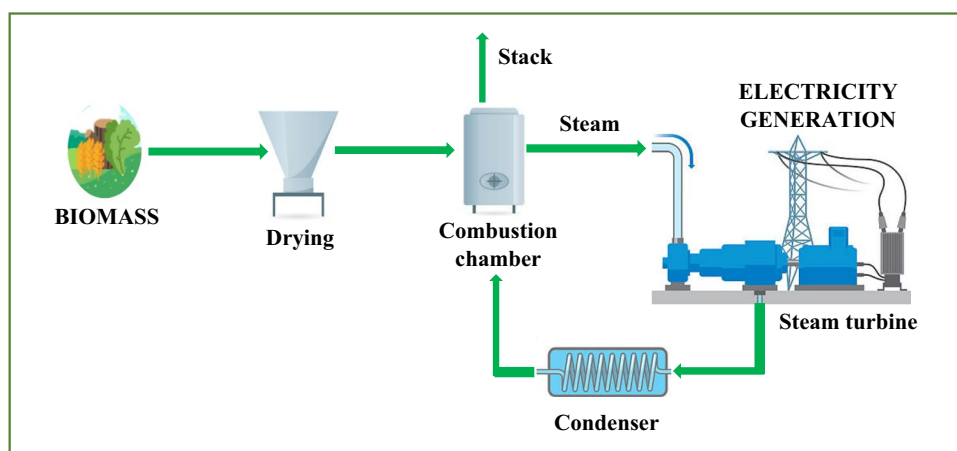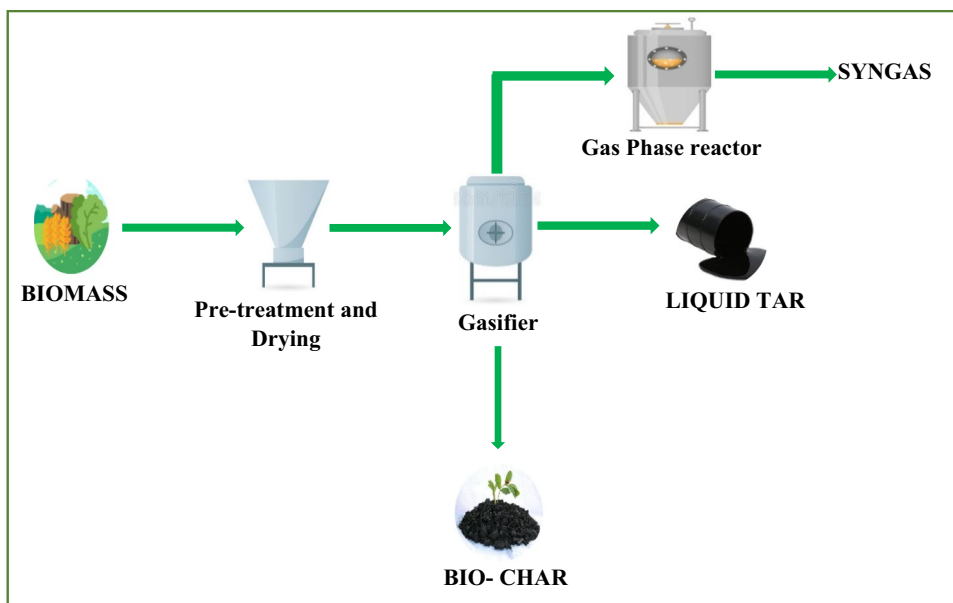
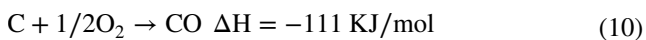**Fig. 11** Schematic for biomass gasification process [19]

condition as shown in Fig. 11. The heat energy required for the process is derived from partial oxidation of the biomass feed. The gasification process follows five major steps in series [255]

i. *Oxidation to generate heat*: The partial oxidation of the biomass is an essential step to generate the heat required for gasification and maintaining the temperature. The oxidation occurring in absence of oxygen (given in reactions 9–11) produces CO, CO$_2$, H2O, and heat [255]. Though all the carbonaceous components present participate in the reactions, it can be simplified to consider the involvement of only char and hydrogen contained in the syngas [255].

Char combustion:

$$C + O_2 \rightarrow CO_2 \quad \Delta H = -394 \text{ KJ/mol} \tag{9}$$

Partial oxidation:

$$C + 1/2O_2 \rightarrow CO \quad \Delta H = -111 \text{ KJ/mol} \tag{10}$$

Hydrogen combustion:

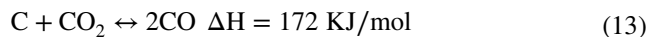$$H_2 + 1/2O_2 \rightarrow H_2O \quad \Delta H = -242 \text{ KJ/mol} \tag{11}$$
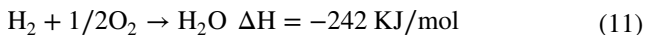
ii. *Drying*: Drying is an essential step for removing moisture from the biomass. The amount of heat required for drying is proportionately dependent on the amount of moisture content. The process of drying can be considered complete when the biomass temperature reaches the temperature of 150 °C [255].

iii. *Pyrolysis*: This is the stage where thermochemical decomposition of the biomass takes place at 250–700 °C. The long chains of hydrocarbon break down into shorter chains of lower molecular weight compounds producing solid, liquid, and gaseous fractions. The solid (biochar) yield is around 5–10 wt% for fluidized bed gasifiers and 20–25 wt% for fixed bed gasifiers. The liquid (tar) yield in downdraft gasifiers is around 1 wt%, 1–5 wt% in bubbling bed gasifiers, and 10–20 wt% for updraft gasifiers. The gaseous fraction (pyrolysis gas) is typically 70–90 wt% and comprises incondensable gases like hydrogen, CO, CO$_2$, and light hydrocarbons. The process of pyrolysis is complex and is governed by numerous factors like heat transfer, diffusion, and kinetics. At low temperatures, the process is kinetic controlled, but it becomes heat transfer controlled at higher temperatures [255]. The overall reaction for pyrolysis is as given below in reaction 12.
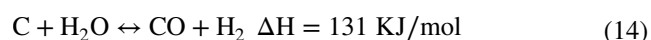
$$Biomass \leftrightarrow H_2 + CO + CO_2 + CH_4 + H_2O(g) + Char + Tar \tag{12}$$
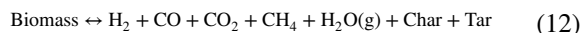
iv. *Reduction*: In the reduction step, the char and gaseous products from the above two stages react together to form the syngas as given in reactions 13–16. As the reactions are reversible, the temperature of the reduction stage defines the composition of the syngas. Higher temperature reduces char formation and increases tar and syngas fraction. However, it may also lead to increased ash sintering and a reduction in the energy content of the syngas [255].
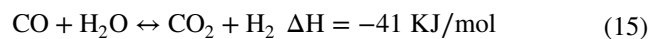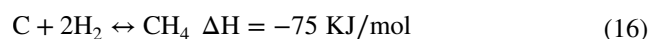
Boudouard reaction:

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H = 172 \text{ KJ/mol} \tag{13}$$

Reforming of the char:

$$C + H_2O \leftrightarrow CO + H_2 \quad \Delta H = 131 \ KJ/mol \qquad (14)$$

Water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41 \ KJ/mol \qquad (15)$$

Methanation reaction:

$$C + 2H_2 \leftrightarrow CH_4 \quad \Delta H = -75 \ KJ/mol \qquad (16)$$

v. *Tar decomposition*: The tar formed during pyrolysis also decomposes and contributes to the reduction step. CH_4 and short-chain hydrocarbons are formed as products from this stage as given in reaction 17.

$$C_nH_m \leftrightarrow C_{n-x}H_{m-y} + H_2 + C + CH_4 \qquad (17)$$
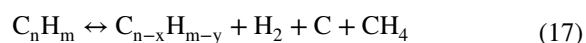
The syngas via gasification can be produced by either the catalytic or non-catalytic route. The non-catalytic process occurs at an extremely high temperature of ~ 1300 °C, whereas the catalytic gasification can be done at a lower temperature of ~ 800 °C [102, 189, 258]. Hu et al. are researching chemical loop biomass gasification (CLG) using F_2O_3/CaO catalyst to produce hydrogen-rich syngas. They observe that the hydrogen production using CLG is 1.88 times more compared to normal steam gasification [258]. For transportation liquid fuel production, Fischer–Tropsch (FT) synthesis or methanol synthesis route of syngas conversion is employed [257]. Recently, efforts are being made to produce renewable aviation fuel via gasification and FT synthesis [257]. Macri et al., in their work, proposed supercritical water gasification (SCWG) as the route to improve bio-hydrogen production [259]. They observe that the presence of excess water during gasification promotes water gas shift reaction as well as steam reforming during the reduction stage increasing hydrogen production. Furthermore, SCWG can be employed on biomass with high moisture content like algal biomass [259]. Biomass integrated gasification with combined cycle (BIG/CC) can convert syngas into electricity at a high conversion efficiency of ~ 40–60% for a plant capacity of 30–60 MW. This is a process that utilizes purified syngas thus reducing further processing costs. However, this process is still in the pilot stage [260, 261]. Similarly, microwave-assisted gasification processes are also being researched at a lab scale [262]. Suárez-Almeida et al. are currently studying solar gasification of biomass in a dual fluidized bed gasifier where the solid particle acts as the thermal energy carrier [263].

Gasification for syngas production or electricity production is at pilot or small-scale developmental stages. One of the major disadvantages is that the producer gas contains contaminants such as particulates, tar, alkali metals, H_2S, and NH_3, which causes blockage and corrosion problems and requires extensive processing before the application [264, 265]. Also, technological advancements are needed to develop compatible engines for syngas applications [255, 259].

Physical Conversion Methods

Mechanical Extraction

The crude oil from crops and microalgae can be extracted by applying mechanical pressure using a screw press [102, 171]. The mechanical pressing can be done either by (i) full pressing or (ii) pre-pressing method. The full pressing employs 95,000 kPa of pressure on the oilseeds to extract up to 3–5% of residual oil. Pre-pressing is normally employed in integration with the solvent extraction process, where 18–20% of oil is removed from the crop using pressing and the rest of it by solvent extraction [102, 266]. This process is commonly employed for biomass with high oil content (~ 30–40%) [102]. Wu et al. have combined enzymatic hydrolysis with intermittent ball milling to increase the lignocellulosic biomass conversion to 84.7% [267]. Mechanical extraction is normally combined with the transesterification process to convert the extracted oil into biodiesel and other value-added bioproducts. This method of oil extraction is well established and orthodox but is often time-consuming and energy inefficient, and demonstrates low yield [268, 269].

Briquetting/Pelleting

The biomass received in bulk is often pre-processed into briquettes and pellets for transportation, storage, and application in biorefineries as feedstock [270]. The most common pre-processing required is the densification of the biomass either by (i) pressing or (ii) maceration (chopping, grinding, etc.). By pressing, the density of the biomass increases proportionately to the amount of pressure inflected [271]. The briquetted biomass is also recommended for usage as primary biofuel for traditional cooking and space heating as it increases burning efficiency and reduces emissions and pollution [272, 273]. The process of briquetting is conventional and widely used but is expensive and needs economic analysis and technical improvements to have commercial success [271].

Distillation

Steam distillation and hydro-distillation are two of the most extensively used techniques to extract oils, essential oils, and many other value-added products from biomass [274]. The volatile matters present in the biomass are allowed to vaporize using steam and then collected and processed [275]. A more recent development is the use of molecular distillation

for the extraction of temperature-sensitive components where conventional methods cannot be applied [276, 277]. In molecular distillation, the distance between the evaporation and condensation surfaces is less than the mean free path of the molecules [277].

Feasibility Analysis — Prospects and Challenges

The biomass to energy conversion technologies is at various stages of development. Table 6 provides a detailed comparison between different biomass to bioenergy conversion technologies, their economics, scale-up possibilities, commercial feasibility, and the current state of development.

Conversion processes like fermentation and anaerobic digestion are well established and economic, and have high commercial feasibility for 1G biomass conversion. However, as first-generation biomass feedstocks, like sugarcane and corn, compete for both food and fuel, their viability for fuel production is low. This is one of the major reasons why, despite being the second-largest producer of sugarcane, countries like India, China, and Brazil are yet to establish commercial large-scale plants for 1G bioethanol production. Lignocellulosic or algal biomass conversion to energy is more lucrative because of their abundant availability; however, their pre-treatment processes and scale-up are a major bottleneck. Furthermore, algal biomass technology is still at its preliminary stages of development and its conversion methodologies are extremely energy-intensive making its commercial feasibility low. Thus, fermentation and anaerobic digestion for 2G bioethanol production have a high possibility but moderate feasibility until the lignin pre-treatments and its scale-up are improved. Viabilities of chemical hydrolysis and enzymatic hydrolysis are also largely decided by the pre-treatment technologies and the cost of production.

Supercritical conversion and liquefaction technologies have enormous potential in terms of fuel production efficiency and fuel quality. However, the high-pressure requirement is a huge barrier to their large-scale productivity. The development of catalysts to improve the reaction pathway and reduction in pressure and temperature requirements for these processes may enhance the possibility. Similarly, processes like combustion and gasification are well understood and are currently used but have problems with GHG emissions. Integration of these processes with CO_2 sequestration and their economic analysis is needed to make the process environment-friendly. Processes like torrefaction, HTC, and pyrolysis are still in the lab and pilot stages of development and lack cost information, optimized process parameters, and post-treatment methodologies leading to uncertainties about their commercial applicability. However, appropriate technological interventions like reactor design and catalyst

development for bio-oil upgradation will allow the processes to be commercially developed. Thermochemical and bio-chemical conversion processes integrated with microwave technology or ultrasound technologies are novel and they improve the conventional methods; however, their scale-up is a challenge. The energy analysis of each of these processes is required to understand the energy efficiencies. Many of these processes like gasification, microwave or ultrasound-assisted processes, or processing that require drying of biomass will have huge energy input. Thus, if this energy is derived from fossil fuels, then they do not serve the purpose. Alternatively, the integration of renewable energy resources is needed to make the system self-sustainable.

Modeling and simulation-based analysis of the bioenergy conversion processes is an alternate route to understand the behavior of the systems, perform parametric analysis and optimization, and improve the design, technology, and overall productivity [32, 33, 278]. These modeling techniques allow holistic development of the processes, reduce time and labor-intensive experiments, and lead to rapid technological advancements. In recent times, a lot of emphases are given to integrating artificial intelligence (AI)/artificial neural networks (ANN) and machine learning (ML) frameworks into these modeling techniques to enhance their performance [278]. Application of various optimization techniques like ant colony algorithm (ACA), genetic algorithm (GA), fuzzy logic, and particle swarm optimization (PSO) to the biological and chemical processes allows improved optimization of parameters like temperature, pH, hydraulic retention time, and substrate concentration [278, 279]. Machine learning frameworks with various optimization algorithms have allowed researchers to optimize different bioenergy conversion technologies like pyrolysis, anaerobic digestion, and the supply chain for biofuel processing involving biomass cultivation, feedstock quality control, processing, and emissions [280–284]. Khan et al. and Ullah et al. applied ANN integrated with various optimization algorithms like GA, PSO, and grey wolf optimization, to predict bio-fuel formation in the pyrolysis process using biomass characteristic and pyrolysis condition data [282–284]. Similarly, Aniza et al. integrated supervised ANN with the Taguchi method to maximize the bio-oil and bio-char yield for pyrolysis and torrefaction processes [285]. Pereira et al. applied AI with a PSO algorithm to optimize industrial bioethanol production [286]. The results show that optimization of the input parameters like biomass purity and pH, fermentation time, and temperature leads to a 10% increase in bioethanol productivity [286].

Thus, these techniques can be successfully implemented to develop a better understanding of the processes and improve their engineering at a reduced cost, time, risk, and labor [278]. These models can be used to optimize the problems of biomass collection, transportation, and segregation

Table 6 A comparison of different biomass to bioenergy conversion methods

Method	Biomass type	Advantages	Disadvantages	Scale-up	Economics	Feasibility	Status
Biochemical conversion methods							
Fermentation	Starch and sugar-based biomass; lignocellulosic biomass; algal biomass; biomass with high moisture content	• An established process • High yield of bioethanol • High purity products can be achieved (e.g., 99.99% ethanol from sugarcane) • Novel techniques can produce bio-hydrogen	• Too many parameters to optimize and control • For lignocellulosic biomass pretreatment and enzymatic hydrolysis is a problem • Separation and reuse of yeast from SSF is difficult	1G — moderately easy to scale up; 2G and 3G — difficult to scale-up	1G — economic; 2G and 3G — expensive	1G — moderate 2G and 3G — low	1G — established; 2G — pilot-scale 3G — lab-scale
Anaerobic digestion	Agricultural residue; municipal solid waste; sewage sludge; biomass with high moisture content	• Biogas produced can generate electricity • Better waste management • Lower investment and costs	• Converts into fuel with less energy content compared to the feedstock • Purification of methane and storage is costly • The process has too many parameters to maintain and control	1G — moderately easy to scale-up; 2G — difficult to scale-up	1G — economic; 2G and 3G — expensive	1G and 2G — moderate; 3G — low	1G and 2G — established; 3G — lab-scale
Enzymatic hydrolysis	Starch and sugar-based biomass; lignocellulosic biomass; algal biomass	• Easy hydrolysis • Can use lignocellulosic and algal biomass	• The pre-treatment cost of lignocellulosic is high • Enzyme cost is expensive • Scale-up is a problem	Difficult to scale-up	Expensive	Moderate to low	Pilot-scale
Physicochemical conversion methods							
Transesterification	Waste vegetable oil; oil-containing seeds like palm and *Jatropha*; algal biomass	• Produces biodiesel • Replacement of diesel in automobiles • Converts waste vegetable oil	• Re-usability of catalyst is difficult • Integration of process with other methods is needed for feasibility • Downstream purification is expensive	Easy to scale-up	Expensive	High to moderate	Established
Chemical conversion methods							
Hydrolysis	Starch and sugar-based biomass; lignocellulosic biomass; algal biomass	• Can be used for different biomass	• Reactor construction is expensive corrosion • Formation of inhibitory components	Easy to scale-up	Expensive	High to moderate	Established
Solvent extraction	Oil-containing seeds like palm and *Jatropha*; algal biomass	• A well-established process	• Conventional extraction is not efficient	Easy to scale-up	Economic	Moderate	Established

Table 6 (continued)

Method	Biomass type	Advantages	Disadvantages	Scale-up	Economics	Feasibility	Status
Supercritical conversion of biomass	Lignocellulosic biomass; biomass with high moisture content	• Lignocellulosic biomass does not need pre-treatment • Produces bio-hydrogen	• Requires high temperature and pressure conditions	Difficult to scale-up	Expensive	Low	Lab-scale
Thermochemical conversion methods							
Liquefaction	Lignocellulosic biomass; algal biomass	• Produces stable bio-oil with a high heating value • Produces bio-crude as a replacement for fossil fuel	• High-pressure requirements for the process • High energy requirement	Difficult to scale-up	Expensive	Moderate to low	Lab-scale
Pyrolysis	Algal biomass; forest residue; municipal sludge; agricultural residue; lignocellulosic biomass	• Produces bio-oil to be used as a transportation fuel • Multiple feedstocks can be used	• The bio-oil produced is corrosive, has low oxygen content, and requires extensive upgradation	Moderately easy to scale-up	Expensive	Moderate	Pilot-scale
Torrefaction	Lignocellulosic biomass; algal biomass; municipal waste	• Produces biochar with coal-like properties • Wet torrefaction does not require pre-drying treatment	• High ash content in the final product • Emission of dibenzo-furans and polychlorinated dibenzo-p-dioxins	Difficult	Expensive	Low	Lab-scale
Combustion	Dry wood; dry leaves; hard vegetable shells; agricultural residues	• Conventional route • It can be integrated with coal-fired • Produces electricity	• Requires pre-treatment and drying • Particulate matter emission if high CO_2 emission	Easy to scale-up	Economic	High	Established
Gasification	Lignocellulosic biomass, forest residues, agricultural residue	• Well-understood process • Produces syngas, electricity, bio-hydrogen, and methanol	• Requires pre-treatment and drying • Contaminants of producer gas need treatment • Syngas based engine compatibility improvements needed	Easy to scale-up	Expensive	High	Small-scale established
Physical conversion methods							
Mechanical extraction	Oil-containing seeds like palm and *Jatropha*; algal biomass	• Well-established process • Inexpensive	• Energy inefficient • Low yield • Environment unfriendly • Time-consuming	Easy to scale-up	Economic	High	Established

Table 6 (continued)

Method	Biomass type	Advantages	Disadvantages	Scale-up	Economics	Feasibility	Status
Briquetting	Lignocellulosic biomass; agricultural residue; woody biomass	• Well-established process • Easy transportation and burning	• Expensive process	Easy to scale-up	Expensive	High	Small-scale established
Distillation	Oil-containing seeds like palm and *Jatropha*; algal biomass	• Well-established process	• Not fully efficient	Easy to scale-up	Economic	High	Established

[280, 287]. However, validation of these models will require lab-scale and pilot-scale experimentations. Moreover, all the AI/ML-based models require a huge amount of data for model development. The authenticity and availability of the data will limit the usability and validity of these models. Thus, authentic data collection, data validation, data cleaning, and sorting will be crucial for these techniques to be successful. Suitable identification of the parameters, network architecture, AI/ML framework, and model validations are also critical when implementing these technology advancements [280, 281, 287].

The commercial feasibility of biomass to energy conversion technology depends upon the type of biomass feed and its cost, ease of biomass collection, segregation, storage and transportation, ease of operation, cost of production, ease of scale-up, product quality, and environmental and government policies.

a) The entire biomass supply chain starting with biomass collection and segregation followed by storage and transportation to the point of conversion is currently an extremely cost-intensive process [288]. The agricultural biomass collection and segregation are normally done at the point of farming. However, collection and segregation of forest residue and municipal waste collection are a major logistics problem due to lack of access and cost [289, 290]. Many technological interventions like chipper, tractor and guillotine blades, multi-tree handling devices, harvesters, and forwarders are employed for forest residue collection; however, the process is cost-intensive and lacks global standardization [289]. The storing of the biomass collected is the next logistic challenge. Biomass containing 15–20% moisture may be stored without drying at a reduced cost of storage, but material loss during handling and loss of heating value needs to be analyzed [288]. However, biomass feedstock with high moisture content requires drying before storage and expensive storage facilities to avoid biomass degradation [288, 290]. Multi-agricultural biomass approach is suggested by Rentizelas et al., to reduce the storage requirement and the cost by combining different agricultural biomass to be stored and transported together [288]. Finally, the transportation of the biomass to the conversion facility is governed by the distance and location of the conversion facility, biomass density, load capacity of the vehicle, and traveling speed [290–294]. The preferable logistics and methodology for collection, storage, and transportation are decided by the cost of the process. AI/ML-based supply chain modeling and analysis can help decide the most optimized options [280, 290].

b) Once biomass feedstock reaches the location, the conversion process is decided based on the type of bio-

mass, product requirement, and cost of production. As discussed previously, lignocellulosic biomass, municipal waste, agricultural and forest residues, etc. have immense potential to become the preferred source of bioenergy provided the pre-treatment processes are made more economical and their technological barriers to scale-up are removed. Biochemical and thermochemical processes like fermentation (normal, dark, and photo), anaerobic digestion, and torrefaction are the most scalable processes that can be commercialized to produce bio-methanol, bio-ethanol, and bio-hydrogen. Large-scale algal biomass generation is also a lucrative option if the challenges of huge water and nutrient requirements, and large energy need for drying are addressed. Moreover, integrated processes and integrated biorefineries demonstrate improved productivities compared to standalone conversion methods but require more technological interventions.

c) Most of the conversion processes being researched are energy-intensive. Drying the biomass for energy conversion requires a huge energy input, which is currently derived from fossil fuels. Also, though we consider biomass as CO_2 neutral process, many of the conversion technologies like pyrolysis, combustion, and gasification produces CO_2 during the process. Furthermore, burning of the bio-char or hydro-char will also release CO_2 and other GHG. Mat Aron et al. has provided a detailed analysis of GHG emissions from different conversion process and concluded that there is no conversion process with net-zero GHG emissions; however, the emissions are much lesser compared to fossil fuel burning [40]. Thus, analysis of energy requirements for the process and the GHF emissions during the process and post-processing is imperative to choose the most energy-efficient and environment-friendly process. Furthermore, fourth-generation (genetically modified) algal biomass may be developed to sequester the GHG and increase lipid production [40].

d) Finally, the policies and government interventions for standardization of biomass price and quality control are necessary. Government subsidies, support plans, and price incentives are also required to encourage industries to invest in the commercialization processes [295]. Policy interventions are also essential to encourage the 1G ethanol producers to move toward 2G ethanol production, thus increasing food security [295, 296]. Another approach to expanding the biofuel sector is to establish small-scale biofuel plants in rural settings to meet their local energy needs via clean and sustainable routes [296]. Finally, to improve the global market for biofuels and create a global need, international collaborations and global market-oriented policies for the biofuel sector are crucial [296, 297].

Conclusions

Biomass as an alternate energy source is lucrative and has immense potential to be developed into a commercially viable solution to energy challenges and waste management. Biomass is abundantly available throughout the world which allows biorefineries to be established at any geographical location. Biomass as a source of energy can fulfill the electricity, heat, and transportation fuel needs. However, policy interventions are required to standardize biomass feedstock collection, distribution, transportation, and cost. Efforts are also needed to make conversion technologies more economic, easy to scale up, user-friendly, and with improved productivity. More emphasis is needed to improve the lignocellulosic biomass, forest and agricultural residues, and municipal waste pre-treatment and conversion processes. The choice of the best conversion technology will be decided by the ease of operation and cost of production along with its energy efficiency and environmental impact. Based on the current analysis, 2G biomass conversion via biochemical and thermochemical pathways holds the most prospects. However, this study is limited to bringing an overview of the entire biomass to energy process and the technological interventions. Some limited discussions on the collection, segregation, transportation of biomass, AI/ML-based modeling, and optimization routes and policies are presented. However, the biomass pricing and economics of the processes are not reviewed here. Furthermore, a more detailed discussion is entailed on challenges in storage and transportation of biomass, policies, and other modeling and simulation-based approaches to improve bioenergy generation.

Author Contribution Dr. Nilanjana Banerjee: conceptualization, data collection, writing and reviewing of the paper. This is a single authorship paper.

Declarations

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