

Review

A Review of Thermochemical Conversion of Waste Biomass to Biofuels

Shivangi Jha ^{1,2}, Sonil Nanda ¹ , Bishnu Acharya ¹ and Ajay K. Dalai ^{1,*}

¹ Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, SK S7N 5A9, Canada

² School of Environment and Sustainability, University of Saskatchewan, Saskatoon, SK S7N 5C8, Canada

* Correspondence: ajay.dalai@usask.ca; Tel.: +1-(306)-966-4771

Abstract: Biofuels are sustainable alternatives to fossil fuels because of their renewable and low-cost raw materials, environmentally friendly conversion technologies and low emissions upon combustion. In addition, biofuels can also be upgraded to enhance their fuel properties for wide applicability in power infrastructures. Biofuels can be produced from a wide variety of biomasses through thermochemical and biological conversion processes. This article provides insights into the fundamental and applied concepts of thermochemical conversion methods such as torrefaction, pyrolysis, liquefaction, gasification and transesterification. It is important to understand the physicochemical attributes of biomass resources to ascertain their potential for biofuel production. Hence, the composition and properties of different biomass resources such as lignocellulosic feedstocks, oilseed crops, municipal solid waste, food waste and animal manure have been discussed. The properties of different biofuels such as biochar, bio-oil, bio-crude oil, syngas and biodiesel have been described. The article concludes with an analysis of the strength, weaknesses, opportunities and threats of the thermochemical conversion technologies to understand their scale-up applications and commercialization.

Keywords: biofuels; pyrolysis; torrefaction; liquefaction; gasification; transesterification



Citation: Jha, S.; Nanda, S.; Acharya, B.; Dalai, A.K. A Review of Thermochemical Conversion of Waste Biomass to Biofuels. *Energies* **2022**, *15*, 6352. <https://doi.org/10.3390/en15176352>

Academic Editors: Federico Galli, Samira Lotfi and James Butler

Received: 6 August 2022

Accepted: 30 August 2022

Published: 31 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Renewable resources such as wind, nuclear and solar power are promising alternative sources of energy to complement fossil fuel resources. However, they cannot produce liquid or gaseous fuels for transportation as well as combined heat and power generation. Furthermore, they are seasonal and largely dependent on the weather, atmospheric, or environmental conditions. It should be noted that some of these renewable resources have certain geographical and environmental limitations. For example, wind and tidal energies account for the channeling of wind and water, whereas solar energy is preferred in regions with adequate hours of sunlight. On the other hand, biomass-derived energy in the form of bioenergy is preferable because they are available in most regions of the world. However, biomass can be converted to energy, energy carriers, and value-added chemicals via thermochemical (e.g., gasification and pyrolysis) and biological conversion processes (e.g., anaerobic digestion and fermentation) [1]. Renewable energy supply attributed to nearly 14% of the world's total primary energy supply in 2018 [2]. It is estimated that the global demand for biofuels can rise to 41 billion liters by 2026 [3]. Currently, the worldwide demands for bioethanol, renewable diesel, biodiesel and bio-jet fuels are 17, 14.5, 7.6 and 1.5 billion L/year. In terms of regions, North America (15.9 billion L/year) has the maximum total demand for biofuels followed by Asia (10.8 billion L/year), Latin America (10.4 billion L/year) and Europe (3.4 billion L/year) [3].

The rising energy consumption, growing demands for fossil fuels, soaring fuel prices, and increasing levels of greenhouse gas (GHG) emissions are some of the issues contributing to the need for a global shift towards renewable energy. Waste biomasses such as oil seed crops, lignocellulosic materials (e.g., agricultural and forest residues), microalgae,

energy crops, manure, food waste and organic fraction of municipal solid waste have a huge potential to provide energy and value-added products via different conversion technologies. Some examples of thermochemical processes are liquefaction, pyrolysis, gasification, torrefaction, carbonization, transesterification and catalytic processes, whereas fermentation, biomethanation and enzymatic processes are widely used biological technologies for biomass conversion [4]. In biological conversion methods, biomass residue is hydrolyzed chemically and enzymatically to release the fermentable components after which responsible microorganisms degrade them to produce high-value products such as biofuels and biochemicals. In the thermochemical conversion processes, the feedstocks undergo thermal breakdown of the organic components regardless of microbially fermentable matter (i.e., saccharides) and non-fermentable components (i.e., lignin) to produce biofuels and biochemical building blocks. Compared to biological conversion processes, thermochemical methods have faster reaction rates due to the involvement of high temperatures, pressures and catalysts.

The composition and characteristics of biomass largely impact the process parameters, reaction rate as well as yields and quality of the conversion products. The main properties of biomass can be determined through proximate and ultimate composition [5]. The proximate composition is measured through the levels of moisture, ash, fixed carbon and volatile matter. On the other hand, the ultimate composition includes carbon, hydrogen, nitrogen, sulfur and oxygen. Ash includes mineral matter that remains as a residue after combustion. Higher ash content could be a challenge for the formation of agglomeration and cause sintering and corrosion during thermochemical conversion, especially in combustion, pyrolysis, gasification and co-firing [6]. In addition, the higher moisture content in biomass results in greater energy input to dry the feedstock before their thermochemical conversion and reduced heating value of the biofuel product. The calorific value of the conversion product can be improved with lower contents of moisture, oxygen and ash [7].

Biomass conversion technologies are variable depending on their processing requirements such as feedstock properties, process parameters, and product types and composition. Hence, it is often difficult to make a comparative assessment of the thermochemical and biological conversion technologies. In addition, an articulate understanding of the sources, classification, origin and physicochemical properties of different waste biomass is lacking, which impacts both upstream and downstream processing of biorefineries. Although the applications of widely used thermochemical technologies are well documented, insights into their fundamental concepts are lacking in the existing pool of literature. With this objective, this article presents an overview of different waste biomass classifications based on their source, origin, composition and physicochemical properties. Subsequently, different thermochemical biomass conversion technologies such as torrefaction, pyrolysis, liquefaction, gasification and transesterification are described based on their fundamental operating principles, parameters, applications and product type and composition. Lastly, the properties of different products from thermochemical conversion of biomass such as biochar, bio-crude oil, bio-oil, syngas and biodiesel are described in this review article.

2. Classification of Waste Biomass and Biogenic Materials

2.1. Lignocellulosic Biomass

Lignocellulosic biomass is a sustainable, cost-effective and carbon-neutral feedstock that characteristically contains cellulose (40–60 wt.%), hemicellulose (20–40 wt.%) and lignin (10–24 wt.%). Some of the sources of lignocellulosic biomass are agricultural crop residues, forestry biomass and energy crops. Agricultural wastes are the residues produced by the harvesting and processing of agricultural vegetative crops. Crop residues are generally divided into two types such as field residues and agro-food processing residues. Since these agro-residues are non-edible, they pose no competition to the food supply or fertile arable lands. Regardless of the environmental, societal, and profitability of woody biomass in different valuable products for household, industrial, construction and power sectors, most of the forestry biomass remain underutilized. Some barricades that restrain the utilization

of agricultural and forest biomass for the production of bioenergy are associated with their seasonal, geographical and climatic variations, which determine their availability and cost.

Research interest in energy crops has augmented worldwide due to their diversity, rapid growth, high production rate, the potential to fix CO₂ during photosynthesis, cost-effectiveness and resilience to grow on marginal quality soils [8]. Therefore, their cultivation can encompass a substantial probability to biofuel industries to fulfill the clean energy necessity. Some common energy crops include switchgrass, elephant grass, timothy grass, *Miscanthus* and hybrid poplar.

2.2. Oilseed Crops

Plant-based oils have traditionally been a significant agrarian commodity. Several species of plants contain oil in the form of fatty acids, lipids, triglycerides and triacylglycerol. These components are stored in plant seeds and cells as reserves of carbon and energy for the improvement of seedlings. The structural similarity of triacylglycerol with long-chain hydrocarbons forms a foundation for a viable alternative to hydrocarbon-based products. Moreover, owing to the physicochemical properties of fatty acids, the non-edible plant-based oils are used to produce biodiesel and components as an integral part of paints, coatings, lubricants and inks. There is a great demand for plant oils in agricultural, nutraceuticals, cosmeceutical, pharmaceutical, food and biorefining industries.

Many plant-based oils are consumed as edible oils in cooking and food processing such as canola oil, vegetable oil, mustard oil, olive oil, sunflower oil, soybean oil, corn oil, almond oil, grapeseed oil and coconut oil. Non-edible plant-based oils are extracted from microalgae, *Ailanthus altissima* (heaven tree), *Azadirachta indica* (Neem), *Jatropha*, *Linum usitatissimum* (flax), *Madhuca longifolia* (Mahua), *Pongamia pinnata* (Karanja), *Ricinus communis* (Castor), *Sapindus mukorossi* (Soapnut), *Toona sinensis* (Juss), *Vernicia fordii* (Tung), rubber seed, silk cotton tree, etc. [9]. The fraction of oil fluctuates noticeably in different oilseed crops. However, it can be inferred that there is scope for genetically engineering the oilseed plants to generate a greater concentration of oils. Using oil seeds for biofuels and biodiesel production is an excellent way to replace petroleum-based sources.

2.3. Municipal Solid Waste

The waste materials (e.g., garbage, recyclable and non-recyclable residues) obtained from municipalities including households are known as municipal solid waste (MSW). MSW could also include Industrial, Commercial and Institutional (ICI) waste such as those discarded residues from businesses, large industries, hospitals, institutions, schools, colleges and universities. It should be mentioned that the composition of MSW and ICI varies depending on the origin, production patterns, household income and geographical location [10]. MSW contains items such as kitchen and household materials, plastic and rubber, metals, paper and cardboards, inert materials, electronic wastes, etc. [11]. MSW also consists of biodegradable and non-biodegradable fractions. It should be mentioned that about 15% of the total waste generated in municipalities is recycled while the remaining is disposed of in landfills or dumped in open sites [12].

The worldwide surge in MSW generation is primarily due to the rise in population, urbanization and industrialization. The global production of MSW has surpassed 1.2 billion tonnes per year with a projection to exceed 2 billion tonnes annually by 2025 [13]. It is projected that in some developing countries and other parts of the world, the MSW generation could reach or exceed that of developed nations without proper regulations and provisions for landfilling and waste recycling facilities [14]. The growth in the rate of generation of MSW is also related to the change in food habits, consumption patterns, consumer behavior and standards of living in rural and urban areas.

MSW generation creates severe environmental pollution when unmanaged. Moreover, its conversion into value-added products could provide a solution to the challenges of energy shortage and sustainable waste management. Various ways by which MSW can be disposed of, recycled or valorized into energy resources are through landfilling, composting,

anaerobic digestion, pyrolysis and gasification [11]. The incineration of 1 ton of MSW could emit 1.3 tons of CO₂ equivalent emissions, which is similar to the amount of CO₂ emissions from petroleum-based power plants [15]. In addition, incineration of MSW emits a considerable amount of pollutants such as particulate matter and fly ash into the atmosphere, making it an unsustainable waste management practice. On the other hand, the fly and bottom ash produced from the incineration of MSW has been proven to contain heavy metals posing risks to ecosystems [16].

The disposal of MSW in landfills is preferred by many municipalities globally for the burial of non-recyclable wastes. Although promising, MSW disposal in landfills faces challenges such as groundwater pollution from landfill leachate and methane gas emissions. MSW landfill leachate exhibits chronic and acute toxicity and often permeates into groundwater biomagnification. Moreover, leachate could also contaminate the flow of water streams [17]. Energy production from MSW helps in minimizing pollution and could facilitate the economic development of a nation in terms of waste management and strengthening energy security.

2.4. Food Waste

Food waste, a component of the organic fraction of MSW, refers to the organic and biodegradable waste produced from various sources including food processing plants, restaurants, kitchens and households. A large amount of food waste is produced annually due to food processing and consumption. Food waste could also be generated because of overproduction, damage to food items including fruits and vegetables by microorganisms, pests and insects, overwhelming purchases and delayed consumption [18]. Approximately 1.3 billion tonnes of food such as processed meat, dairy products, fruits, and vegetable are lost along the food supply chain every year [19].

Landfilling and incineration are not feasible waste management practices for food waste. Landfilling of food waste can lead to the emissions of methane, a more potent GHG than CO₂. On the other hand, incineration or combustion is suitable for dry biomass. Hence, high-moisture containing food waste may result in greater energy requirements for the incinerator leading to high operating costs. In such a scenario, anaerobic digestion of food waste is a reasonable alternative to producing biogas (or biomethane) through biomethanation by methanogenic bacteria [20].

Food waste consists of carbohydrates, organic acids, fatty acids, lipids, proteins and cellulose. Moreover, the carbohydrates present in food waste could undergo hydrolysis to produce oligosaccharides and monosaccharides suitable for biological conversion [19]. Owing to its organic composition, food waste can also be a crucial resource to produce bioethanol [21], biobutanol [22] and biohydrogen [23] through fermentation. As biohydrogen is gaining popularity, food waste can prove to be an eco-friendly and cost-effective feedstock for its production through photo/dark fermentation and gasification. Thermally, food waste can also be converted to produce bio-oil and biochar by pyrolysis [24] and hydrogen-rich syngas by hydrothermal gasification [18]. Food waste has also shown promising results for biochar and activated carbon production [25]. The parameters such as the composition of food waste, pretreatment methods and processing parameters influence the production of biofuels.

2.5. Animal Manure

Animal manure refers to the metabolic and waste by-products of livestock and poultry farming. Manure is a valuable material containing organic matter and nutrients essential for the cultivation of crops. Moreover, animal manure could also contain different types of pathogens posing ecological risks. Typically, animal manure contains metabolic waste or feces, waste feed and waste feedwater. Despite being a major source of agricultural nutrients, livestock manure can also contribute to the emission of GHGs such as CH₄ by microbial decomposition [26]. It should be mentioned that greenhouse gas emission from animal manure accounts for 10% of the overall emissions from agricultural production [27].

Some other traditional manure treatment includes composting and vermicomposting [27]. These treatments are very common in developing countries because of their simplicity and cost-effectiveness. Furthermore, composting also ensures the availability of nutrients to plants. Composting also leads to an increase in the aeration and water infiltration of clay soils. Animal manure could be valorized by several methods such as anaerobic digestion [28], dark fermentation [29], fermentation [30], pyrolysis [31], hydrothermal liquefaction [32], hydrothermal gasification [33] and torrefaction [34] to produce biomethane, biohydrogen, bioethanol, bio-oil, bio-crude oil, syngas and torrefied biomass, respectively. The digestate left behind after the anaerobic digestion of manure could be used as feedstock for biochar, bio-oil and syngas production through pyrolysis, liquefaction and gasification, respectively.

Animal manure has shown significant potential for biofuels and biochemicals production via thermochemical and biological conversion processes. Nanda et al. [33] showed that horse manure is an effective feedstock for hydrogen production via hydrothermal gasification. In another study, chicken manure was used as feedstock for bioethanol production via co-anaerobic digestion with ethanol plant effluent [35]. A mixture of poultry manure and *Eucalyptus* wood was used for hydrogen production via catalytic hydrothermal gasification [36].

3. Thermochemical Conversion Technologies

3.1. Torrefaction

Torrefaction is a clean and promising thermochemical technology that is often used as a thermal pretreatment of biomass resources [37]. It has been evident that torrefaction enhances the performance of thermochemical conversion processes such as pyrolysis, liquefaction and gasification by removing moisture and partially degrading the biomass [38]. Torrefaction has received substantial attention not only because torrefied and densified biomass encompasses better properties, but the technologies linked with torrefaction are close to being marketable. Some of the superior properties of torrefied biomass as compared to raw biomass are hydrophobicity, grindability, higher heating value and low-moisture content and pelletizable nature [37]. Torrefaction accounts for increasing the percentage of carbon and reducing the oxygen content consequently enhancing the heating value of biomass.

Figure 1 illustrates a typical torrefaction process flow diagram. Torrefaction refers to the drying of feedstock typically at a temperature range of 200–300 °C under an inert atmosphere. The temperature range determines the type of torrefaction, which can be classified as light (200–235 °C), mild (235–275 °C) and severe (275–300 °C) [39]. It can also be regarded as the slow heating of biomass under oxygen-free conditions. The volatile matters that are emitted during the torrefaction process move to the condenser in the form of hot vapors for condensation. The condensed liquid product of torrefaction contains water and carboxylic acids along with traces of aldehydes, ketones, ethers, esters and alcohols [40]. The non-condensable gases contain CO₂, CO, CH₄ and traces of H₂. The torrefied solids that are left behind have properties similar to coal and hence can be used as their green alternatives. The advantage of using torrefaction is that it does not emit any GHGs. Instead, it fixed the carbon in the form of densified and dehydrated biomass for further thermochemical processing. Table 1 summarizes some notable studies on the torrefaction of waste biomass to solid fuels.

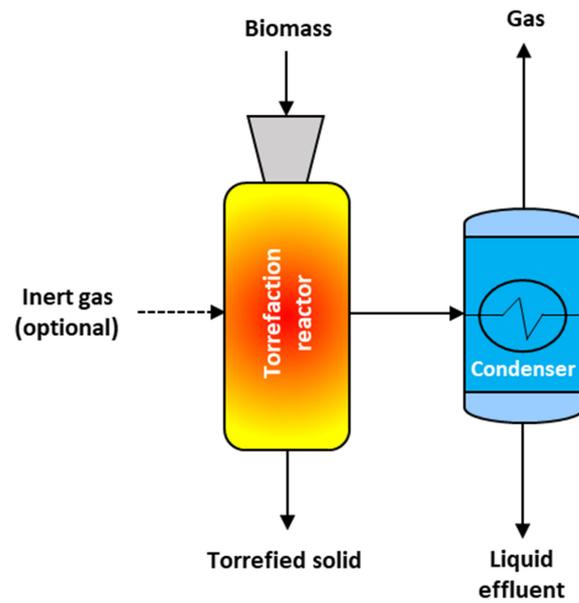


Figure 1. Typical process representation of torrefaction of biomass.

Table 1. Summary of notable works on torrefaction of waste biomass.

Feedstock	Temperature (°C)	Residence Time (min)	Observations	Reference
<i>Acacia nilotica</i> (Babul)	225–300	15–60	<ul style="list-style-type: none"> Oxygen removal efficiency and carbon densification were amplified by 40% and 52%, respectively at 300 °C in 30 min. An increase of 42% of higher heating value when compared to biomass in its raw form was observed. There was an improvement in the physical property of water. During the process, the overall aromatic carbon and aromaticity of the liquid condensate were augmented. 	Singh et al. [41]
Cotton stalk, sugarcane bagasse, rice straw and rice husk	250–300	30	<ul style="list-style-type: none"> Microwave drying cracked the surface of biomass, which consequently released additional volatiles with lower crystallinity. Torrefied rice husk, sugarcane bagasse and cotton stalk demonstrated higher elemental carbon and heating value similar to that of bituminous coal. Carbon in torrefied rice straw presented high crystallinity (around 50%), whereas that in rice husk and sugarcane bagasse was amorphous. 	Amer et al. [42]
Oats, willow and poultry litter	200–300	15–45	<ul style="list-style-type: none"> The torrefied products had up to 42% more heating value as compared to the untreated biomass. The mass and energy yields by oat residues were the fastest, whereas it was the least in poultry litter. Mass yield varied from 42% to 91%, whereas the yield of energy varied by 49%. All products displayed hydrophobic characteristics. 	Acharya and Dutta [43]

Table 1. Cont.

Feedstock	Temperature (°C)	Residence Time (min)	Observations	Reference
Pinewood, <i>Miscanthus</i> , and wheat straw	250–300	45	<ul style="list-style-type: none"> • Mass balance ranged from 96 wt.% to 103 wt.%. • Several condensable species were identified including anhydrous sugars, terpenes and terpenoids. • The type of biomass along with temperature affected the yields of condensable species. 	Lê Thành et al. [44]
Soybean straw, corn straw, rice straw and rice husk	300	-	<ul style="list-style-type: none"> • The flowability of ground biomass was enhanced by torrefaction. • Rice husk had the highest flowability, whereas rice straw had the least. 	Xu et al. [45]
Switchgrass	200–400	-	<ul style="list-style-type: none"> • The volatile content reduced while the fixed carbon content upsurged. • Severe torrefaction conditions resulted in a higher mass loss. 	Nhuchhen et al. [46]

3.2. Pyrolysis

In pyrolysis, the organic material present in the biomass undergoes an irreversible thermochemical decomposition reaction to produce biofuels. Pyrolysis technologies can be classified as slow, intermediate and fast (Table 2). The fast heating rate and short vapor residence times result in rapid condensation of the volatile hydrocarbon vapors into bio-oil, whereas slow pyrolysis results in greater biochar production due to slower carbonization of biomass due to slow heating rate and longer vapor residence time [47].

Table 2. Typical operating conditions for slow, intermediate and fast pyrolysis.

Process	Temperature (°C)	Heating Rate (°C/min)	Vapor Residence Time	Bio-Oil (wt.%)	Biochar (wt.%)	Gas (wt.%)
Slow pyrolysis	300–500	<50	>30 min	20–50	25–35	20–50
Intermediate pyrolysis	400–600	200–300	10 min	35–50	25–40	20–30
Fast/Flash pyrolysis	400–900	10–1000	<2 s	60–75	10–25	10–30

Figure 2 displays a typical process flow diagram for pyrolysis. Pyrolysis is a thermal cracking method for biomass at higher temperatures of 300–700 °C in absence of oxygen to obtain bio-oil, biochar and non-condensable gases (H₂, CH₄, CO and CO₂). Bio-oil contains an organic phase and a watery phase. The organic phase of bio-oil consists of tar and hydrocarbon-rich heavier compounds that can be upgraded to obtain clean transportation fuels. Bio-oil requires upgrading through catalytic and non-catalytic processes to remove oxygen, nitrogen and sulfur compounds, which lower the heating value of the fuel and could lead to NO_x and SO_x emissions upon combustion [48]. The watery phase of the bio-oil contains water, esters, ethers, aldehydes, ketones, phenols, alcohols, acids and other biochemicals [8]. The gas phase especially H₂ and CO can be converted to liquid hydrocarbons through catalytic Fischer-Tropsch synthesis.

A variety of lignocellulosic biomass is utilized by the technology of pyrolysis for attaining sustainable energy. Characteristics of the products of pyrolysis vary considerably depending upon the process temperature, heating rate, composition of biomass and residence time. Microwave heating has been established as a fast and energy-efficient means of heating. The heating caused by microwaves takes place via direct absorption of microwave energy by components of the material. Microwave radiation can be defined as an electromagnetic wave having a wavelength in the range of 300 MHz to 300 GHz. The introduction of microwave heating into the pyrolysis process has been recognized as a capable solution [49]. There are various advantages of using microwave-assisted pyrolysis over traditional pyrolysis such as faster heating rate, quicker and consistent heating of voluminous feedstocks, increased energy efficiency, bio-oil with low aqueous content and

prompt response of pyrolyzer for start-up and shut down. Table 3 summarizes some recent studies on the pyrolysis of biomass.

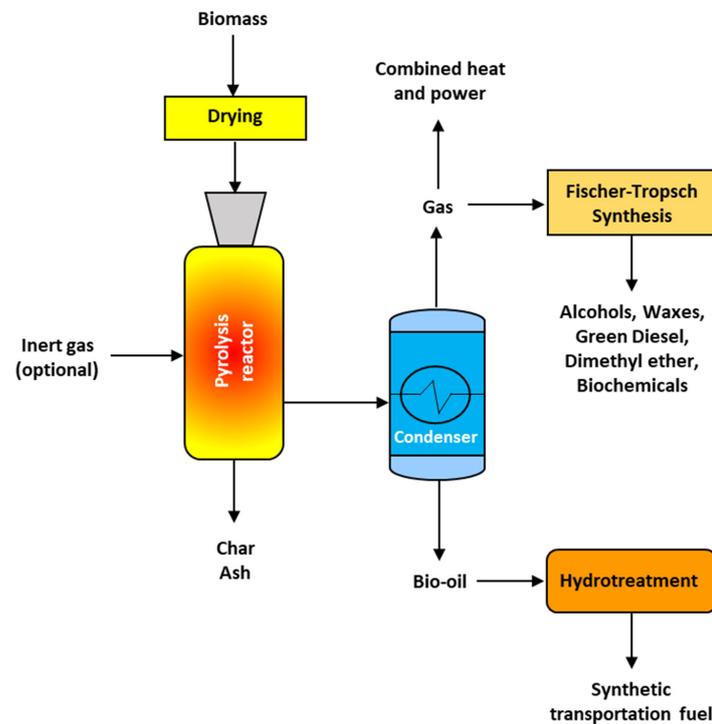


Figure 2. Typical process representation of pyrolysis of biomass.

Table 3. Summary of notable works on pyrolysis of waste biomass.

Feedstock	Catalyst	Reactor	Temperature (°C)	Observations	Reference
Bamboo and pigeon pea stalk biomass	No catalyst	Muffle furnace	400–600	<ul style="list-style-type: none"> The yield and characteristics of biochar from both biomasses were significantly influenced by the biomass composition. Due to higher lignin content in bamboo biomass, more biochar was produced compared to that from pigeon pea stalk. 	Sahoo et al. [50]
Coconut shell, palm kernel shell, rice husk, cotton stalk, wheat straw, sugarcane bagasse and biomass model compounds (hemicellulose, cellulose and lignin)	10 wt.% NiAl ₂ O ₃	Two-stage fixed bed reactor	550	<ul style="list-style-type: none"> The existence of steam and catalyst notably elevated the percentage of gas production (specifically H₂). Lignin was responsible to generate maximum H₂ when compared to hemicellulose and cellulose. 	Akubo et al. [51]
Food waste, canola hull and oat hull	No catalyst	Tubular reactor	300–600	<ul style="list-style-type: none"> The highest yield of biochar was obtained from oat hull (29.1 wt.%) followed by canola hull (28.8 wt.%) and food waste (28.4 wt.%). High-temperature biochar also demonstrated increased carbon aromaticity and thermal stability. The phenolic and aromatic chemicals were found in bio-oil produced at higher temperatures. 	Patra et al. [24]

Table 3. Cont.

Feedstock	Catalyst	Reactor	Temperature (°C)	Observations	Reference
Hinoki cypress	No catalyst	Fixed bed reactor	350–600	<ul style="list-style-type: none"> Biochar yield decreased from 33 wt.% at 350 °C to 20 wt.% at 600 °C. Biochar attained a microporous structure at 500 °C. 	Yu et al. [52]
<i>Miscanthus</i>	5 wt.% Pd/C	Fluidized bed and fixed bed reactor	350–550	<ul style="list-style-type: none"> Oxygen and sulfur contents in the bio-oil reduced significantly while the heating value augmented. A maximum degree of deoxygenation of bio-oil was noticed with improved viscosity. The bio-oil revealed the potential to replace traditional combustion fuels. 	Wang and Lee [53]
Peanut shell, corncob Jatropha seeds de-oiled cake and bagasse	Org-CaO/Nano-ZSM-5	A dual-catalyst fixed-bed reactor system	50–320	<ul style="list-style-type: none"> The percentage of aromatics in the pyrolysis liquid product from Jatropha cake (after removal of oil) with Org-CaO/NZSM-5 augments to 93%. The yield of benzene, toluene and xylene (BTX) along with naphthalene (70%) nearly doubled than that obtained with the traditional CaO/ZSM-5. The thermal cracking ability of biomass was better with Org-CaO. When compared with the pyrolysis of corncob, peanut shell and bagasse, de-oiled Jatropha cake generated more aromatics with Org-CaO/NZSM-5. 	Yi et al. [54]
Pinewood, peanut shell and rice straw	K ₂ CO ₃	Fixed bed reactor	300–700	<ul style="list-style-type: none"> The fraction of liquids in pinewood and peanut shells drastically decreased, whereas that of rice straw showed the least decline. Pinewood had the highest catalytic effect followed by peanut shell and rice straw. 	Fan et al. [55]
Sugarcane bagasse, straw and acid-treated biomass	No catalyst	Fixed bed reactor	450–650	<ul style="list-style-type: none"> Sugarcane bagasse produced more biochar (50 wt.%) and bio-oil (26 wt.%) at 450 °C. The elemental analysis of biochar produced from various feedstocks revealed a higher carbon content (65–81 wt.%) and a lower oxygen content (23–31%) than sugarcane bagasse. 	de Almeida et al. [56]
Switchgrass and <i>Miscanthus</i>	Trace minerals	Fast pyrolysis reactor	500	<ul style="list-style-type: none"> The fraction of product varied from 12–18 wt.% for biochar and ash, 45–53 wt.% for bio-oil and 24–27 wt.% for gases. 	Zaimes et al. [47]
Wheat straw	1–10 wt.% coal fly ash		450–750	<ul style="list-style-type: none"> With the increase in fly ash content (1–10 wt.%) in wheat straw, the alteration of biomass augmented. Methylene blue was removed by the use of heterogeneous wheat straw fly ash biochar. Fly ash could be a cost-effective catalyst for biomass pyrolysis concurrently fabricating heterogeneous sorbents with improved adsorption capacities for organic pollutants. 	Gao et al. [57]

Table 3. Cont.

Feedstock	Catalyst	Reactor	Temperature (°C)	Observations	Reference
Willow, sugarcane bagasse, Ugu plant and rice straw	10 wt.% Ni/Al ₂ O ₃	Two-stage pyrolysis-catalytic hydrogenation reactor	500	<ul style="list-style-type: none"> • CH₄ yield was augmented with the use of catalysts. • CH₄ yield produced from hemicellulose and cellulose was higher than that obtained from lignin. 	Jaffar et al. [58]

3.3. Liquefaction

Liquefaction is another thermochemical process for biomass conversion that predominantly produces bio-crude oil. Bio-crude oil is formed because of hydrogenation and high-pressure thermal disintegration of biomass. Hydrothermal liquefaction (HTL) requires the usage of water and catalysts to transform high-moisture containing solid waste into bio-crude oil. Figure 3 shows the process flow diagram for liquefaction. Liquefaction generally operates at a temperature range of 240–380 °C and pressures of 5–30 MPa. The reaction mechanism of liquefaction can be summarized by the following basic routes [59]:

- (i) Hydrolysis of biomass → smaller monomer
- (ii) Smaller monomer → smaller compounds (by cleavage and decarboxylation)
- (iii) Recombination of the smaller fragments → new compounds (by condensation, polymerization)

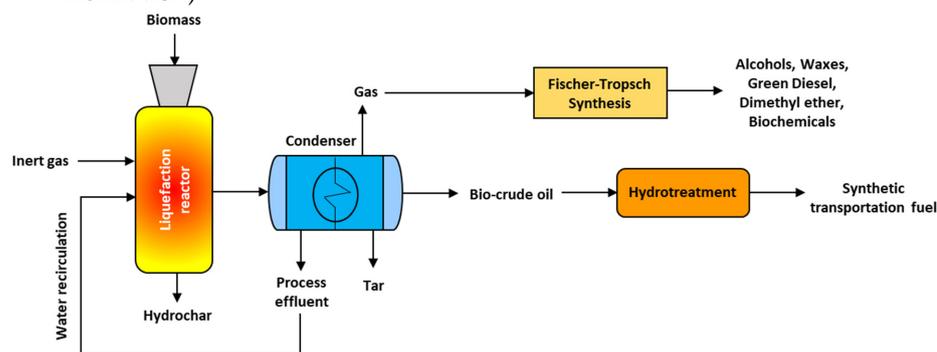


Figure 3. Typical process representation of liquefaction of biomass.

Ethanol and subcritical water are some commonly used solvents in liquefaction. The role of solvents is critical in the dissolution of biomass by breaking hemicellulose, cellulose, and lignin into the volatile matter [59]. Thereafter, two phases are formed, i.e., the tar phase and the watery phase similar to pyrolysis. The watery phase containing water and biochemicals (as discussed earlier) can be recycled back and utilized as a solvent in the process [60]. Bio-crude obtained from liquefaction requires minimal upgrading by hydrotreating unlike pyrolysis-derived bio-oil because of low oxygen content, more hydrocarbon yields, better energy density and flowability. Table 4 shows some promising studies on the liquefaction of biomass to bio-crude oil.

Table 4. Summary of notable works on liquefaction of waste biomass.

Feedstock	Catalyst	Reactor	Temperature (°C)	Observations	Reference
Cellulose and lignin	KOH	High pressure autoclave	280	<ul style="list-style-type: none"> The yield of bio-crude oil and cellulose conversion was affected by an alkaline catalyst. Low molecular weight compounds were found in the liquid products due to the hydrolysis of cellulose and lignin. 	Singh et al. [61]
Corn stover	-	Autoclave reactor	250–375	<ul style="list-style-type: none"> The yield of hydrocarbons was highest at 350 °C. The rise in pressure negatively affected hydrochar yield while retention time has negligible effects. The formation of agglomerates at higher temperatures was due to repolymerization reactions. 	Mathanker et al. [62]
Loblolly pine, sewage sludge and cow manure	-	Bench-top reactor	250–300	<ul style="list-style-type: none"> Wet feedstocks have the potential to be utilized to generate bio-crude which can further be utilized as liquid fuels and other value-added products. 	Saba et al. [63]
Microbial biomass	-	-	200–300	<ul style="list-style-type: none"> Effective conversion of wastewater sludge, fast-growing algae and bacteria having a low fraction of lipids into biofuels was demonstrated. 	Goswami et al. [64]
Potato starch, Casein and sunflower oil	-	Stainless-steel batch reactors	350–600	<ul style="list-style-type: none"> Energy content and nutrients in food waste can be recovered via HTL. HTL proved to be an efficient method to turn food waste into bio-crude which is dense in energy. 	Gollakota and Savage [65]
Spruce wood	Potassium fluoride doped alumina catalyst	Bench-top reactor	250–350	<ul style="list-style-type: none"> Homogeneous alkali catalysts proved suitable for biofuel production and impede the formation of char. Heterogeneous catalysts were preferred for HTL of lignocellulosic biomass. 	Alper et al. [66]
Tomato plant waste	H ₂ SO ₄ and KOH	Autoclave reactor	220–280	<ul style="list-style-type: none"> Wet food waste demonstrated potential as a bioresource to produce liquid fuels through HTL. 	Zhang et al. [67]
Wood biomass (larch and Mongolian oak)	K ₂ CO ₃	Batch reactor	300	<ul style="list-style-type: none"> The quantity of hydrochar obtained was highest when no catalyst was used. With the addition of catalysts, the conversion of biomass to bio-crude oil notably increased. 	Hwang et al. [68]

3.4. Gasification

Gasification is termed a thermochemical process that has the potential to transform any carbonaceous material into syngas [69]. Gasification provides flexibility for using a variety of feedstocks to generate gaseous products (e.g., H₂, CO, CO₂ and CH₄) and char. Using syngas, several different forms of energy such as heat, power, biofuel, biomethane, chemicals and hydrogen can be generated [70]. Figure 4 illustrates a simplistic process flow diagram for gasification. While thermal gasification of coal and complex biomass uses high temperatures (800–1200 °C), hydrothermal gasification can operate at relatively moderate temperatures (400–700 °C). Apart from the main gaseous products, gasification also results in condensable liquids rich in water and biochemicals. Due to higher temperature, there is restricted tar formation, making cleaning and recovery of the gas fairly simple [69]. Moreover, high temperatures in gasification contribute to a faster reaction rate favored by endothermic reactions such as water-gas shift, methanation and steam reforming leading to near-complete decomposition of biomass to gases. The syngas can be converted to clean fuels and value-added products by Fischer-Tropsch catalysis [71].

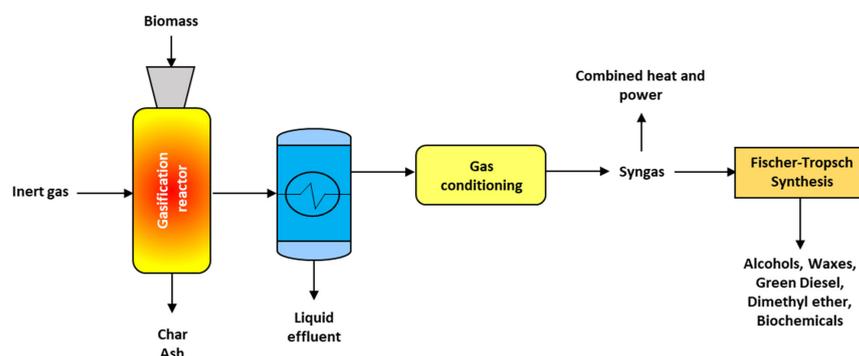


Figure 4. Typical process representation of gasification of biomass.

Hydrothermal gasification (HTG) utilizes subcritical or supercritical water as a reaction media to produce syngas. Subcritical and supercritical water occur below and beyond the critical temperature (374 °C) and critical pressure (22.1 MPa) of water, respectively. The chief benefit of using HTG is that it can efficiently transform biomass comprising high moisture, which would otherwise involve cost-intensive and energy-intensive drying steps before gasification [72]. In contrast, converting wet biomass through pyrolysis, liquefaction and gasification tends to be inefficient as the heat of moisture evaporation generally surpasses the heat of combustion of biomass. The product of HTG has several different applications such as chemical synthesis, power generation and fuel cells related to hydrogen production.

It is a challenge to enhance the levels of H₂ and CO in the syngas. However, several strategies that can address this issue are the application of catalysts that can promote water-gas shift, steam reforming, tar reforming and syngas redox reactions [73,74]. In addition, optimizing the gasification process conditions such as temperature, pressure, reaction time, reaction medium, feedstock concentration, equivalence ratio and catalyst loading can result to improve gasification efficiency, carbon conversion efficiency, hydrogen selectivity and calorific value of syngas [75]. Table 5 summarizes some recent studies on the gasification of waste biomass to syngas.

Table 5. Summary of notable works on gasification of waste biomass.

Feedstock	Catalyst	Reactor	Temperature (°C)	Observations	Reference
Cotton stalks, corn stalks and rice straw	Marly clay, calcium hydroxide, dolomite, and cement kiln dust	Bench-scale fixed-bed reactor	700–850	<ul style="list-style-type: none"> Ca(OH)₂ and cement kiln dust were effective in increasing the yield of gas and decreasing tar and char yields. Cotton stalks contributed a greater percentage of gases compared to rice straw and corn stalks. 	Hamad et al. [76]
MSW and wastepaper	K ₂ CO ₃ , Li ₂ CO ₃ , Rb ₂ CO ₃ , CaCO ₃ , CsCO ₃ , CaSO ₄ and Na ₂ CO ₃	-	800–950	<ul style="list-style-type: none"> Catalytic activity was enhanced by using CaCO₃, Li₂CO₃ and Na₂CO₃ for the gasification of sewage sludge, wastepaper and MSW, respectively. 	Vamvuka et al. [77]
Poplar wood chips	Ru/activated carbon, Ni/activated carbon, KOH, Dolomite, Trona and Borax	Batch reactor	300–600	<ul style="list-style-type: none"> All the catalysts irrespective of their type improved gasification yields. KOH resulted in a high gas yield and low residue yield. Ru/activated carbon had the best activity for increasing H₂ yields. 	Gökkaya et al. [78]
Willow wood chips	-	Bubbling fluidized bed reactor	600–850	<ul style="list-style-type: none"> High thermal stability and high carbon conversion efficiency of willow chips were observed. 	Hai et al. [79]

3.5. Transesterification

Transesterification is the process by which non-edible oils react with alcohols (methanol and ethanol) to produce biodiesel. These alcohols are widely used since they are easily

available and inexpensive. Transesterification is known to decrease the viscosity of non-edible oils and facilitate the formation of triglycerides into esters with easy miscibility in diesel [80]. Figure 5 represents the process flow diagram for biodiesel production through transesterification. The waste fat and oil are mixed with alcohol to produce methyl esters and methanol. The methyl esters can be catalytically converted into glycerol and biodiesel. The biodiesel methanol mixture can be further separated and re-used, whereas methyl ester can be catalytically converted to glycerol and biodiesel [81].

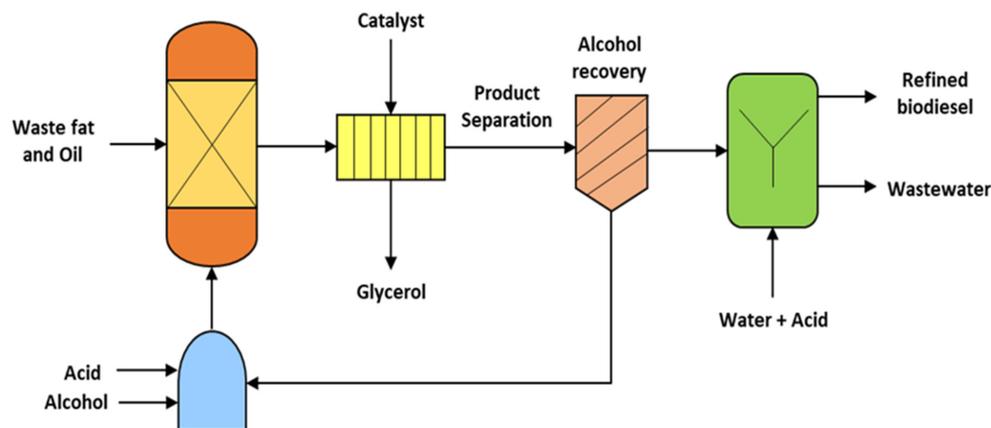


Figure 5. Typical process representation of transesterification of waste fats and oil.

Biodiesel can be produced using homogeneous and heterogeneous acid and alkaline catalysts. Due to their high activity, homogeneous catalysts are typically used in chemical reactions. However, due to the difficulty in recovering the spent homogeneous catalysts, the operating cost of the process could increase. Heterogeneous catalysts are relatively easier for recovery and subsequent recyclability [82]. Additionally, mineral acids and heterogeneous base catalysts are combined in solid acids catalysts of Brønsted type (e.g., materials containing sulfonic acid) and Lewis type (e.g., mixed sulfated oxides). However, the production of soap during transesterification using heterogeneous catalysts is a drawback leading to challenges in product purification and separation [83].

The application of alkali catalysts can make the transesterification process faster with better yields and product selectivity. Catalytic conversion of oil to biodiesel consists of acid-catalyzed esterification and base-catalyzed transesterification. Acid catalysts are utilized for esterification or free fatty acids (FFA). Some examples of acid catalysts are phosphoric acid, sulfuric acid, organic sulfonic acids and hydrochloric acid [84]. Even though the use of acid catalysts for transesterification makes it slower in comparison to alkali catalysis, they are appropriate for glycerides that contain more water and FFAs. Some of the alkali catalysts used for transesterification are NaOH, KOH, carbonates and alkoxides such as sodium methoxide (CH_3NaO) and sodium ethoxide ($\text{C}_2\text{H}_5\text{ONa}$) [85]. The alkali-catalyzed transesterification is rapid as compared to acid catalysts. Regardless of catalytic or non-catalytic routes, transesterification requires the separation of alcohol, oil, applied catalyst and other impurities from the liquid products.

Some of the benefits of using solid acid catalysts include recyclability, product selectivity, regeneration and minimization of reactor corrosion [86]. Nevertheless, heterogeneous catalytic processes can produce high-quality oils due to their sensitivity toward high FFAs. Heteropoly acids (HPAs) are among the several solid acid catalysts effective for biodiesel production due to their strong acidity and elevated tolerance to high FFA levels and water content [87]. Some other advantages of HPAs are their elastic structure, exceptional dispersion and appropriate interaction with support materials. The surface area and thermal stability of the catalyst are increased when HPAs are immobilized on a suitable support material [88]. Careful consideration should be given to the support material's surface area and porosity, which can increase the catalyst's effectiveness and activity.

In enzyme-catalyzed transesterification, lipase enzyme acts as a bio-catalyst for transesterification reactions [89]. Enzymes have a huge possibility for dropping the necessity of high energy requirements and reducing the environmental complications in biodiesel refineries. Enzymatic transesterification takes place at a comparatively lower temperature as compared to other acid and base-catalyzed transesterification reactions to avoid the loss of lipase activity. Since the lipase-catalyzed reactions require moderate temperature, enzymatic transesterification is less energy-intensive. There are several benefits of enzymatic transesterification such as high selectivity, mild reaction conditions and availability of a wide range of substrates. Nevertheless, the cost, stability and low recyclability of enzymes are some of the limitations that require more research [90]. Table 6 summarizes some notable work on the conversion of waste oils to biodiesel via transesterification.

Table 6. Summary of notable works on transesterification of waste oil and biomass to biodiesel.

Feedstock	Catalyst	Reactor	Temperature (°C)	Observations	Reference
Biomass from the oleaginous yeast <i>Yarrowia lipolytica</i> cultivated on waste cooking oil	H ₂ SO ₄	-	65–110	<ul style="list-style-type: none"> The optimized conditions for transesterification involved the temperature of 50 °C, reaction time of 8 h, sonication time of 5 min, 100 mL methanol, 10 mL chloroform, 1 mL/g catalyst and 4 g biomass. 	Katre et al. [91]
Soybean oil	NaOH	Stirred tank reactor	50	<ul style="list-style-type: none"> The rate of reaction was strongly influenced by catalyst loading, reaction rate, oil-to-methanol ratio and temperature. 	Bashiri and Pourbeiram [92]
Waste cooking oil	CaO and Clay	Heater equipped with a magnetic agitator	45–55	<ul style="list-style-type: none"> The conversion rate of 97% was obtained under optimal conditions such as a temperature of 55 °C, the oil-to-methanol ratio of 1.94, catalyst loading of 9.6 wt.%, toluene concentration of 16.1 wt.% and reaction time of 74 min. The catalyst was reusable up to 5 times. 	Mohadesi et al. [93]
Waste frying oil	NaOH	Shake flask	55	<ul style="list-style-type: none"> The blending of biodiesel with commercial diesel was an effective method to reduce its viscosity for direct use in diesel engines. 	Duti et al. [94]
Wet sewage sludge	H ₂ SO ₄	Hydrothermal reactor	70–160	<ul style="list-style-type: none"> A high percentage of biodiesel was obtained implying that the hydrothermal process can stimulate the transfer of lipids from feedstock to the separating solvent. 	Hu et al. [95]

4. Major Biofuel Products

4.1. Biochar

Biochar, a solid co-product of pyrolysis and high-temperature torrefaction, is rich in carbon and can be prepared from several kinds of raw materials such as crop residues, woody biomass and other solid wastes. Biochar is primarily composed of carbon and smaller fractions of minerals based on the precursor or feedstock. It has been revealed that the higher yields of biochar are inversely proportional to the pyrolysis temperatures. Hence, the low pyrolysis temperature contributes to high yields of biochar, electrical conductivity and cation-exchange capacity in addition to high levels of volatiles [96]. In contrast, biochar obtained at higher temperatures has a greater surface area as well as carbon content.

Biochar is gaining popularity owing to its exclusive features such as a high percentage of carbon and cation exchange capacity, greater surface area and thermally stable structure [96,97]. Similarly, due to the presence of a high percentage of carbon, the char encompasses high energy content that in turn can be utilized to produce heat to prepare activated carbon. Other applications of biochar are as a nutrient for soil remediation and as a filtrate for pollutants. Biochar is also used as an adsorbent to sequester heavy metals and organic micro-pollutants. Its ability to be used as an adsorbent results from its physico-chemical properties such as distribution of pore size, surface area, functional groups and

cation exchange capacity [98]. Recently, the utilization of biochar as a catalyst supports particularly for the processes of upgrading bio-oil such as esterification, hydrotreating, and hydrodeoxygenation is gaining a lot of attention [99]. Biochar is recently being recognized as a promising bioresource as a fuel and reducing agent to replace coal and coke in metallurgical processes [100].

Hydrochar is a carbon-rich product of hydrothermal conversion processes such as hydrothermal gasification, hydrothermal liquefaction and hydrothermal carbonization. They exhibit dissimilar physicochemical properties when compared with biochar due to different operating conditions involved in their production. The atomic ratios of H/C and O/C of hydrochar are relatively higher when compared to that of biochar [96]. Moreover, hydrochar contains more oxygenated functional groups and is slightly acidic compared to biochar [101]. On the other hand, biochar tends to display alkaline characteristics due to the presence of alkali and alkaline earth metals [102]. This property of biochar is beneficial for application to acidic soils for neutralization of the soil pH levels. Hydrochar also exhibits a relatively low specific surface area and porosity when compared to biochar. However, the properties of hydrochar could be tailored for various industrial applications including catalysts support, activated carbon production, wastewater treatment, and soil remediation [103].

4.2. Bio-Crude Oil

Bio-crude oil is an energy-rich liquid product that can be produced via thermochemical routes such as hydrothermal liquefaction. Nevertheless, bio-crude oil obtained from both the above-mentioned routes has some unwanted properties including a high amount of moisture, high acidity, high tendency to corrode. These undesirable properties should be eliminated before utilizing the bio-crude oil in refineries for co-processing or to be used as a commercial fuel in transportation [104].

Algae are considered suitable as a feedstock for bio-crude oil production via HTL owing to their higher efficiency for photosynthesis, fast growth, no requirement of agricultural lands, cultivation in wastewater, less dependency on nutrients, CO₂ capture and fixation and higher production of lipids [105]. Nowadays, bio-raw oil production from microalgae is gaining popularity. The nitrogen recovery from unrefined oil is lower than that from pure algae [106].

Bio-crude oil and bio-oil have a few unsought characteristics such as a high percentage of moisture, high viscosity, greater ash content, a high fraction of oxygen, and a tendency to corrode the reactors due to high acidity. These undesirable properties need remedy before utilizing the bio-oil in the refineries and the power sectors. This is achieved by catalytic and non-catalytic upgrading technologies (discussed earlier) that reduce the contents of oxygen, nitrogen and sulfur from bio-crude and bio-oil along with enhancing their fuel properties such as heating value, viscosity, reduced corrosivity, reduced polymerization and lower emissions [107]. Therefore, it is imperative to enhance the bio-crude oil properties to make it commercially viable via catalytic upgrading or any other economically viable upgrading technologies. Specifically, a catalyst with high product selectivity, reactive performance, low cost, durability, reusability and resistance to high temperatures and coking is mostly preferred for upgrading bio-crude oil and bio-oil.

4.3. Bio-Oil

Bio-oil is defined as the key product derived from the pyrolysis of biomass. The feature and yield of bio-oil are dependent on the residence time, temperature, heating rate and biomass composition [108]. The major constituent of bio-oil is water which generally comprises 30–40 wt.% of bio-oil [109]. The reason for the presence of water could be attributed to the amount of moisture in the biomass as well as dehydration and decarboxylation reactions taking place during pyrolysis [110]. Bio-oil also contains phenols, hydrocarbon derivatives and esters, concentrations of which depend on biomass properties and process parameters. Bio-oil particularly obtained from the lignocellulosic biomass is a

combination of the degraded product obtained from the hemicellulose, cellulose and lignin. The specific degraded product from the cellulose and hemicellulose that are present in bio-oil are acids, furans, sugars, aldehydes, esters and oxygenates [111].

The chemical composition of the biomass feedstock also performs a key role in the characteristic and yield of bio-oil during thermochemical conversion processes. The major issues related to the utilization of bio-oil are its low energy density, tendency to corrode the reactor, high viscosity, thermal instability, polymerization and presence of a high percentage of heteroatoms (e.g., oxygen, nitrogen and sulfur) [110]. In addition, bio-oil is known to be chemically unstable and highly oxygenated in its raw form, thus requiring upgrading as discussed earlier.

4.4. Syngas

Syngas is a major product of biomass to gas technologies such as gasification. It comprises gaseous mixtures such as H_2 , CO_2 , CO and CH_4 as the key components. Syngas is an important intermediate in the chemical industry that can be used for the manufacture of transportation fuels and green chemicals [70]. Another application of syngas is its direct use as a fuel for generating electricity [112]. Hydrogen is an important constituent of syngas. Owing to its exceptional properties has appeared as an ideal renewable future energy carrier. Hydrogen is used in a variety of industrial applications including fuel cells, synthesis of platform chemicals, medicines, aerospace, maritime purposes, metallurgy and electrical devices.

The hydrogen economy is an anticipated system where hydrogen produced is widely utilized as an energy carrier. The effective deployment of hydrogen economy will result in several benefits concerning profitability, energy security, environment and end-users [113]. Although hydrogen energy is considered substitute energy, currently, its usage is restricted only to small-scale operations. The major challenge associated with the large-scale production of hydrogen energy is difficulty in the distribution and commercial application of hydrogen energy [114]. As competition is absent in, hydrogen energy currently, the governments are recommended to execute policies to promote the portable, stationary and transportation applications of hydrogen energy.

4.5. Biodiesel

Biodiesel is one of the extensively recognized sustainable biofuels. The crucial fact for the industrial manufacturing of biodiesel is the low cost of its feedstock, i.e., non-edible oils as well as waste fats and oils. Biodiesel is preferred over traditional petrol and diesel due to its characteristics such as non-toxicity, biodegradability and negligible levels of aromatics and sulfur. With these properties, biodiesel or its blended counterparts can also perform better than ultra-low sulfur fuel [115]. In most countries, B20 biodiesel blended fuel is used, which is made of 6–20 vol.% biodiesel in fossil-based diesel fuel. The low biodiesel fraction in B20 blended fuel makes it suitable for direct use in many diesel-fueled vehicles worldwide without engine modification.

The commonly used precursors for generating biodiesel are triglyceride-based materials such as animal fat, vegetable oil (edible and non-edible), waste cooking oil, waste industrial oil and algal oil. A variety of oilseed crops contribute to biodiesel production such as mustard, soybean, camelina, cottonseed, canola, sunflower seed, peanuts and rapeseeds as discussed earlier. Oilseeds have adequate quantities of fat that make their extraction easy.

Biodiesel can be produced via transesterification using homogeneous and heterogeneous catalysts. Potassium methoxide ($KOCH_3$), sodium hydroxide ($NaOH$), sodium methoxide ($NaOCH_3$), hydrochloric acid (HCl), sulfonic acid, organic sulfonic acid, sulfuric acid (H_2SO_4) and iron sulfate are some common homogeneous alkali catalysts used for biodiesel production. Some of the heterogeneous catalysts used are CaO , $Ca(OH)_2$ and $CaCO_3$. Heterogeneous catalysts are recyclable, non-corrosive and more effective as compared to homogenous catalysts [116]. It has been observed that biodiesel contributes to

fewer emissions in comparison to diesel fuel. There are several reasons for biodiesel being used as a substitute fuel such as sustainable and renewable energy solution, lesser influence on climate, decrease in GHG emissions and feasible drop-in substitute to petro-diesel. By replacing traditional fuels with biodiesel, emissions of particulate matter, CO₂, CO and unburned hydrocarbons can also be lessened.

5. Strengths, Weaknesses, Opportunities and Threats Analysis

As discussed in this review, some promising thermochemical technologies for bio-fuel production from biomass are torrefaction, pyrolysis, liquefaction, gasification and transesterification. Each of these technologies has advantages and limitations that are critical to understanding to determine their performance, commercialization aspects, techno-economics and marketability of the products. The key summary of this review in the form of strengths, weaknesses, opportunities and threats of these thermochemical waste-to-energy technologies are shown in Table 7.

Table 7. Summary of strengths, weaknesses, opportunities and threats of thermochemical biomass conversion technologies.

Technology	Strengths	Weaknesses	Opportunities	Threats
Torrefaction	<ul style="list-style-type: none"> • It can be used both as a pretreatment and biomass conversion technology. • High energy content per unit volume. • Improves the calorific value of biomass. • Pelletizing torrefied biomass makes its transportation easy for long-distance. • Reduces moisture content. • Low energy input. • Reduced operating costs. 	<ul style="list-style-type: none"> • Lower overall efficiency. • Optimization of torrefaction reactors is essential to meet the end-use necessities financially and reach product standardization for the market. 	<ul style="list-style-type: none"> • Torrefaction improves the characteristics of feedstock in numerous ways and can be used as a direct fuel. • No catalyst is required. 	<ul style="list-style-type: none"> • Volatilization of phenol, acetone, and other contaminants, makes flue gas cleaning more challenging.
Pyrolysis	<ul style="list-style-type: none"> • High efficiency. • Probable applications of produced compounds (e.g., tar, bio-oil, and char). • Reduces greenhouse gases and wastes going to landfills. • Requires lower energy input for slow pyrolysis. • Requires higher energy input for fast pyrolysis. 	<ul style="list-style-type: none"> • Complex product stream • Difficulty in venting out product gases without treatment owing to high concentrations of CO. • Issues with recyclability of homogeneous and carbon-based catalysts. 	<ul style="list-style-type: none"> • Extensive expertise • Development of the market for pyrolysis liquid and char products. 	<ul style="list-style-type: none"> • Feasibility is established only in large-scale plants • Not much efficient for sewage sludge. • High cost.
Liquefaction	<ul style="list-style-type: none"> • A promising method for wet biomass. • Drying is not necessary. • Easy recovery of inorganics. • Lower critical point. • High-energy bio-crude is obtained via hydrothermal liquefaction and the product is low in oxygen and moisture content as compared to pyrolysis bio-crude. 	<ul style="list-style-type: none"> • Possibility of corrosion. • Salt deposition in the reactor. • No harmful solvents are involved. • Issues with recyclability of homogeneous and carbon-based catalysts. 	<ul style="list-style-type: none"> • High energy efficiency. • Apt for generating biofuels. 	<ul style="list-style-type: none"> • The feedstock and the conditions of the production frequently influence the chemical and physical attributes of bio-oil. • Difficulty in eluting heavy compounds that remains uncharacterized in the column.

Table 7. Cont.

Technology	Strengths	Weaknesses	Opportunities	Threats
Gasification	<ul style="list-style-type: none"> Syngas can be directly utilized as a fuel or for value-added products such as synthetic natural gas, chemicals, hydrogen, kerosene, naphtha, etc. 	<ul style="list-style-type: none"> High operating cost. High maintenance cost. Issues with recyclability of homogeneous and carbon-based catalysts. 	<ul style="list-style-type: none"> Large-scale operations are possible. High unexploited potential. 	<ul style="list-style-type: none"> Lack of subsidies to farmers. High cost.
Transesterification	<ul style="list-style-type: none"> Short reaction times. The cost of the production process is relatively lower. The reaction condition can be regulated. The methanol generated in the process can be recycled. 	<ul style="list-style-type: none"> Incidence of unsought reactions Sensitivity of the catalysts towards the existence of water in the feedstock. High concentrations of glycerol and methanol are obtained as wastes. Issues with recyclability of homogeneous catalysts. 	<ul style="list-style-type: none"> Large-scale production is possible. High conversion of the feedstocks. 	<ul style="list-style-type: none"> High biodiesel blending requires engine modification.

6. Conclusions

Waste biomass is an exceptional bioresource for valorization to usable forms of energy carriers such as bio-oil, bio-crude oil, biodiesel, syngas, hydrogen and biochar. As reviewed in this article, biomass can be categorized into agricultural and forestry biomass, energy crops, oilseed crops, food waste, municipal solid waste and animal manure. These waste resources can be converted to biofuel products through thermochemical technologies such as torrefaction, pyrolysis, gasification, liquefaction and transesterification. Torrefaction results in the production of torrefied biomass with reduced moisture content and increased heating value in a densified form factor. Pyrolysis and liquefaction lead to the production of bio-oil and bio-crude oil because of the thermal cracking of cellulose, hemicellulose, lignin and other organic matter present in biomass under inert atmospheres and process conditions optimal to produce bio-oil and bio-crude oil, respectively. Gasification results in the production of syngas, a mixture of H₂ and CO along with CO₂ and CH₄ under inert, air or hydrothermal conditions (i.e., steam and/or supercritical water). Biochar is a co-product of pyrolysis and gasification that has a higher content of fixed carbon. The aromaticity, thermal stability, calorific value, surface area and porosity of biochar can be improved at higher temperatures. Biodiesel is generated through transesterification of fatty acids and lipids in waste vegetable oil and/or animal fat mostly in the presence of chemical or biocatalysts. Nonetheless, the yield and quality of the biofuel products as well as the process efficiency depend on factors including biomass composition and process conditions (i.e., temperature, pressure, reaction time, reactor type, applied catalyst, etc.). The biofuel products can be used as drop-in alternatives to fossil fuels or as blends to reduce GHG emissions, pollution, global warming and dependency on fossil fuels.

Author Contributions: Conceptualization, S.J., S.N., B.A. and A.K.D.; investigation, S.J., S.N. and B.A.; resources, B.A. and A.K.D.; data curation, S.J., S.N. and B.A.; writing—original draft preparation, S.J., S.N. and B.A.; writing—review and editing, S.N., B.A. and A.K.D.; supervision, B.A. and A.K.D.; project administration, B.A. and A.K.D.; funding acquisition, A.K.D. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to thank the funding received from the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Research Chairs (CRC) program, Agriculture and Agri-Food Canada (AAFC) and BioFuelNet Canada to support this research.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jha, S.; Okolie, J.A.; Nanda, S.; Dalai, A.K. A review of biomass resources and thermochemical conversion technologies. *Chem. Eng. Technol.* **2022**, *45*, 791–799. [CrossRef]
2. World Bioenergy Association. *Global Bioenergy Statistics 2020*; World Bioenergy Association: Stockholm, Sweden, 2020; Volume 3, p. 49.
3. IEA. Renewables 2021: Biofuels. Available online: <https://www.iea.org/reports/renewables-2021/biofuels?mode=transport®ion=World&publication=2021&flow=Consumption&product=Ethanol> (accessed on 22 August 2022).
4. Lee, S.Y.; Sankaran, R.; Chew, K.W.; Tan, C.H.; Krishnamoorthy, R.; Chu, D.T.; Show, P.L. Waste to bioenergy: A review on the recent conversion technologies. *BMC Energy* **2019**, *1*, 4. [CrossRef]
5. Xing, J.; Luo, K.; Wang, H.; Gao, Z.; Fan, J. A comprehensive study on estimating higher heating value of biomass from proximate and ultimate analysis with machine learning approaches. *Energy* **2019**, *188*, 116077. [CrossRef]
6. Namkung, H.; Lee, Y.J.; Park, J.H.; Song, G.S.; Choi, J.W.; Kim, J.G.; Park, S.J.; Park, J.C.; Kim, H.T.; Choi, Y.C. Influence of herbaceous biomass ash pre-treated by alkali metal leaching on the agglomeration/sintering and corrosion behaviors. *Energy* **2019**, *187*, 115950. [CrossRef]
7. Güleç, F.; Pekaslan, D.; Williams, O.; Lester, E. Predictability of higher heating value of biomass feedstocks via proximate and ultimate analyses—A comprehensive study of artificial neural network applications. *Fuel* **2022**, *320*, 123944. [CrossRef]
8. Singh, A.; Nanda, S.; Guayaquil-Sosa, J.F.; Berruti, F. Pyrolysis of *Miscanthus* and characterization of value-added bio-oil and biochar products. *Can. J. Chem. Eng.* **2021**, *99*, S55–S68. [CrossRef]
9. Khan, I.U.; Chen, H.; Yan, Z.; Chen, J. Extraction and quality evaluation of biodiesel from six familiar non-edible plants seeds. *Processes* **2021**, *9*, 840. [CrossRef]
10. Kumar, A.; Samadder, S.R. An empirical model for prediction of household solid waste generation rate—A case study of Dhanbad, India. *Waste Manag.* **2017**, *68*, 3–15. [CrossRef]
11. Nanda, S.; Berruti, F. Municipal solid waste management and landfilling technologies: A review. *Environ. Chem. Lett.* **2021**, *19*, 1433–1456. [CrossRef]
12. Rajendran, N.; Gurunathan, B.; Han, J.; Krishna, S.; Ananth, A.; Venugopal, K.; Priyanka, R.S. Recent advances in valorization of organic municipal waste into energy using biorefinery approach, environment and economic analysis. *Bioresour. Technol.* **2021**, *337*, 125498. [CrossRef]
13. Gunarathne, V.; Ashiq, A.; Ramanayaka, S.; Wijekoon, P.; Vithanage, M. Biochar from municipal solid waste for resource recovery and pollution remediation. *Environ. Chem. Lett.* **2019**, *17*, 1225–1235. [CrossRef]
14. Fazeli, A.; Bakhtvar, F.; Jahanshaloo, L.; Sidik, N.A.C.; Bayat, A.E. Malaysia's stand on municipal solid waste conversion to energy: A review. *Renew. Sustain. Energy Rev.* **2016**, *58*, 1007–1016. [CrossRef]
15. Ouda, O.K.; Cekirge, H.M.; Raza, S.A. An assessment of the potential contribution from waste-to-energy facilities to electricity demand in Saudi Arabia. *Energy Convers. Manag.* **2013**, *75*, 402–406. [CrossRef]
16. Clavier, K.A.; Paris, J.M.; Ferraro, C.C.; Townsend, T.G. Opportunities and challenges associated with using municipal waste incineration ash as a raw ingredient in cement production—A review. *Resour. Conserv. Recycl.* **2020**, *160*, 104888. [CrossRef]
17. Mishra, S.; Tiwary, D.; Ohri, A.; Agnihotri, A.K. Impact of municipal solid waste landfill leachate on groundwater quality in Varanasi, India. *Groundw. Sustain. Dev.* **2019**, *9*, 100230. [CrossRef]
18. Nanda, S.; Isen, J.; Dalai, A.K.; Kozinski, J.A. Gasification of fruit wastes and agro-food residues in supercritical water. *Energy Convers. Manag.* **2016**, *110*, 296–306. [CrossRef]
19. Kiran, E.U.; Trzcinski, A.P.; Ng, W.J.; Liu, Y. Bioconversion of food waste to energy: A review. *Fuel* **2014**, *134*, 389–399. [CrossRef]
20. Ren, Y.; Wang, C.; He, Z.; Qin, Y.; Li, Y.Y. Enhanced biomethanation of lipids by high-solid co-digestion with food waste: Biogas production and lipids degradation demonstrated by long-term continuous operation. *Bioresour. Technol.* **2022**, *348*, 126750. [CrossRef]
21. Kiran, E.U.; Liu, Y. Bioethanol production from mixed food waste by an effective enzymatic pretreatment. *Fuel* **2015**, *159*, 463–469. [CrossRef]
22. Qin, Z.; Duns, G.J.; Pan, T.; Xin, F. Consolidated processing of biobutanol production from food wastes by solventogenic *Clostridium* sp. strain HN4. *Bioresour. Technol.* **2018**, *264*, 148–153. [CrossRef]
23. Yasin, N.H.M.; Mumtaz, T.; Hassan, M.A.; Rahman, N.A. Food waste and food processing waste for biohydrogen production: A review. *J. Environ. Manag.* **2013**, *130*, 375–385. [CrossRef] [PubMed]
24. Patra, B.R.; Nanda, S.; Dalai, A.K.; Meda, V. Slow pyrolysis of agro-food wastes and physicochemical characterization of biofuel products. *Chemosphere* **2021**, *285*, 131431. [CrossRef] [PubMed]
25. Patra, B.R.; Nanda, S.; Dalai, A.K.; Meda, V. Taguchi-based process optimization for activation of agro-food waste biochar and performance test for dye adsorption. *Chemosphere* **2021**, *285*, 131531. [CrossRef]
26. Nguyen, B.T.; Trinh, N.N.; Bach, Q.V. Methane emissions and associated microbial activities from paddy salt-affected soil as influenced by biochar and cow manure addition. *Appl. Soil Ecol.* **2020**, *152*, 103531. [CrossRef]
27. Khoshnevisan, B.; Duan, N.; Tsapekos, P.; Awasthi, M.K.; Liu, Z.; Mohammadi, A.; Angelidaki, I.; Tsang, D.C.; Zhang, Z.; Pan, J.; et al. A critical review on livestock manure biorefinery technologies: Sustainability, challenges, and future perspectives. *Renew. Sustain. Energy Rev.* **2021**, *135*, 110033. [CrossRef]

28. Yao, Y.; Huang, G.; An, C.; Chen, X.; Zhang, P.; Xin, X.; Shen, J.; Agnew, J. Anaerobic digestion of livestock manure in cold regions: Technological advancements and global impacts. *Renew. Sustain. Energy Rev.* **2020**, *119*, 109494. [[CrossRef](#)]
29. Dareioti, M.A.; Vavouraki, A.I.; Tsigkou, K.; Zafiri, C.; Kornaros, M. Dark fermentation of sweet sorghum stalks, cheese whey and cow manure mixture: Effect of pH, pretreatment and organic load. *Processes* **2021**, *9*, 1017. [[CrossRef](#)]
30. Yan, Q.; Liu, X.; Wang, Y.; Li, H.; Li, Z.; Zhou, L.; Qu, Y.; Li, Z.; Bao, X. Cow manure as a lignocellulosic substrate for fungal cellulase expression and bioethanol production. *AMB Exp.* **2018**, *8*, 190. [[CrossRef](#)]
31. Su, G.; Ong, H.C.; Zulkifli, N.W.M.; Ibrahim, S.; Chen, W.H.C.; Chong, C.T.; Ok, Y.S. Valorization of animal manure via pyrolysis for bioenergy: A review. *J. Clean. Prod.* **2022**, *343*, 130965. [[CrossRef](#)]
32. Liu, Q.; Xua, R.; Yan, C.; Han, L.; Lei, H.; Ruan, R.; Zhang, X. Fast hydrothermal co-liquefaction of corn stover and cow manure for biocrude and hydrochar production. *Bioresour. Technol.* **2021**, *340*, 125630. [[CrossRef](#)]
33. Nanda, S.; Dalai, A.K.; Gökalp, I.; Kozinski, J.A. Valorization of horse manure through catalytic supercritical water gasification. *Waste Manag.* **2016**, *52*, 147–158. [[CrossRef](#)] [[PubMed](#)]
34. Itoh, T.; Iwabuchi, K.; Maemoku, N.; Sasaki, I.; Taniguro, K. A new torrefaction system employing spontaneous self-heating of livestock manure under elevated pressure. *Waste Manag.* **2019**, *85*, 66–72. [[CrossRef](#)] [[PubMed](#)]
35. Cheong, D.Y.; Harvey, J.T.; Kim, J.; Lee, C. Improving biomethanation of chicken manure by co-digestion with ethanol plant effluent. *Int. J. Env. Res. Public Health* **2019**, *16*, 5023. [[CrossRef](#)] [[PubMed](#)]
36. Yong, T.L.K.; Matsumura, Y. Catalytic gasification of poultry manure and eucalyptus wood mixture in supercritical water. *Ind. Eng. Chem. Res.* **2012**, *51*, 5685–5690. [[CrossRef](#)]
37. Sarker, T.R.; Nanda, S.; Dalai, A.K.; Meda, V. A review of torrefaction technology for upgrading lignocellulosic biomass to solid biofuels. *BioEnergy Res.* **2021**, *14*, 645–669. [[CrossRef](#)]
38. Basu, P.; Sadhukhan, A.K.; Gupta, P.; Rao, S.; Dhungana, A.; Acharya, B. An experimental and theoretical investigation on torrefaction of a large wet wood particle. *Bioresour. Technol.* **2014**, *159*, 215–222. [[CrossRef](#)]
39. Chen, W.H.; Peng, J.; Bi, X.T. A state-of-the-art review of biomass torrefaction, densification and applications. *Renew. Sustain. Energy Rev.* **2015**, *44*, 847–866. [[CrossRef](#)]
40. Acharya, B.; Dutta, A.; Minaret, J. Review on comparative study of dry and wet torrefaction. *Sustain. Energy Technol. Assess.* **2015**, *12*, 26–37. [[CrossRef](#)]
41. Singh, S.; Chakraborty, J.P.; Mondal, M.K. Torrefaction of *Acacia nilotica*: Oxygen distribution and carbon densification mechanism based on in-depth analyses of solid, liquid, and gaseous products. *Energy Fuels* **2020**, *34*, 12586–12597. [[CrossRef](#)]
42. Amer, M.; Nour, M.; Ahmed, M.; Ookawara, S.; Nada, S.; Elwardany, A. The effect of microwave drying pretreatment on dry torrefaction of agricultural biomasses. *Bioresour. Technol.* **2019**, *286*, 121400. [[CrossRef](#)]
43. Acharya, B.; Dutta, A. Fuel property enhancement of lignocellulosic and nonlignocellulosic biomass through torrefaction. *Biomass Convers. Bioref.* **2016**, *6*, 139–149. [[CrossRef](#)]
44. Lê Thành, K.; Commandré, J.M.; Valette, J.; Volle, G.; Meyer, M. Detailed identification and quantification of the condensable species released during torrefaction of lignocellulosic biomasses. *Fuel Process. Technol.* **2015**, *139*, 226–235. [[CrossRef](#)]
45. Xu, G.; Li, M.; Lu, P. Experimental investigation on flow properties of different biomass and torrefied biomass powders. *Biomass Bioenergy* **2019**, *122*, 63–75. [[CrossRef](#)]
46. Nhuchhen, D.R.; Dutta, A.; Abhi, T.D. Correlations to predict properties of torrefied biomass using mass loss fraction and experimental validation. *Energy Fuels* **2020**, *34*, 11091–11102. [[CrossRef](#)]
47. Zaimes, G.G.; Soratana, K.; Harden, C.L.; Landis, A.E.; Khanna, V. Biofuels via fast pyrolysis of perennial grasses: A life cycle evaluation of energy consumption and greenhouse gas emissions. *Environ. Sci. Technol.* **2015**, *49*, 10007–10018. [[CrossRef](#)]
48. Kumar, R.; Strezov, V. Thermochemical production of bio-oil: A review of downstream processing technologies for bio-oil upgrading, production of hydrogen and high value-added products. *Renew. Sustain. Energy Rev.* **2021**, *135*, 110152. [[CrossRef](#)]
49. Suresh, A.; Alagusundaram, A.; Kumar, P.S.; Vo, D.V.N.; Christopher, F.C.; Balaji, B.; Viswanathan, V.; Sankar, S. Microwave pyrolysis of coal, biomass and plastic waste: A review. *Environ. Chem. Lett.* **2021**, *19*, 3609–3629. [[CrossRef](#)]
50. Sahoo, S.S.; Vijay, V.K.; Chandra, R.; Kumar, H. Production and characterization of biochar produced from slow pyrolysis of pigeon pea stalk and bamboo. *Clean. Eng. Technol.* **2021**, *3*, 100101. [[CrossRef](#)]
51. Akubo, K.; Nahil, M.A.; Williams, P.T. Pyrolysis-catalytic steam reforming of agricultural biomass wastes and biomass components for production of hydrogen/syngas. *J. Energy Inst.* **2019**, *92*, 1987–1996. [[CrossRef](#)]
52. Yu, S.; Park, J.; Kim, M.; Ryu, C.; Park, J. Characterization of biochar and byproducts from slow pyrolysis of hinoki cypress. *Bioresour. Technol. Rep.* **2019**, *6*, 217–222. [[CrossRef](#)]
53. Wang, W.C.; Lee, A.C. The study of producing “drop-in” fuels from agricultural waste through fast pyrolysis and catalytic hydro-processing. *Renew. Energy* **2019**, *133*, 1–10. [[CrossRef](#)]
54. Yi, L.; Liu, H.; Li, S.; Li, M.; Wang, G.; Man, G.; Yao, H. Catalytic pyrolysis of biomass wastes over Org-CaO/Nano-ZSM-5 to produce aromatics: Influence of catalyst properties. *Bioresour. Technol.* **2019**, *294*, 122186. [[CrossRef](#)] [[PubMed](#)]
55. Fan, H.; Chang, X.; Wang, J.; Zhang, Z. Catalytic pyrolysis of agricultural and forestry wastes in a fixed-bed reactor using K₂CO₃ as the catalyst. *Waste Manag. Res. J. Sustain. Circular Econ.* **2020**, *38*, 78–87. [[CrossRef](#)]
56. de Almeida, S.G.; Tarelho, L.A.; Hauschild, T.; Costa, M.A.M.; Dussán, K.J. Biochar production from sugarcane biomass using slow pyrolysis: Characterization of the solid fraction. *Chem. Eng. Process. Process Intens.* **2022**, *179*, 109054. [[CrossRef](#)]

57. Gao, L.; Goldfarb, J.L. Solid waste to biofuels and heterogeneous sorbents via pyrolysis of wheat straw in the presence of fly ash as an in situ catalyst. *J. Anal. Appl. Pyrolysis* **2019**, *137*, 96–105. [[CrossRef](#)]
58. Jaffar, M.M.; Nahil, M.A.; Williams, P.T. Pyrolysis-catalytic hydrogenation of cellulose-hemicellulose-lignin and biomass agricultural wastes for synthetic natural gas production. *J. Anal. Appl. Pyrolysis* **2020**, *145*, 104753. [[CrossRef](#)]
59. Gollakota, A.R.K.; Kishore, N.; Gu, S. A review on hydrothermal liquefaction of biomass. *Renew. Sustain. Energy Rev.* **2018**, *81*, 1378–1392. [[CrossRef](#)]
60. Hu, Y.; Feng, S.; Bassi, A.; Xu, C.C. Improvement in bio-crude yield and quality through co-liquefaction of algal biomass and sawdust in ethanol-water mixed solvent and recycling of the aqueous by-product as a reaction medium. *Energy Convers. Manag.* **2018**, *171*, 618–625. [[CrossRef](#)]
61. Singh, R.; Krishna, B.B.; Bhaskar, T. Hydrothermal liquefaction of lignocellulosic biomass components: Effect of alkaline catalyst. In *Biofuels*; Agarwal, A.K., Agarwal, R.A., Gupta, T., Gurjar, B.R., Eds.; Springer: Singapore, 2017; pp. 69–84.
62. Mathanker, A.; Pudasainee, D.; Kumar, A.; Gupta, R. Hydrothermal liquefaction of lignocellulosic biomass feedstock to produce biofuels: Parametric study and products characterization. *Fuel* **2020**, *271*, 117534. [[CrossRef](#)]
63. Saba, A.; Lopez, B.; Lynam, J.G.; Reza, M.T. Hydrothermal liquefaction of loblolly pine: Effects of various wastes on produced biocrude. *ACS Omega* **2018**, *3*, 3051–3059. [[CrossRef](#)]
64. Goswami, G.; Makut, B.B.; Das, D. Sustainable production of bio-crude oil via hydrothermal liquefaction of symbiotically grown biomass of microalgae-bacteria coupled with effective wastewater treatment. *Sci. Rep.* **2019**, *9*, 15016. [[CrossRef](#)] [[PubMed](#)]
65. Gollakota, A.; Savage, P.E. Hydrothermal liquefaction of model food waste biomolecules and ternary mixtures under isothermal and fast conditions. *ACS Sustain. Chem. Eng.* **2018**, *6*, 9018–9027. [[CrossRef](#)]
66. Alper, K.; Tekin, K.; Karagoz, S. Hydrothermal liquefaction of lignocellulosic biomass using potassium fluoride-doped alumina. *Energy Fuels* **2019**, *33*, 3248–3256. [[CrossRef](#)]
67. Zhang, Y.; Minaret, J.; Yuan, Z.; Dutta, A.; Xu, C. Mild hydrothermal liquefaction of high water content agricultural residue for bio-crude oil production: A parametric study. *Energies* **2018**, *11*, 3129. [[CrossRef](#)]
68. Hwang, H.; Lee, J.H.; Choi, I.G.; Choi, J.W. Comprehensive characterization of hydrothermal liquefaction products obtained from woody biomass under various alkali catalyst concentrations. *Environ. Technol.* **2019**, *40*, 1657–1667. [[CrossRef](#)]
69. Makwana, J.P.; Pandey, J.; Mishra, G. Improving the properties of producer gas using high temperature gasification of rice husk in a pilot scale fluidized bed gasifier (FBG). *Renew. Energy* **2019**, *130*, 943–951. [[CrossRef](#)]
70. Centi, G.; Perathoner, S. Chemistry and energy beyond fossil fuels. A perspective view on the role of syngas from waste sources. *Catal. Today* **2020**, *342*, 4–12. [[CrossRef](#)]
71. dos Santos, R.G.; Alencar, A.C. Biomass-derived syngas production via gasification process and its catalytic conversion into fuels by Fischer Tropsch synthesis: A review. *Int. J. Hydrogen Energy* **2020**, *45*, 18114–18132. [[CrossRef](#)]
72. Pecchi, M.; Baratieri, M. Coupling anaerobic digestion with gasification, pyrolysis or hydrothermal carbonization: A review. *Renew. Sustain. Energy Rev.* **2019**, *105*, 462–475. [[CrossRef](#)]
73. Gupta, P.; Velazquez-Vargas, L.G.; Fan, L.S. Syngas Redox (SGR) Process to produce hydrogen from coal derived syngas. *Energy Fuels* **2007**, *21*, 2900–2908. [[CrossRef](#)]
74. Nguyen, N.M.; Alobaid, F.; Dieringer, P.; Epple, B. Biomass-based chemical looping gasification: Overview and recent developments. *Appl. Sci.* **2021**, *11*, 7069. [[CrossRef](#)]
75. Gopirajan, P.V.; Gopinath, K.P.; Sivaranjani, G.; Arun, J. Optimization of hydrothermal gasification process through machine learning approach: Experimental conditions, product yield and pollution. *J. Clean. Prod.* **2021**, *306*, 127302. [[CrossRef](#)]
76. Hamad, M.A.; Radwan, A.M.; Heggo, D.A.; Moustafa, T. Hydrogen rich gas production from catalytic gasification of biomass. *Renew. Energy* **2016**, *85*, 1290–1300. [[CrossRef](#)]
77. Vamvuka, D.; Karouki, E.; Sfakiotakis, S.; Salatino, P. Gasification of waste biomass chars by carbon dioxide via thermogravimetry—Effect of catalysts. *Combust. Sci. Technol.* **2012**, *184*, 64–77. [[CrossRef](#)]
78. Gökkaya, D.S.; Çokkuvvetli, T.; Sağlam, M.; Yüksel, M.; Ballice, L. Hydrothermal gasification of poplar wood chips with alkali, mineral, and metal impregnated activated carbon catalysts. *J. Supercrit. Fluids* **2019**, *152*, 104542. [[CrossRef](#)]
79. Hai, I.U.; Sher, F.; Yaqoob, A.; Liu, H. Assessment of biomass energy potential for SRC willow woodchips in a pilot scale bubbling fluidized bed gasifier. *Fuel* **2019**, *258*, 116143. [[CrossRef](#)]
80. Singh, D.; Sharma, D.; Soni, S.L.; Sharma, S.; Sharma, P.K.; Jhalani, A. A review on feedstocks, production processes, and yield for different generations of biodiesel. *Fuel* **2020**, *262*, 116553. [[CrossRef](#)]
81. Rezania, S.; Oryani, B.; Park, J.; Hashemi, B.; Yadav, K.K.; Kwon, E.E.; Hur, J.; Cho, J. Review on transesterification of non-edible sources for biodiesel production with a focus on economic aspects, fuel properties and by-product applications. *Energy Convers. Manag.* **2019**, *201*, 112155. [[CrossRef](#)]
82. Avhad, M.R.; Marchetti, J.M. A review on recent advancement in catalytic materials for biodiesel production. *Renew. Sustain. Energy Rev.* **2015**, *50*, 696–718. [[CrossRef](#)]
83. Veljković, V.B.; Banković-Ilić, I.B.; Stamenković, O.S. Purification of crude biodiesel obtained by heterogeneously-catalyzed transesterification. *Renew. Sustain. Energy Rev.* **2015**, *49*, 500–516. [[CrossRef](#)]
84. Borges, M.E.; Díaz, L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 2839–2849. [[CrossRef](#)]

85. Jayakumar, M.; Karmegam, N.; Gundupalli, M.P.; Gebeyehu, K.B.; Asfaw, B.T.; Chang, S.W.; Ravindran, B.; Awasthi, M.K. Heterogeneous base catalysts: Synthesis and application for biodiesel production—A review. *Bioresour. Technol.* **2021**, *331*, 125054. [[CrossRef](#)] [[PubMed](#)]
86. Mansir, N.; Taufiq-Yap, Y.H.; Rashid, U.; Lokman, I.M. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. *Energy Convers. Manag.* **2017**, *141*, 171–182. [[CrossRef](#)]
87. Negm, N.A.; Betiha, M.A.; Alhumaimess, M.S.; Hassan, H.M.; Rabie, A.M. Clean transesterification process for biodiesel production using heterogeneous polymer-heteropoly acid nanocatalyst. *J. Clean. Prod.* **2019**, *238*, 117854. [[CrossRef](#)]
88. Hanif, M.A.; Nisar, S.; Rashid, U. Supported solid and heteropoly acid catalysts for production of biodiesel. *Catal. Rev.* **2017**, *59*, 165–188. [[CrossRef](#)]
89. Canet, A.; Bonet-Ragel, K.; Benaiges, M.D.; Valero, F. Lipase-catalysed transesterification: Viewpoint of the mechanism and influence of free fatty acids. *Biomass Bioenergy* **2016**, *85*, 94–99. [[CrossRef](#)]
90. Pikula, K.; Zakharenko, A.; Stratidakis, A.; Razgonova, M.; Nosyrev, A.; Mezhuev, Y.; Tsatsakis, A.; Golokhvas, K. The advances and limitations in biodiesel production: Feedstocks, oil extraction methods, production, and environmental life cycle assessment. *Green Chem. Lett. Rev.* **2020**, *13*, 275–294. [[CrossRef](#)]
91. Katre, G.; Raskar, S.; Zinjarde, S.; Kumar, V.R.; Kulkarni, B.D.; RaviKumar, A. Optimization of the in situ transesterification step for biodiesel production using biomass of *Yarrowia lipolytica* NCIM 3589 grown on waste cooking oil. *Energy* **2018**, *142*, 944–952. [[CrossRef](#)]
92. Bashiri, H.; Pourbeiram, N. Biodiesel production through transesterification of soybean oil: A kinetic Monte Carlo study. *J. Mol. Liquids* **2016**, *223*, 10–15. [[CrossRef](#)]
93. Mohadesi, M.; Aghel, B.; Gouran, A.; Razmehgir, M.H. Transesterification of waste cooking oil using Clay/CaO as a solid base catalyst. *Energy* **2022**, *242*, 122536. [[CrossRef](#)]
94. Dutti, I.J.; Maliha, M.; Ahmed, S. Biodiesel production from waste frying oil and its process simulation. *J. Mod. Sci. Technol.* **2016**, *4*, 50–62.
95. Hu, W.; Zhou, X.; Tan, J.; Hou, J.; Xie, Y.; Wang, X.; Wang, Y.; Zhang, Y. In situ transesterification of wet sewage sludge via hydrothermal process: Biodiesel production and residue utilization. *Biomass Bioenergy* **2020**, *141*, 105715. [[CrossRef](#)]
96. Nanda, S.; Dalai, A.K.; Berruti, F.; Kozinski, J.A. Biochar as an exceptional bioresource for energy, agronomy, carbon sequestration, activated carbon and specialty materials. *Waste Biomass Valor.* **2016**, *7*, 201–235. [[CrossRef](#)]
97. Bartoli, M.; Giorcelli, M.; Jagdale, P.; Rovere, M.; Tagliaferro, A. A review of non-soil biochar applications. *Materials* **2020**, *13*, 261. [[CrossRef](#)]
98. Panwar, N.L.; Pawar, A.; Salvi, B.L. Comprehensive review on production and utilization of biochar. *SN Appl. Sci.* **2019**, *1*, 168. [[CrossRef](#)]
99. Kang, K.; Nanda, S.; Hu, Y. Current trends in biochar application for catalytic conversion of biomass to biofuels. *Catal. Today* **2022**. [[CrossRef](#)]
100. Koveria, A.; Kieush, L.; Svetkina, O.; Perkov, Y. Metallurgical coke production with biomass additives. Part 1. A review of existing practices. *Can. Metal. Quarter.* **2020**, *59*, 417–429. [[CrossRef](#)]
101. Salimi, M.; Safari, F.; Tavasoli, A.; Shakeri, A. Hydrothermal gasification of different agricultural wastes in supercritical water media for hydrogen production: A comparative study. *Int. J. Ind. Chem.* **2016**, *7*, 277–285. [[CrossRef](#)]
102. Shen, Y.; Yu, S.; Yuan, R.; Wang, P. Biomass pyrolysis with alkaline-earth-metal additive for co-production of bio-oil and biochar-based soil amendment. *Sci. Total Environ.* **2020**, *743*, 140760. [[CrossRef](#)]
103. Zhang, Z.; Zhu, Z.; Shen, B.; Liu, L. Insights into biochar and hydrochar production and applications: A review. *Energy* **2019**, *171*, 581–598. [[CrossRef](#)]
104. Chand, R.; Borugadda, V.B.; Qiu, M.; Dalai, A.K. Evaluating the potential for bio-fuel upgrading: A comprehensive analysis of bio-crude and bio-residue from hydrothermal liquefaction of agricultural biomass. *Appl. Energy* **2019**, *254*, 113679. [[CrossRef](#)]
105. Enamala, M.K.; Enamala, S.; Chavali, M.; Donepudi, J.; Yadavalli, R.; Kolapalli, B.; Aradhyula, T.V.; Velpuri, J.; Kuppam, C. Production of biofuels from microalgae-A review on cultivation, harvesting, lipid extraction, and numerous applications of microalgae. *Renew. Sustain. Energy Rev.* **2018**, *94*, 49–68. [[CrossRef](#)]
106. Chen, W.T.; Zhang, Y.; Zhang, J.; Yu, G.; Schideman, L.C.; Zhang, P.; Minarick, M. Hydrothermal liquefaction of mixed-culture algal biomass from wastewater treatment system into bio-crude oil. *Bioresour. Technol.* **2014**, *152*, 130–139. [[CrossRef](#)] [[PubMed](#)]
107. Saber, M.; Nakhshiniev, B.; Yoshikawa, K. A review of production and upgrading of algal bio-oil. *Renew. Sustain. Energy Rev.* **2016**, *58*, 918–930. [[CrossRef](#)]
108. Zhang, T.; Cao, D.; Feng, X.; Zhu, J.; Lu, X.; Mu, L.; Qian, H. Machine learning prediction of bio-oil characteristics quantitatively relating to biomass compositions and pyrolysis conditions. *Fuel* **2022**, *312*, 122812. [[CrossRef](#)]
109. Salehi, E.; Abedi, J.; Harding, T. Bio-oil from sawdust: Effect of operating parameters on the yield and quality of pyrolysis products. *Energy Fuels* **2011**, *25*, 4145–4154. [[CrossRef](#)]
110. Gupta, S.; Gupta, G.K.; Mondal, M.K. Slow pyrolysis of chemically treated walnut shell for valuable products: Effect of process parameters and in-depth product analysis. *Energy* **2019**, *181*, 665–676. [[CrossRef](#)]
111. Joshi, N.; Lawal, A. Hydrodeoxygenation of pyrolysis oil in a microreactor. *Chem. Eng. Sci.* **2012**, *74*, 1–8. [[CrossRef](#)]
112. Adnan, M.A.; Xiong, Q.; Muraza, O.; Hossain, M.M. Gasification of wet microalgae to produce H₂-rich syngas and electricity: A thermodynamic study considering exergy analysis. *Renew. Energy* **2020**, *147*, 2195–2205. [[CrossRef](#)]

113. Abe, J.O.; Popoola, A.P.I.; Ajenifuja, E.; Popoola, O.M. Hydrogen energy, economy and storage: Review and recommendation. *Int. J. Hydrogen Energy* **2019**, *44*, 15072–15086. [[CrossRef](#)]
114. Tian, M.W.; Yuen, H.C.; Yan, S.R.; Huang, W.L. The multiple selections of fostering applications of hydrogen energy by integrating economic and industrial evaluation of different regions. *Int. J. Hydrogen Energy* **2019**, *44*, 29390–29398. [[CrossRef](#)]
115. Alam, S.S.; Churkunti, P.R.; Depcik, C. Comparison of waste plastic fuel, waste cooking oil biodiesel, and ultra-low sulfur diesel using a Well-to-Exhaust framework. *Int. J. Environ. Sci. Technol.* **2022**, *19*, 5857–5876. [[CrossRef](#)]
116. Ling, J.S.J.; Tan, Y.H.; Mubarak, N.M.; Kandedo, J.; Saptorio, A.; Nolasco-Hipolito, C. A review of heterogeneous calcium oxide based catalyst from waste for biodiesel synthesis. *SN Appl. Sci.* **2019**, *1*, 810. [[CrossRef](#)]