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Review

Bioenergy and biofuel production from biomass using thermochemical conversions technologies—a review

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Abstract: Biofuel and bioenergy production from diverse biomass sources using thermochemical technologies over the last decades has been investigated. The thermochemical conversion pathways comprise dry processes (i.e., torrefaction, combustion, gasification, and pyrolysis), and wet processes (i.e., liquefaction, supercritical water gasification, and hydrothermal carbonisation). It has been found that the thermochemical processes can convert diverse biomass feedstocks to produce bioenergy sources such as direct heat energy, as well as solid, liquid and gaseous biofuels for instance biochar, bio-oil and syngas. However, some of these processes have limitations that impede their large-scale utilisation such low energy efficiency, high costs, and generation of harmful chemicals that cause environmental concerns. Efforts are being made extensively to improve the conversion technologies in order to reduce or solve these problems for energy efficiency improvement. In this review, the emerging developments in the thermochemical techniques for producing biofuel and bioenergy from biomass are presented and evaluated in terms of their technological concepts and projections for implementation. It is suggested that an integration of torrefaction or hydrothermal carbonisation with combustion and/or gasification may optimise biomass energy use efficiency, enhance product quality, and minimise the formation of noxious compounds.

Keywords: bioenergy; biofuel; biomass; combustion; hydrothermal carbonisation; hydrothermal liquefaction; gasification; pyrolysis; supercritical water gasification; torrefaction

1. Introduction

The world's total energy demand is expected to reach about 865 exajoules per year (EJ/y) by 2040 [1,2]. The major problem related to meeting this demand is the dependence on fossil fuels, as their uses increase Greenhouse gas (GHG) emissions and contribute to air pollution and climate change. International protocols such as the Paris Agreement encourages countries to reduce the consumption of fossil fuels by substituting with renewable energy as a means of assisting the fight against global climate change. As a result, the goal and desire of many countries around the world today is towards the production of renewable energy from sources such as wind, solar and biomass.

Biomass is any type of living or recently living organic material that comes from plants and animals. Biomass can be lignocellulosic such as wood and agriculture residuals or non-cellulosic, like animal manure, sewage sludge, and municipal solid wastes (MSWs) [3]. Biofuel production from biomass and its application offer economic benefits through employments and business incomes, rural economy diversification, import substitution with direct and indirect influences on the trade balance, energy supply, and diversification by the establishment of new industries [4]. The major challenge with biomass usage for biofuel/bioenergy production is the efficient management of land usage for crop production to prevent food vs. energy conflict and reduction of Greenhouse gas (GHG) emissions to prevent climate change [4]; as the application of synthetic fertilisers to improve crop yield leads to the emissions of N_2O from agricultural land [5]. Sustainable biomass residues or waste biomass feedstocks such as residues from plantation fields, agricultural and food waste, animal manure, sewage sludge, and MSW do not depend on agricultural land and are readily available [6,7]. Utilising biomass residues and waste contribute to waste minimisation, thus leading to the mitigation of carbon footprint and reduction of GHG emissions; as these wastes would have otherwise decomposed to generate CO_2 and other pollutant gases.

Biomass is the only renewable energy source that can be converted into any form of fuel comprising solid, liquid, and gaseous [8]. Biomass has been an important source of fuel for cooking and heating in developing countries. However, using simple cookstoves has impact on human health and the environment [9]. In many developed countries, the use of biomass fuels for electricity generation and transportation is increasing as a means of minimising CO_2 emissions from the use of fossil fuels. Biomass has a lower calorific value than coal or gas, but produces less CO_2 emissions (about 77 g CO_2 eq/kWhe), compared with 1054 g CO_2 eq/kWhe produced by coal [10]. Biomass has lower ash, sulphur and nitrogen contents (except manure and sludge) than coal; hence, GHG emissions from biomass production and energy generation are significantly lower than those for fossil, about 66–99% lower than for current coal-fired power generation [11].

Energy from biomass (bioenergy) accounts for about 1/10th of the global total energy supply [9], which is projected to increase to about 50% by 2050 [12]. In 2020, about 4,532 trillion British thermal units (TBtu) or 4.5 quadrillion Btu, which is nearly 4.9% of total primary energy consumption in the United States was from biomass. Of the 4.9%, roughly 46.36% (i.e., 2,101 TBtu) was from wood and wood-derived biomass, about 44.13% (i.e., 2,000 TBtu) was from biofuels (mainly ethanol), and 9.49% (i.e., 430 TBtu) was from the biomass in municipal wastes [13]. In 2020, there was a record increase in bioenergy production in the Great Britain, with bioenergy and waste accounting for about 12.7% of electricity generation, which represented 37% of the total generation of primary energy from low carbon sources [14]. In Asian countries, China has contributed to the highest renewable energy production, making up 9.7% of total energy supply (13.7 EJ) in 2019. Of this, modern bioenergy (residential use of biomass) represented 12% (1.8 EJ) and 25% (3.4 EJ) was from traditional bioenergy (i.e., use of biomass for residential heating) [15]. This is followed by India, with renewable energy sources making up of total energy supply (8.8 EJ) in 2019, with 88% of it being bioenergy, which is mostly traditional use of biomass for residential heating [16]. Next is Japan with 6.3% renewables of the total energy supply, of which 40% was bioenergy from biomass, with solid biomass representing 90% of bioenergy whilst the other types of bioenergy (biogas, liquid biofuels, renewable MSW) were much lower [17]. In South Africa, nearly 85% of renewable energy is from biomass, which is almost entirely used for heat production (residential and in industry) [18].

Using bioenergy produced from biomass as renewable energy minimises emissions of air pollutants including GHGs, particularly CO_2 during combustion, reducing the overall pollution load and other environmental impacts [4,19–21]. Also, biofuels production and their utilisation are described as been a carbon-neutral path as they are produced from biomass, which absorbs the greater amount of CO_2 from the environment [4,22,23]. The contribution of bioenergy to the energy mix has increased interests for using biomass in the production of heat, electricity, and transport biofuels [13,24,25], largely due to higher levels of policy support [13]. However, bioenergy has challenges that affect its handling and utilisation. Except when dry biomass such as dry wood is used, biomass with high moisture content such as sludge, manure, etc are difficult to handle and transport and has a lower calorific value, which affects their energy efficiency. Hence, biomass needs to be processed to overcome these drawbacks and to improve the energy efficiency. Also, bioenergy has technological obstacles affecting the commercialisation of advanced biofuels [4], which varies depending on the biofuel conversion technology.

There are several types of biofuels generation technologies, which can be categorised into biological/biochemical and thermochemical technologies. Biochemical conversion technologies, namely anaerobic digestion and fermentation use microorganisms, bacteria and enzymes to breakdown biomass into gaseous and liquid biofuels such as biogas and bioethanol, respectively. Thermochemical biofuels and bioenergy generation technologies have gain research and technical attention over the past years due to their ability to process diverse biomass feedstocks to produce a variety of bioenergy sources including direct heat energy, solid, liquid and gaseous biofuels such as biochar, bio-oil and syngas. Therefore, the general objective of this review is to provide a detailed discussion of the different thermochemical technologies for biofuels and bioenergy production. The conversion technologies covered in this review include combustion, torrefaction, pyrolysis, gasification (which are ‘dry’ processes), and hydrothermal processes namely liquefaction, supercritical water gasification, and hydrothermal carbonisation (HTC). The ‘dry’ thermochemical processes are viable for biomass with low moisture content (<20 wt%); so, they will require energy intensive pre-drying of the biomass, especially to remove the surface water. Combustion is a simple and an already available technology for generating heat energy and electricity in steam turbines [13], but it has adverse effects on the environment caused by the generation of by-products such as CO, CO_2, soot, dust and ash; and for biomass such as manure and sludges, NOx and SOx are generated. Gasification can process diverse biomass feedstocks to produce syngas with high efficiency [26], which can be further treated using Fischer-Tropsch process to produce liquid fuels [13]. However, extensive cleaning of the syngas is required to remove tar, char, ash and dust, and H_2S especially when a feedstock like sewage sludge is used. Pyrolysis can be used for different sources of biomass to produce a variety of products (biochar, bio-oil, and syngas) [27], but the syngas requires extreme cleaning to remove tar, char, ash and dust. Also, feedstock such as sewage sludge and manure generate H_2S [28].

Recent developments have been focusing on pre-treating the biomass to remove inorganics that contribute to the formation of ash and other pollutants in the products. Pre-treating biomass using torrefaction and HTC have been found to improve combustion performance of biomass [29], and reduce pollutant emissions, while enhancing energy efficiency and syngas quality in gasification [30]. However, there are still challenges even when the biomass is pre-treated, which requires further attention. For example, there is high ash and tar contents in torrefied biomass, which cause problems in combustion and gasification systems [31]. Microwave-assisted pyrolysis (MAP) and catalytic pyrolysis are new technologies that improve the pyrolysis process in terms of yield production and quality [32,33]. The challenges in these emerging technologies include high operating costs in MAP and catalyst deactivation caused by coke deposition in catalytic pyrolysis [34]. The deactivated catalyst can be regenerated to remove the thermal coke, but after regeneration, the coke still blocks the active sites of the catalyst. There are also irreversible chemical changes to the catalyst structure, leading to loss of activity [35], thus posing challenges in large-scale applications.

The hydrothermal techniques can process all kinds of biomass feedstocks, including those with high moisture content, but generally there is a high energy demand to heat the high moisture fraction to reach the reaction temperature. Hydrothermal liquefaction (HTL) produces bio-oil and a variety of other useful products depending on the biomass feedstock. Catalyst deactivation caused by coking reduces bio-oil yield and quality. Also, HTL of feedstock containing very high minerals could lead to reactor clogging as a result of salt deposition in the reactor [36]. Hydrothermal gasification produces high-quality syngas with high carbon efficiency (than direct gasification), which is free from char and tar at comparatively low temperatures. However, coke and tar will still form in the parts of the biomass that is not gasified, and salt precipitation could lead to clogging problems [37]. The reactors for HTC are simple and scalable with a relatively low energy requirement. The main product of HTC is char or hydrochar, which has improved energy characteristics (calorific value and energy ratio) than the biomass feedstock. One downside of the HTC process is that, the liquid by-product contains dissolved inorganics and organics transferred from the biomass [38]; hence, will require post-treatment. To improve the energy efficiency of the process, attention has been on anaerobic digestion (AD) of the liquid by-products for biogas production [39,40], but further investigations are still needed, especially using different biomass feedstock and optimisation of the process.

The present review will analyse and discuss the recent progress in thermochemical technological routes of converting biomass residues and waste to biofuels and bioenergy by covering the up-to-date information in this rapidly growing area. The significant constraints and challenges facing these technologies are discussed in detail, such as technological challenges, conversion efficiency, and the environmental impacts of the bioenergy production technologies. Future research should focus on biomass pre-treatment and process integration to address these challenges.

2. Biomass sources for thermochemical technologies

Biomass is any type of living or recently living organic material that comes from plants and animals. Biomass is available in different sources. Some of the biomass is specifically cultivated for energy purpose such as Miscanthus and poplar. However, biomass residues and waste are generated as by-products when the preferred raw products are planted, processed, and consumed [6]. These can be classified into three groups namely, primary, secondary, and tertiary residues/wastes. Primary residues are created during plantation of food crops and forest products in the field. Examples include corn stems, stalks, straw, and leaves. Secondary biomass residues are wastes generated when agricultural and food crops are processed into final products, such as woodchips, sawdust, rice husk and hulls, coffee husk, palm kernel cake, sugarcane bagasse, pulp and paper waste, textiles. Tertiary residues are generated after biomass-derived products have been consumed by humans and/or animals, which are present in the form of MSWs [7,41] and are later converted to wastewater and/or sewage sludge. These groups can further be categorised into sub-groups as shown in Figure 1.

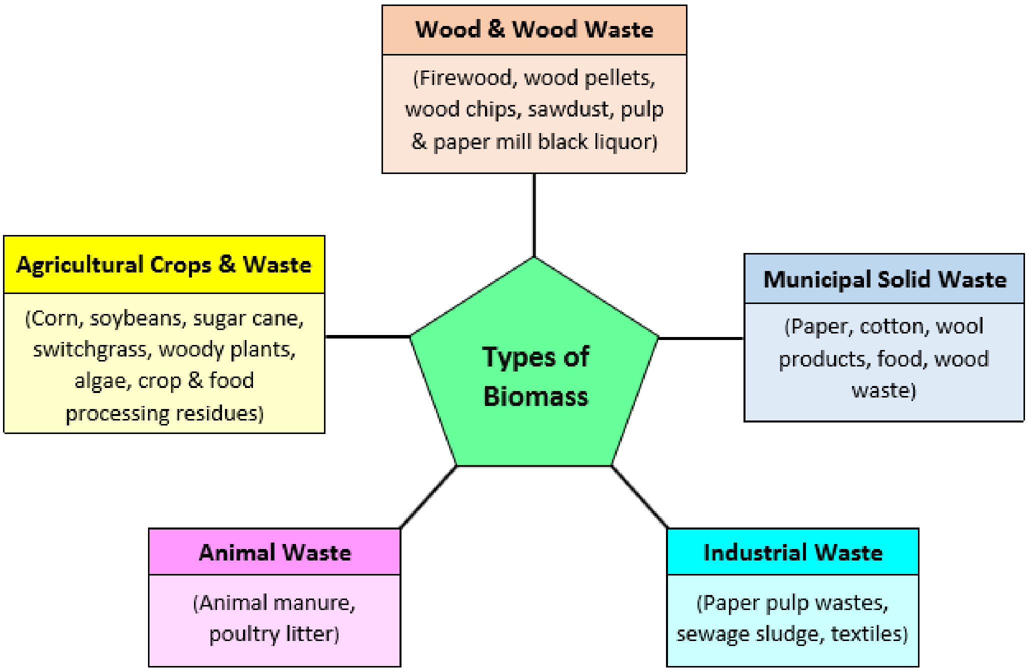

Figure 1. Biomass sources for energy.

The US Department of Energy and Agriculture estimated the total sustainable biomass feedstock that can be harvested from US forest and agriculture land to be 1.18 billion dry tons, and have projected a 30 percent replacement of the current U.S. petroleum consumption with biofuels by 2040 [42].

Characteristics of some biomass feedstocks are presented in Table 1. The biomass composition shown in Table 1 reveals that biomass characteristics is feedstock dependent. Early research has shown that feedstock characteristics such as chemical composition, energy content, and physical properties such as moisture content, particle size, volatile matter, and non-combustible or ash component considerably influence the conversion efficiencies and the characteristics of the final product [43,44].

2.1. Wood and agricultural feedstocks

Feedstock for biofuels can be obtained from wood processing wastes that are generated through sawmill and lumber processing activities. These include sawdust, wood chips, firewood or discarded logs [45]. Other source of wood waste is black liquor obtained from pulp and paper mill.

China is the world leading producer of straw, which is estimated to be around 700 Mt of straw per year [46,47]. Straw is agricultural residues or by-products of harvested food crops like corn, rice, wheat, cotton, beans, and sugar crops. About 50% of this straw is available for energy production per year in China [47]. In tropical countries, sugarcane bagasse, which is a residue of sugarcane has economic utilisation for producing biofuels such as biochar [48].

Animal manure and poultry litter can also be classified as agricultural waste. About 1.18 billion dry tons of sustainable biomass feedstock can be harvested from the US agricultural land [42]. This includes MSW, animal manures, crop residues, corn fibre, and grains. Of this biomass feedstock, animal manures represent a large proportion (i.e., 18%); however, studies on its application for biofuels/bioenergy production is not as extensive as the other plant-based biomass. Carbonisation has been the environmentally acceptable means of converting animal manures to biofuels [43]. As indicated in Table 1, the characteristics of animal manure feedstock can differ extensively. Dairy and swine manures usually contains more than 90% moisture content, whilst manures from poultry and feedlot processes typically have low water content (less than 50%).

Table 1. Biomass feedstock characteristics in relation to thermochemical conversion techniques.

Feedstock	Elemental composition (%, daf)					Volatile matter (% db)	Ash (% db)	Moisture content (% fresh wt.)	HHV (MJ/kg^{db})	Particle size (mm)
	C	H	N	O	S					
Wood [a]	50–55	5–6	0.1–0.2	39–44	0–0.1	70–90	0.1–8	5–20 (dried wood) 35–60 (green wood)	19–22	NA
Grasses [b]	46–51	6–7	0.4–1.0	41–46	<0.02–0.08	75–83	1.4–6.7	NR	18.3–20.6	N/A
Sugarcane bagasse [c]	45.3	6.1	0.2	46.8	–	N/R	N/R	N/R	16.7	0.56–0.85
Grape pomace [c]	50.3	6.1	2.0	33	–	N/R	N/R	N/R	20.0	0.56–0.85
Microalgae [c]	42.4	6.1	3.6	38.7	–	N/R	N/R	N/R	17.0	0.56–0.85
Manures [d]	52–60	6–8	3–6	26–36	0.7–1.2	57–70	19–31	21–99.7*	13–20	N/A
Primary sewage sludge [e]	43–53.3	6.5–7.2	3.8–5.3	32–46.6	2.1	60–80**	16–25	90–96**	18–29	<5 (82% wt. <0.1 mm) [#]
MSW [f]	27–55	3–9	0.4–1.8	22–44	0.04–0.18	41–71	12–50	15–40	2–14	Average”: 180–200
Rapeseed [g]	62.1	9.1	3.9	24.9	–	81.7	5.5	4.9	26.7	N/A

[a] Data from 22 samples of soft and hard wood [49].

[b] Grass varieties (such as poplar pannonia, energy grass pellets, and tree heaven) [50].

[c] Values estimated based on dry basis (db) [51]. [d] Data from [52, 53]. * Data from [54]. [e] Values from [44, 55].

** Moisture content after thickening [44, 56]. [#] Model values for % (wt.) of solids with particle size <0.1 mm [57].

[f] Data from [58, 59]. [g] Data from [60]. “Neglecting bulky items.

db = dry basis; daf = Dry ash-free basis; NA = Not applicable; NR = Not reported; HHV = Higher Heating Value.

2.2. Municipal solid waste

Municipal solid waste (MSW) comprises of product packaging, newspapers, magazines, food waste, grass clippings, yard waste and recyclables. Combustion ash, construction, demolishing waste, industrial and municipal wastewaters are not classified as MSW [43]. MSW is widely abundant in most countries but remains a largely untapped energy resource because electricity generation from MSW is generally cost intensive [61]. The rate of MSW generation differs and depends on geographical location and it is found to correlate with average income, which vary from 0.1 tons per person a year in low-income countries to 0.8 tons per person a year in high income countries [62].

MSW (unless segregated) is a heterogenous feedstock with varying composition and chemical properties (see Table 1), which may be contaminated. This makes it difficult in its use as a feedstock for most of the technologies for biofuel/bioenergy generation. To reduce operation and maintenance problems, MSW needs to be sorted and shredded before feeding to the process [58,59,63–65]. Mostly, the level of sorting of the different MSW fractions determines the choice of technology to be used. Also, rigorous regulation over emissions is needed resulting in high costs in relation to emissions control in waste-to-energy facilities [61]. Incineration has been the conventional thermochemical method of treating MSW; however, it is not globally preferred as its pollution has been a problem, resulting in public opposition. Recently, compositing followed by calcination to produce activated carbon have been found as an efficient way of managing MSW [66,67].

2.3. Industrial waste

Pulp and paper sludges are classified as industrial waste. Pulp and paper sludge is generated as waste from pulp and paper processes. They are naturally wet feedstock; hence, high energy requirements are needed to dry them before they can be used for some other thermochemical processes. Some degree of management, processing and/or pre-treatment are required to meet environmental regulations. Sewage sludge is a municipal waste, which is obtained from the treatment of human waste (i.e., excreta and faecal sludges) mostly using centralised wastewater treatment plants (WWTP). Hence, sewage sludge may be classified as an industrial waste. Management of human waste comes with substantial collection and pre-treatment costs [43] from the WWTP. Sewage sludge contains proteins, lipids, fibre, non-fibrous carbohydrates, inorganic matter, and ash [68]. The amount of human waste (i.e., untreated excrement and faecal sludges) and sewage sludge (i.e., primary and secondary sludges from WWTP) has been increasing remarkably. This is because of increasing population growth, and the installation of new sanitation facilities especially in developing countries as well as increase in WWTPs in developed countries [69]. It is estimated that, globally, between 0.6 to 1.0 billion tons of human faeces are generated annually [70,71]. By the end of 2019, sewage sludge production in China was 39.04 million tons (80% water content), obtained from 5476 municipal WWTPs operating in China [72]. The yearly US biosolids production was estimated to be nearly 4.75 million dry metric tons (dmt) in 2019, based on EPA annual reports collected form Publicly Owned Treatment Works (POTWs) [73]. The EU generated about 9.0–9.5 million tons of sewage sludge (on dry basis) in 2017 [74]. The current (2019) data show that the generation rates of member countries have increased significantly, but data from some of the most important sludge producers (such as Italy, Spain, Germany, and UK) were missing, so the current data cannot be used.

3. Thermochemical biomass to energy conversion pathways

Thermochemical conversion is the decomposition of the biomass by means of heat into useful energy or energy sources. This is a high-temperature reformation process, which involves breaking of the biomass macromolecules and reforming of organic matter, converting the biomass into various forms of fuel namely, direct fuel (heat and power), solid fuel (bio char), gaseous fuel (synthesis gas), and highly oxygenated liquid fuel (bio-oil or biocrude). Thermochemical technologies include direction combustion, torrefaction, gasification (direct), pyrolysis, and hydrothermal processes (i.e., liquefaction, hydrothermal gasification and hydrothermal carbonisation) (Figure 2). The choice of conversion technology is influenced by many factors such as the type and quantity of biomass feedstock, the preferred type of energy (e.g., the end use conditions), financial circumstances, environmental principles, and precise aspects of the project [75]. Combustion, torrefaction, gasification, and pyrolysis typically require pre-drying of feedstock with high moisture content (>20%). The availability of industrial infrastructure to provide highly developed thermochemical technologies equipment has given them more attention coupled with their ability to produce energy from wastes that cannot be converted by non-thermochemical processes [76].

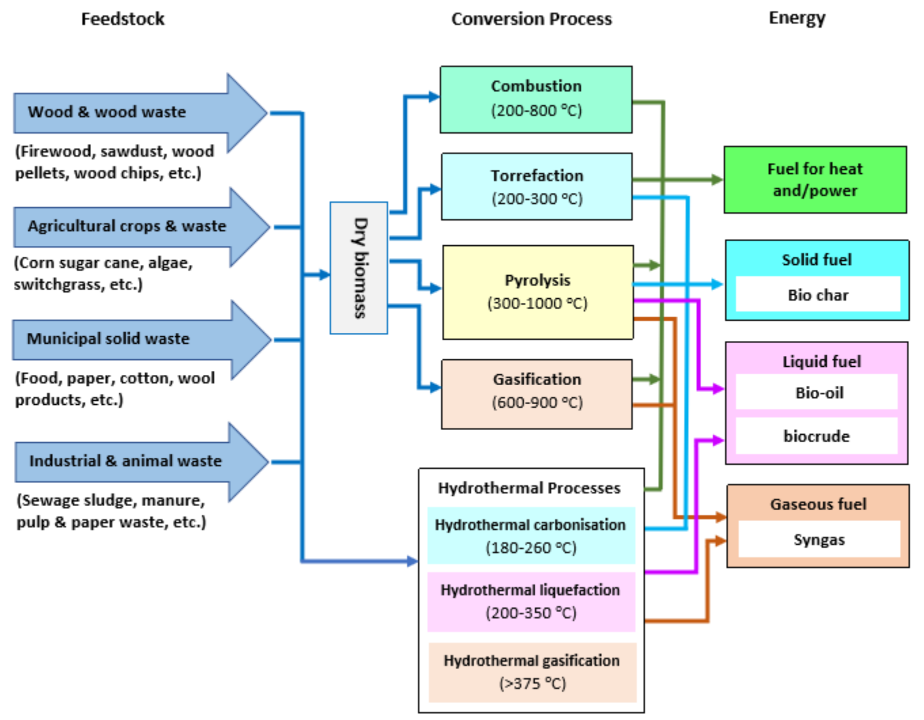

Figure 2. Potential biomass to bioenergy pathways via thermochemical conversion.

3.1. Combustion technology

Direct combustion is the most common technique for converting biomass to useful energy. This requires burning the biomass to generate heat energy, which can be utilised for industries process heat, for generation of electricity in steam turbines, or combined heat and power (CHP) co-generation systems [12,77]. It has been found that co-generation can reduce the cost of power production by 40–60%

for stand-alone plants ranging between 1–30 MWe [61]. In developing countries, especially in Africa, combustion is the most utilised process for biomass conversion to energy [78].

Combustion of biomass involves heating/burning the biomass in a combustion reactor with sufficient amount of oxygen to produce carbon dioxide, water vapour and heat (energy) as shown in the following generalised reaction:

$$\text{Biomass} + \text{Oxygen} \underset{\Delta}{\rightarrow} \text{Carbon Dioxide} + \text{Water Vapour} + \text{Heat} \tag{1}$$

The amount of heat that is produced differs depending on the heating or calorific value and moisture content of the biomass, the amount of air (oxygen) used to burn the biomass, and the construction of the furnace [79]. Generally, 20 MJ of energy is produced per kg of biomass [80].

Typical biomass combustion reactors include fireplace, stoves, furnaces (furnace with boilers, wood-chip and pellet furnace), and industrial combustion systems (downdraft, updraft and fluidised bed combustion systems). The combustion process involves three main stages namely drying, pyrolysis and oxidation [79]. The residual moisture in the biomass must be removed (at low temperatures up to 150 ℃) before combustion can take place. The heat used for the drying is provided by radiation from flames and from stored heat from the combustion process. During the pyrolysis stage, the combustion temperature reaches between 200–450 ℃ with continuous presence of oxygen [81], releasing the volatile gases (CO, CO_2 and CH_4) and high molecular wight compounds (tar), which condense to liquid when cooled. After all the volatiles have been burned off, the remaining material is char [79]. At the final stage, the char burns and oxidises after 450 ℃ with addition of oxygen for some types of wood biomass such as masson pine, Chinese fir, willow, slash pine, poplar, cottonwood, switchgrass [81,82]; and this is the slow oxidation and decomposition stage of the carbon layer [81]. For other kinds of wood and biomass such as beefwood, palm kernel shell and rice husk, the oxidation starts up to 530–680 ℃ [83,84]. Oxidation of the carbon occurs at the fire bed, and above the fire bed, oxygen mixes with carbon monoxide to form carbon dioxide that is released to the atmosphere. Hence, sufficient air and residence time are required for complete combustion. The combustion process is complete when all the energy in the biomass is extracted [79].

3.2. Torrefaction technology

The dry torrefaction process involves heating biomass in the absence of oxygen at a temperature of 200–300 ℃, converting the biomass to a coal-like product [85,86]. The torrefied biomass has low moisture content and high caloric value than the original biomass and can be used in place of coal. The produced biochar is more hydrophobic (less prone to absorb moisture) and less likely to undergo biological degradation, which gives it longer storage life [87]. Also, compared to fresh biomass, the biochar is more brittle, so it is easy to grind with less energy [88].

During torrefaction, the initial heating of biomass removes unbound water. Further heating led to the removal of bound water through chemical reactions. Most of the bound water is assumed to be removed by a thermo-condensation process, which occurs above 160 ℃ when the formation of CO_2 begins [89]. Further heating to between 180–270 ℃ results in an exothermic reaction and starts the decomposition of hemicellulose in the biomass, which causes the biomass to change colour due to loss of water, CO_2, and large amounts of acetic acid and phenols. This leads to a significant increase in the energy density of the biomass. At temperatures above 280 ℃, the process becomes completely exothermic, resulting in significant increases in the production of CO_2, phenols, acetic acid, and other higher hydrocarbons [89]. For lignocellulosic biomass, torrefaction causes decomposition of more hemicellulose than lignin and cellulose, which results in the destruction of more hydroxyl groups (OH) and further increase in the density and specific heating value of the bio coal [87].

It has been reported that an increase in torrefaction temperature causes a decrease in solid biochar yield and an increase in the volatile fractions, including liquid and non-condensable gases. This is due to the competition between charring and devolatilisation reactions that become more intense at higher temperatures [90]. A study by Deng et al. [91] reported a decrease in solid yield from 59.85% (wt.) to 36.57% (wt.) for raw straw torrefied between 200–300 ℃ with an increased in HHV from 17.16 to 18.68 MJ/kg. In the same work, solid yield of torrefied rape stalk decreased from 63.26% (wt.) to 25.30% (wt.) with an increase in HHV from 19.50 to 21.59 MJ/kg at the same range of torrefaction temperature.

The disadvantages of torrefaction are that, the process requires dry biomass; hence, feedstock containing moisture content higher than 20% will require pre-drying, especially to remove free water, making the process energy intensive. Also, the torrefied biomass contains all the ash components of the fresh biomass, hence the corrosive deposits on boiler tube are not reduced. Commercial implementation of torrefaction requires enough knowledge on process performance, properties of the torrefied material and composition of volatiles.

3.3. Pyrolysis technology

Pyrolysis requires heating the biomass at temperatures typically between 300–800 ℃ or higher, in a near complete absence of free air or oxygen resulting in the decomposition or carbonisation of the biomass. The products are biochar, bio-oil, and syngas [43,92]. The distribution of the products depends on the pyrolysis process conditions. Pyrolysis has many benefits including: (i) it can be more easily adapted to changes in feedstock composition, that is, it can be used for a variety of dry biomass; (ii) it is scalable and can be operated as a batch process; (iii) it is a low-pressure process and requires minimal feedstock pre-processing; (iv) it can produce a variety of valuable products (biochar, bio-oil or py-oil and hydrocarbons, syngas, monomers, nitrogen-rich compounds for fertilizers); (v) pyrolysis technology can be designed to produce minimal amounts of unwanted by-products) [93]; (vi) the bio-oil can be stored directly and readily transported; and (vii) the bio-oil can be an alternative for fuel oil in the application of static heating or in the generation of electricity [94]. The bio-oil can be further treated with hydrogen under elevated temperatures (260–430 ℃) and pressures (up to 6895 kPa) in the presence of catalyst to produce renewable diesel, renewable gasoline, and renewable jet fuel [13]. However, pyrolysis is limited to dry feedstocks containing moisture content up to 20%; hence, an energy intensive pre-drying stage is required to treat high moisture feedstocks. Also, comparatively, pyrolysis requires high energy input in relation to the extreme process temperatures required, and generates potential toxic GHG and carbon monoxide. Hence, commercial pyrolysis plants will need an air purification system to treat flue gases that are generated.

There are six types of pyrolysis processes, and the differences are due to their operation conditions (see Figure 3). These are vacuum pyrolysis, slow pyrolysis, fast pyrolysis, flash pyrolysis, microwave pyrolysis, and catalytic pyrolysis [33,35,95,96]. The classification between slow, fast and flash pyrolysis is categorised base on the temperature ramp or heating rate.

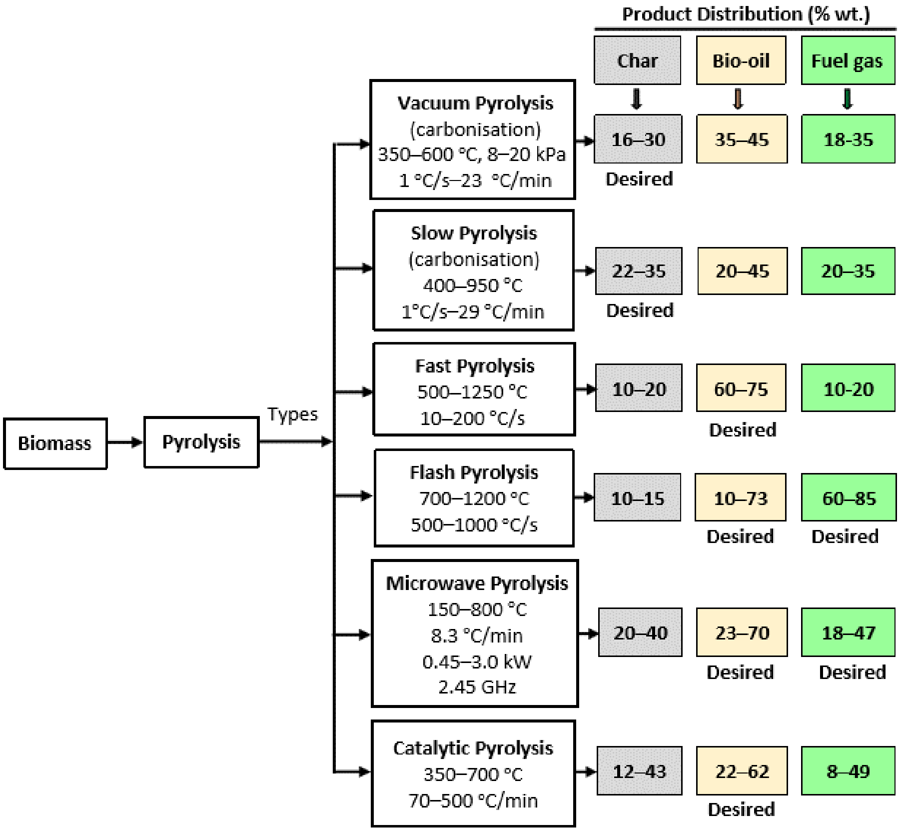

Figure 3. Illustration of different types of pyrolysis processes and product distributions.

3.3.1. Vacuum pyrolysis

In vacuum pyrolysis, the biomass is decomposed at comparatively moderate temperatures between 350–600 °C and lower pressure ranging from 8–20 kPa [97,98]. The heating rate used in vacuum pyrolysis is the same as in slow pyrolysis, but different procedures are used in these processes to eliminate vapour from the reaction zone [98]. Fast heating rates up to 0.1–1.0 °C/s has been reported for vacuum pyrolysis of biomass at a temperature of 300–600 °C for a holding time up to 1 min and pressure between 10–20 kPa [98]. Heating rates between 9–23 °C/min were utilised for vacuum pyrolysis of sugar cane bagasse at 350–530 °C for a residence time of 60 min and a pressure of 8 kPa [99]. A recent study by Ma et al. [100] utilised a heating rate of 5 °C/min for vacuum pyrolysis of cotton rose wood at a relatively high temperature of 800 °C for a longer residence time of 3 h and pressures between 5–20 Pa with the objective of producing biochar electrodes. Vacuum pyrolysis uses vacuum or low pressure to remove the vapours in substitute of purge gas used in slow pyrolysis. The low pressure enables decomposition of the organic material into its fragments at relatively low temperatures [101]. Higher bio-oil yield is produced because vapours formed during the primary pyrolysis stage are rapidly removed, with less residence time of vapours thereby reducing secondary reactions [102].

The advantages of vacuum pyrolysis are that, unlike the atmospheric processes, the biomass usually spends shorter residence time in the reactor, which consequently reduces unwanted chemical reactions, resulting in higher bio-oil yield and higher amounts of aromatic compounds, which eventually enhance the octane number of the bio-oil [103].

3.3.2. Slow pyrolysis

Slow pyrolysis involves decomposing the biomass at temperatures up to 400–950 ℃ with a low heating rate and long residence time to produce high char or biochar yields, as the vapour does not leave as quickly, reacting to produce more solids, with small amount of bio-oil (tar) and gaseous products [98,104]. The residence time for pyrolysis may differ for each biomass feedstock. Fast heating rates of between 0.1–1 ℃/s and residence times ranging from 5–30 min have been reported for slow pyrolysis of biomass at temperatures between 500–950 ℃ [98,104]. Heating rates of 5–29 ℃/min have been reported for slow pyrolysis of sugar cane bagasse at a temperature up to 570 ℃ and residence time of 60 min [99]. Residence times between 10 to 60 min has been used for pine wood, grasses and dry algae at pyrolysis temperatures ranging from 300–750 ℃ [105], and about 5–10 h for wheat straw and poplar and spruce wood pyrolysed at 400–525 ℃ [106].

3.3.3. Fast pyrolysis

In fast pyrolysis, the biomass is heated at a controlled temperature up to 1250 ℃ at a short residence time and high heating rates producing higher yields of bio-oil (thinner), as the gases do not have enough residence time to react to form solids. High heating rates in the range 10–200 ℃/s and a short residence time of 0.5–5 s have been reported for fast pyrolysis of biomass at temperatures between 850–1250 ℃ at a pressure of 100 kPa [95,98]. Uzun and Sarioğlu [107] investigated rapid pyrolysis of corn stalks at 400–600 ℃ at heating rate of 300 ℃/min for a residence time of 10 min. Maximum char yield (29%) and minimum gas yield were obtained at 400 ℃, while liquid yield reached a maximum value of 30% at a pyrolysis temperature of 500 ℃. Increasing the temperature up to 600 ℃ improved gas products only, which was caused by gasification of the tar that had been formed as well as secondary reactions of the liquid fraction of volatiles and further decomposition of the char particles. The effect of heating rate on product yields was also studied by varying the heating rate within 5–700 ℃/min and utilising pyrolysis temperature at 500 ℃. Uzun and Sarioğlu [107] found that increasing the heating rate from 300 to 500 ℃/min increased the bio-oil yields from 31.55 to 33.30%, whilst there were decrease in the char yields. However, the liquid yields decreased after 500 ℃/min. The increased in bio-oil yields was because the high heating rates surpassed the heat and mass transfer limitations in the pyrolysis environment, preventing secondary reactions, which led to maximum oil-yields. The bio-oil produced from fast pyrolysis has a low pH value, which makes it very corrosive [108]. One limitation of fast pyrolysis is that it requires feedstock with comparatively low moisture content, requiring high heating rate and temperatures [95].

3.3.4. Flash pyrolysis

Flash or ultra-fast pyrolysis is a modified and improved method of fast pyrolysis. The reaction temperature can range between 700 to 1000 ℃, or even higher up to 1200 ℃ with higher heating rate than fast pyrolysis (>1000 ℃/s) and an extremely short reaction time of 0.1–1 s [104,109]. The faster heating rate coupled with the higher temperature and short residence time of vapours result in higher bio-oil yield with low resulting water content, and lower char yield [98]. The main products are gases and bio-oil. Products yields are typically: gases ~ 60–85%; bio-oil (liquid condensate) ~10–20%; and char ~10–15%. The product distribution is influenced by the reaction temperature, heating rate and reaction time. Higher bio-oil yields have been reported for flash pyrolysis of rapeseed at lower reaction temperatures; that is 42.1% (wt.) at 550 ℃ [110] and 73% (wt.) at 600 ℃ [60]. If more oxygen is allowed in the reactor to partially combust the biomass at higher temperatures above 800 ℃, the process becomes gasification maximising stream gas production [43]. Small biomass feedstock particle, normally about 105–250 μm is required to obtain such high heating and heat transfer rates.

Table 2 presents an overview of recent studies of conventional biomass pyrolysis. The pyrolysis process is more important to influence the products types than feedstock types. Factors that favour biochar formation include lower temperature, slower heating rates, slower volatilisation rates, and longer feedstock residence times.

Table 2. Overview of yield distribution from conventional pyrolysis of biomass.

Feedstock	Operating condition	Bioenergy type	Yield (wt. %)	Reference
Rapeseed	Slow pyrolysis Heating rate: 30 ℃/min Temperature: 550 ℃ Fast pyrolysis Heating rate: 300 ℃/min Temperature: 550 ℃ Flash pyrolysis Temperature: 550–600 ℃		Slow: 49.0 Fast: 68.0 Flash: 73.0	[60]
Sugar cane bagasse	Slow pyrolysis Heating rate: 21.3 ℃/min Temperature: 420 ℃ Reaction time: 60 min	Biochar, bio-oil	32.6 19.4	[99]
Sugar cane bagasse	Vacuum pyrolysis Heating rate: 12 ℃/min Temperature: 501 ℃ Reaction time: 60 min Pressure: 8 kPa	Biochar, bio-oil	16.0 23.3	[99]
Cotton rose wood	Vacuum pyrolysis Heating rate: 5 ℃/min Temperature: 800 ℃ Residence time: 3 h Pressure: 5–20 Pa	Carbon (biochar)	28.1	[100]
Rapeseed	Flash pyrolysis Temperature: 550 ℃	Biol-oil	42.1	[110]
Sugarcane leaves and tops	Fast pyrolysis Temperature: Sugarcane leaves: 429 ℃ Sugarcane tops: 403 ℃ Nitrogen gas flow: 7 L/min Biomass feed rate: 300 g/h	Bio-oil	Sugarcane leaves: 52.5 Sugarcane tops: 59.0	[115]
Kaner (*Thevetia peruviana*) Seed	Fast pyrolysis Temperature: 600 ℃	Bio-oil	81.2	[116]

In general, as the biomass is heated, there is a competition between the three processes, which are: biochar and gas formation, liquid and tar formation, gasification and carbonisation [111] and the relative rates of these processes depend on the highest temperature treatment (HTT), heating rate, volatile removal rate and feedstock residence time [112]. Degradation of lignocellulose starts above 120 ℃ and is dominated by the biochar- and gas-formation pathway at HTTs below 300 ℃, which is found to be a free-radical process initiated by homolytic cleavage of the bonds [112]. Carboxyl and carbonyl groups are formed and afterward cleaved to produce CO and CO_2 [113,114]. The dehydration reactions cause release of water. Finally, some of the free-radicals recombine in various ways with each other and with the substrate to produce a biochar residue [112].

At HTTs of between 300–600 ℃, there is a different liquid- and tar-forming pathway, which results in a significant decrease in biochar production over this temperature range [113]. The proportion of free radicals trapped in the biochar increases with HTT for a given residence time and reaches a maximum at HTTs between 500 ℃ to 600 ℃ [117]. Therefore, biochars produced in this temperature range are very reactive towards oxidation, normally to the point of being pyrophoric. At HTTs above 600 ℃, there is high mass- and heat-transfer rates and gas-forming pathway dominates, which results in minimum formation rates of biochar, tar and liquid [112].

3.3.5. Microwave-assisted pyrolysis

Microwave-assisted pyrolysis (MAP) is a new thermochemical process that converts biomass to bio-oil. Compared with the conventional heating pyrolysis, MAP is controllable, flexible and ensures generation of more rapid heating within the material, it is efficient, selective, and does not require fluidisation [32,118,119]. MAP has higher heating rates and conversion efficiencies than conventional heating pyrolysis, which make the biomass feedstocks decompose at lower temperatures such as 100–150 ℃ [120], resulting in more bio-oil under MAP than under conventional heating pyrolysis [118]. The MAP process is significantly influenced by many factors, e.g., pyrolysis temperature, microwave power, heating time, feedstock type and characteristics, particle size, etc. [118,121]. The optimal pyrolysis temperature for the bio-oil obtained from MAP of biomass feedstock have been reported in a wide range (400–800 ℃) and found to depend on the feedstocks and parameters used [122]. However, the bio-oil yield would exhibit different changes at different temperatures within the optimal pyrolysis temperature range. Temperatures lower than the optimal pyrolysis temperature would result in a monotonous increase in the bio-oil yield, but there would be a decrease in the bio-oil yield if the pyrolysis temperatures are higher than the optimal pyrolysis temperature. If pyrolysis starts at a lower temperature and ends at a higher value than the optimal pyrolysis temperature, the bio-oil yield would increase initially and reduce finally [118].

The MAP process can be categorised into three, namely moderate MAP, fast MAP, and catalytic fast MAP [118]. The moderate MAP process requires microwave heating of the biomass feedstock to reach a high temperature (300 ℃ or even higher). Usually, insulation materials such as asbestos and bricks are used to protect the microwave oven from high temperature damage and to avoid heat losses [118]. MAP in a quartz reactor can be generally divided into three basic processes, namely drying, pyrolysis I, and pyrolysis II. The average temperature rising rates for drying, pyrolysis I, and pyrolysis II processes are reported to be 100–150 ℃/min, 10–50 ℃/min, and ~0 ℃/min, respectively [120]. During the pyrolysis I process, the feedstock particles are decomposed to release vapours including condensables (bio-oil) and non-condensables (syngas). During the pyrolysis II process, the feedstock particles continue to be decomposed, releasing vapours including condensables (bio-oil) and non-condensables (syngas) [118]. Salema et al. [123] carried out MAP of corn stalk biomass briquettes in a developed microwave reactor supplied with 2.45 GHz frequency using 3 kW power generator. Highest bio-oil, biochar, and gas yield of 19.6%, 41.1%, and 54.0%, respectively, were achieved at different process conditions. In terms of quality, the biochar has a high HHV (32.0 MJ/kg) than the bio-oil (2.47 MJ/kg).

Fast microwave-assisted pyrolysis (FMAP) uses a constant pyrolysis temperature, which may sometimes fluctuate slightly around a constant set pyrolysis temperature. For FMAP, both the drying and pyrolysis I processes are achieved within a much shorter time without noticeable differences in the pyrolysis temperatures, while the pyrolysis II dominates the whole pyrolysis process also with no obvious differences in the pyrolysis temperatures [118]. Exogenous microwave absorbents are used in FMAP of biomass to improve heating of the biomass. Typical microwave absorbents used in FMAP include SiC, activated carbon, carbon, char, and graphite [124]. Mixing the biomass feedstock with microwave absorbents increase the heating rates and pyrolysis temperature, and reduce the residence times. Suriapparao and Vinu [124] reported that when the biomass feedstock was heated by a 450 W microwave, its temperature reached about 325 °C at 34 min with an average heating rate of 8.3 °C/min. However, its temperature reached about 605 °C at 7.5 min with an average heating rate of 75.9 °C/min when the microwave absorbent of activated carbon was added. The initial high heating rate and increased pyrolysis temperature as a result of using microwave adsorbent lead to an increase in bio-oil yield, however, too high a temperature especially in the later stage of MAP may cause secondary reactions that break down vapours to non-condensable gases, decreasing the bio-oil yield [123,125]. Fast MAP generally results in higher bio-oil yield than moderate MAP process. Bio-oil yields between 50.18–64.74 wt.% have been reported for fast MAP of soapstock over pyrolysis temperatures of 400–550 °C, compared with yields of 48.16–62.91 wt.% for moderate MAP. The optimal pyrolysis temperature was 550 °C, after which the bio-oil yield decreased when the pyrolysis temperature was raised to 600 °C. Generally, fast MAP resulted in higher alkanes, aromatics, and oxygenates, whereas lower alkenes, alkadienes, cycloalkenes, and cycloalkanes than moderate MAP [126]. Ravikumar et al. [127] studied fast MAP of corn cob, corn stover, saw dust and rice straw at a temperature of about 400–500 °C for a residence time of 10 min using a maximum microwave power of 800 W. Corn cob gave the highest bio-oil yield up to 42.1%, leading to a low char yield (32%), whiles rice straw resulted in watery like liquid with low bio-oil yield of about 15.3%, with high biochar yield (62.9%). However, the addition of catalyst $MgCl_2$ in corn cob pyrolysis was not effective in increasing bio-oil yield; resulting in yield of 39.8%.

3.3.6. Catalytic pyrolysis

Utilisation of catalysts in biomass pyrolysis influences the decomposition behaviour of biomass and affects the quantity of pyrolysis products. Catalysts also affect the distribution and chemical composition of the pyrolysis products. Catalytic pyrolysis of biomass produces transportation liquids that are compatible with the current petroleum products and the existing infrastructure as the catalyst can remove oxygen in the bio-oil, whilst the carbon number is preserved [128]. Zeolite ZSM-5 is the catalyst of choice for the production of BTX (Benzene, Toluene, and Xylenes) from biomass as it is usually highly efficient in catalytic upgrading of oxygenate-containing vapours [33,35].

Catalytic pyrolysis of corn stalks at 500 °C and heating rate of 500 °C/min indicated that catalyst type influences the pyrolysis process differently. USY catalyst produced the maximum gas yield (37.17%), while the maximum bio-oil yield was obtained with ZSM-5 as 26.46% and the maximum char yield was obtained with H–Y, due to the higher tendency of coking over H-Y zeolite catalyst caused by the catalyst acidity and larger pore size [107]. During catalytic fast pyrolysis of rice stalk in a fluidised bed at 550 °C for 30 min, ZSM-5 zeolites were found to be effective in improving deoxygenated aromatic content (12.8%) and C_2-C_4 olefins (10.5%) of pyrolysis products while reducing liquid yield. ZSM-5 also shows the highest selectivity of naphthalene (12.1%), whereas spent FCC catalyst presents the highest selectivity of benzene (45.5%) [129]. In catalytic pyrolysis of Lignocel HBS 150–500 originated from beech wood at 500 °C for 30 min using H-ZSM-5/Al-MCM-41 catalyst mixture, the organic fraction yield of the catalytic process (22.51 wt%) was lower than the organic yield of the non-catalytic process (25 wt%) due to the more extensive deoxygenation in the catalytic than the non-catalytic pyrolysis process. Catalytic pyrolysis resulted in a decrease in CO and CO_2 yields due to the deoxygenation in catalytic pyrolysis with a catalyst mixture occurring via decarbonylation, decarboxylation, and dehydration mechanisms [33]. Catalytic fast pyrolysis of pine wood at 500 °C at three different time-on-stream (10, 60, and 180 min) revealed that the organic fractions produced are mostly converted to gas, water, and coke, especially at the shortest time-on-stream (i.e., highest catalyst/biomass ratio) caused by dehydration, decarbonylation and decarboxylation reactions, which contributed to deoxygenation of the biomass [35].

3.3.6.1. Catalytic microwave-assisted pyrolysis

Catalytic fast microwave-assisted pyrolysis is another approach to improve microwave-assisted pyrolysis of biomass. When the reaction catalysts are used in microwave-assisted pyrolysis, the heating rates and pyrolysis temperatures would be increased due to the microwave absorbance of the reaction catalysts [118]. The reaction catalysts used in microwave-assisted pyrolysis (MAP) of biomass for bio-oil production mostly include metals (Al, Ni, Fe, Cu, etc.), metal oxides (CaO, CuO, MgO, Fe_2O_3, NiO, TiO_2, ZrO_2, Al_2O_3, HZSM-5, etc.), metal salts (NaCl, KCl, $CaCl_2$, $MgCl_2$, $AlCl_3$, $ZnCl_2$, $FeCl_2$, $CuCl_2$, NaOH, KOH, KAc, etc.), and acids (H_2SO_4, H_3PO_4, H_3BO_3, etc.). The function of these catalysts is to: (a) improve the catalytic cracking of biomass feedstock into products; and (b) improve the bio-oil quality through catalyst selectivity [126], thus improving the microwave-assisted pyrolysis of biomass for bio-oil production [118].

Application of activated carbon and lignite char as catalysts during catalytic fixed-bed and microwave pyrolysis of palm kernel shell at a temperature range of 400–600 °C showed that addition of catalyst increased the bio-oil yield, but decreased the selectivity of phenol in fixed-bed, with 500 °C being the optimum temperature for obtaining the highest bio-oil yield. Microwave pyrolysis produced lower bio-oil yields compared to that in fixed-bed pyrolysis due to the rapid heating obtained in the presence of microwave receptors. Microwave pyrolysis led to higher gas yield than that in fixed-bed pyrolysis conditions. Microwave pyrolysis favored the formation of non-condensable gases at higher temperatures, resulted in higher gas yield compared to that in fixed-bed pyrolysis conditions [130].

Table 3. Overview of yield distribution from microwave-assisted and catalytic pyrolysis of biomass.

Feedstock	Operating condition	Bioenergy type	Yield (wt. %)	Reference
Corn stalk biomass briquettes	Microwave pyrolysis:	Biochar	41.1	[123]
	Temperature: 150–250 ℃	Bio-oil	19.6	
	Residence time: 2 h	Syngas	54.0	
	Power: 3 kW			
	Frequency: 2.45 GHz			
Corn cob, corn stover, saw dust and rice straw	Microwave pyrolysis:	Bio-oil: corn cob	42.1	[127]
	Temperature: 400–500 ℃	corn cob + MgCl$_2$	39.8	
	Residence time: 10 min	Biochar: corn cob	32.0	
	Max Power 800 W	Corn cob + MgCl$_2$	35.3	
	Catalyst: MgCl$_2$	Syngas: corn cob	25.9	
		Corn cob + MgCl$_2$	24.9	
Corn stover and scum	Microwave pyrolysis:	Biochar	25.9–71.1	[131]
	Temperature: 450–600 ℃	Bio-oil	17.4–29.2	
	Power: 750 W	Syngas	11.5–48.0	
	Frequency: 2.45 GHz			
	Catalyst: CaO/HZSM-5	+Catalyst: bio-oil	10.7–38.3	
Bamboo, gumwood, pine, rosewood	Microwave pyrolysis + catalytic: reforming	Biochar	14.5–22.2	[132]
		Bio-oil	3.2–11.4	
	Temperature: 600–800 ℃	Syngas	66.7–81.1	
	Power: 3 kW			
	Frequency: 2.45 GHz			
	Conventional pyrolysis	Biochar	8.2–26.5	
	Temperature: 600–800 ℃	Bio-oil	8.2–13.6	
	Residence time: 15 min	Syngas	61.2–81.6	
	Microwave pyrolysis + catalytic reforming	Biochar	22.8–24.1	
		Bio-oil	0.3–2.2	
		Syngas	74.3–76.9	
	Conventional pyrolysis + catalytic reforming	Biochar	20.5–22.8	
		Bio-oil	0.8–2.8	
		Syngas	75.2–78.1	
Corn stover	Microwave pyrolysis	Biochar	26.4	[133]
	Temperature: 425 ℃, 550 ℃	Bio-oil	41.6	
	Catalyst: ZSM-5	Syngas	35.2	
Lignocel HBS 150-500 from beech wood	Catalytic pyrolysis:	Biochar	39.85	[33]
	Temperature: 500 ℃	Organic fraction	2.1	
	Residence time: 30 min	Syngas	18.33	
	Catalyst: H-ZSM-5/Al-MCM-41	Coke	2.80	
		Non-catalytic		
		Biochar	40.0	
		Organic fraction	24.6	
		Syngas	10.1	
		Coke	0.0	

Continued on next page

Feedstock	Operating condition	Bioenergy type	Yield (wt. %)	Reference
Pine wood	Catalytic pyrolysis: Temperature: 500 ℃ Residence time: 10, 60, 180 min Catalyst: HZSM-5/Al_2O_3	Biochar Organics Water Syngas Coke	18.0 10.0–28.0 13.0–24.0 16.0–37.0 2.0–12.0	[35]
Corn stalks	Catalytic pyrolysis: Heating rate: 500 ℃/min Temperature: 500 ℃ Catalysts: zeolites	Biochar Liquids Gas	30.0 27.6 37.2	[107]
Spent coffee grounds loaded with cobalt	Catalysis: Co-biochar Generation of H_2: CO_2 at atmospheric pressure Reaction time: 110 min Generation of CO: Temperature: 700 ℃	Syngas (H_2 and CO)	Yield concentration: H_2: 1.6% (mol) CO: 4.7% (mol)	[134]
Greenhouse vegetable waste and coal	Catalytic co-pyrolysis: Temperature: 500 ℃ Catalysts: calcite, dolomite, and zeolite Nitrogen gas flow rate: 1450 mL/min	Biochar, bio-oil, and gas	Biochar yield: 40.2, 54.7, 45.9	[135]
Beech wood	Hydrotreatment Temperature: 250 ℃ Catalyst: NiCu/Al_2O_3	Bio-oil	86.1	[136]
Pinyon-juniper wood chips	Catalytic pyrolysis: Temperature: 400 ℃ Catalyst: Red mud Feeding rate: 0.9 kg/h HDO of oil produced: Temperature: 350 ℃ Catalyst: Ni/Red mud	Bio-oil	47..8	[137]

Fast microwave-assisted catalytic co-pyrolysis of corn stover and scum using CaO and HZSM-5 as the catalyst for the production of bio-oil showed that the use of catalyst resulted in a decrease in bio-oil yield as the pyrolysis vapours had to pass through the catalyst particles, which increases the gas residence time. CaO catalyst caused a reduction in bio-oil yield, whiles the maximum yield of 38.34 wt.% was obtained using CaO:HZSM-5 mixed catalysts in a ratio of 1:4. The optimal temperature of 550 ℃ gave the maximum bio-oil and aromatic yields. A further increased in temperature led to secondary thermal cracking reaction of the volatile compounds converting to lower molecular weight organic products or other non-condensable gases, which caused a significant increase in gas yield whilst the biochar yield was reduced as temperature was raised from 450–600 ℃) [131]. In a recent study, MAP of wood biomass at temperatures between 600–800 ℃ (max power of 3 kW, 2.45 GHz) was combined with catalytic reforming of the pyrolytic gas using activated carbon as a catalyst. Conventional pyrolysis produced higher bio-oil yield in comparison to the yield from microwave pyrolysis.

Reforming of the pyrolytic gas fraction resulted in reductions in bio-oil yield to <3.0 wt.%, with a simultaneous increase in syngas yield and H_2 selectivity. The use of microwave pyrolysis with activated carbon reforming produced 85 vol% syngas fractions containing 55 vol% H_2 compared to 74 vol% syngas fractions with 30 vol% H_2 obtained without the reforming. This is because, cracking reactions were improved with microwave heating, while deoxidation and dehydrogenation reactions were enhanced by activated carbon, which created a reduction environment. Consequently, these reactions generated H_2-rich syngas formation [132].

An overview of recent studies on microwave-assistant pyrolysis and catalytic pyrolysis of biomass is presented in Table 3.

3.3.7. Bio-oil upgradation methods

In recent times, more attention is given to bio-oil production from fast pyrolysis than for biochar yield. This is because of the high yield of bio-oil that can be obtained (up to 75% wt.) and the merits of the technology such as cost effectiveness, high energy efficiency, and the environmental friendliness [96,138]. Bio-oil is a dark brown, high viscose liquid with low calorific value. It is a complex mixture of various carbon compounds many of which contain oxygen in their structure. It contains acids, alcohols, aldehydes, phenols and oligomers that originate from lignin [139]. Pyrolysis bio-oil has lower higher heating value (HHV), which is comparatively half than that of crude oil, therefore, it is necessary to upgrade bio-oil before its utilisation [140]. Recent concern has been on improving the properties of bio-oil so that it could be used as substitute to crude oil. This can be achieved through physical, chemical and catalytic methods.

3.3.7.1. Physical upgradation

The most commonly used physical upgradation method is hot vapour filtration, which reduces the initial molecular weight of the bio-oil, slowing down be rate of aging of the bio-oil [112] and improves the viscosity and stability of the oil [141]. This process also eliminates char and inorganic substances from the oil, which is initiated as a result of the removal of the highly unstable compound of ring-conjugated olefinic substituents and the conversion of guaiacol-type compounds to catechol- and phenol-type compounds [142].

3.3.7.2. Hydrodeoxygenation (HDO) upgradation

HDO upgradation, also known as hydrotreatment, is another process used to increase bio-oil yield, improve oil quality and carbon recovery. The process involves removing oxygen from oxygenated hydrocarbons through a catalytic reaction at a high pressure (up to 200 bar), hydrogen supply and a moderate temperature (up to 400 °C) [96]. This process is found to enhance the quality of bio-oil by refining the oil stability and increases the energy density [143]. Four key reactions affect the HDO of bio-oil, namely (a) hydrogenation of C-O, C=O and C=C bonds, (b) dehydration of C-OH group, (c) condensation and decarbonylation of C-C bond cleavage using retro-aldol, and (d) hydrogenolysis of C-O-C bonds. Deactivation of the catalyst is the main problem concerning HDO of bio-oil, therefore, there is the need to synthesise an effective catalyst for the HDO process [112].

3.3.7.3. Catalytic upgradation

Catalysts can also be used for upgrading bio-oil. In this process, the vapour produced by pyrolysis goes through extra cracking within the catalyst pore for the formation of low molecular weight compounds. Carboxylic and carbonyl groups are the undesired products in the bio-oil, which cause the increase in oil acidity and viscosity. Zeolitic catalysts are the most used in oil refineries, as they have the capacity to convert the organic acids into alcohols by breaking the long chain compounds, promoting the formation of aromatic hydrocarbons [144]. When using zeolitic catalysts, it is essential to take into consideration the size of micropore/mesopore to ensure the entry of huge biomass chains into the zeolite pores to increase yield of hydrocarbons [145].

Two methods can be used to improve the quality of pyrolysis oil. The first method involves the downstream process by bi-functional or metallic (hydrogenating and acidic) catalysts [94], in which the pyrolysis vapours are converted via acid-catalysed reactions leading to the breaking of C-O and C-C bonds among guaiacyl, syringyl and p-hydroxylphenyl and produces intermediates that cause coke formation on the zeolite surface [139]. The second method is in-situ enhancement by means of integrated catalytic pyrolysis [94]. According to Hoff et al. [146], by using rich-ZSM5 obtained through desilication increased the mesoporosity of the zeolite. The enhanced mesoporosity of the zeolite results in an increase in the aromatic yields during the pyrolysis of red oak [146]. The in-situ way of reaction is the preferred for bio-oil upgradation as it can be achieved at several operating temperatures and catalyst loading ratios [139].

3.4. Gasification technology

Standard or dry gasification involves heating the biomass at extreme temperatures between 500–1400 ℃ in a gasifier, from atmospheric pressures up to 33 bar and with the injection of controlled amounts of oxygen in the presence of a gasification agent and a catalyst, resulting in a partial oxidation to produce synthetic gas or syngas. Alternatively, the biomass is passed through steam, causing a steam reforming reaction producing hydrogen (H_2) and methane (CH_4) in higher quantities, but the process requires large amounts of energy [147]. Syngas comprises of H_2, carbon monoxide (CO), carbon dioxide (CO_2), CH_4, higher hydrocarbons and nitrogen (N_2). Syngas has a low caloric value and can be used as fuel for heating, diesel engines, and electricity generation in gas turbines. Also, the syngas can be further treated to produce liquid fuels using Fischer-Tropsch process, and can also be processed to separate the hydrogen, which can be used in fuel cells or burned [13]. Table 4 presents different studies of biomass gasification.

The syngas composition varies depending on the type of gasifier, gasification agent, catalyst type and particle size of the catalyst. Gasification of feedstock containing high amount of carbon and oxygen generate high amount of CO and CO_2. Agricultural residue and MSW have been found to generally produce syngas with greater CO and CO_2 contents [28]. Biowaste feedstocks usually contains <1.5% (wt.) of sulphur, among which animal waste and sewage sludge comprises of the highest quantity of sulphur with 0.55 (wt.) and 1.0% (wt.) respectively. Gasification of such feedstock emits sulphur in the form of H_2S, which cause complexity in gas separation and treatment. Hence, gas treatment methods are needed for such feedstocks [28].

Table 4. Overview of yield distribution from gasification of biomass.

Feedstock	Gasification method/Operation condition	Syngas Composition (%)	Calorific value (MJ/m^3)	Reference
Rice straw	Temperature: 600–800 ℃ Oxygen ratio: 33% Air flow: 0.6 Nm^3/h Feed rate: 1.12 kg/h Equivalence ratio: 0.2	CO: 2.01 H_2: 5.48 CH4: 0.51 Efficiency: 33.78%	–	[148]
Eucalyptus chips and coffee husk	Eucalyptus chip Temperature: 22.1 ℃ Air input flow: 182.7 NM^3/s Coffee husk Temperature: 22.1 ℃ Air input flow: 182.7 NM^3/s	–	Eucalyptus chips: 6.81 [a] Coffee husk: 7.76 [a]	[149]
MSW and hazardous waste	Co-gasification using plasma gasifier. MSM composition: 90% (wt.) Oxygen volume: 96%	Plant efficiency: 41.1% Power: 81 MW	–	[150]
Sewage sludge	Circulating fluidised bed gasifier	H_2: 13.87 CO: 6.5 CO_2: 15.84 CH_4: 2.37	3.2	[151]
Sewage sludge	Updraft gasifier	H_2: 5.0–15.0 CO: 16.0–28.0 CO_2: 0.0–12.0 CH_4: 0.0–9.0	3.2–6.8 [b]	[152]
Sewage sludge	Bubbling fluidised bed gasifier	H_2: 13.3 CO: 13.8 CO_2: 13.0 CH_4: 4.2	4.7	[153]
Pine woodchips	Dual circulation fluidised-bed gasifier Temperature: 700–900 ℃ Steam to fuel ratio: 0.3 kg/kg	H_2: 26–42 CO: 25–37 CO_2: 16–19 CH4: 8–11	–	[154]
Wheat straw pellets	Downdraft gasifier	H_2: 17.0–19.0 CO:14.0–17.0 CO_2: 11.0–14.0	4.50	[155]
Coconut shells	Downdraft gasifier	H_2: 10.0–15.0 CO: 19.0–24.0 CO_2:11.0–15.0	7.20	[155]
Corn cobs	Downdraft gasifier	H_2: 16.5 CO: 18.6 CH_4: 6.4	6.29	[156]

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Feedstock	Gasification method/Operation condition	Syngas Composition (%)	Calorific value (MJ/m^3)	Reference
Rice hulls pelleted	Downdraft gasifier	H_2: 9.6 CO: 16.1 CH_4: 0.95	3.25	[156]

[a] HHV (MJ/N-m^3); [b] LHV ((MJ/N-m^3)

Four types of gasifiers are usually used in biomass gasification, namely fixed bed, fluidised bed, entrained flow, and plasma gasifiers (shown in Table 5). Fixed bed gasifiers have two different types, which are downdraft gasifier and updraft gasifier. Downdraft gasifiers are the most used among the two because of its flexibility to handle biomass of variable moisture content and the ability to quickly produce high yield of good syngas [157]. The advantages of a fixed bed gasifier are as follows: (i) it has a high tolerance of ash content; (ii) low accumulation of tar; (iii) minimum sensitivity towards feedstock size and quantity; and (iv) it is able to withstand feedstock with high moisture content [144]. Fluidised bed gasifier on the other hand has high heat transfer rate, requires moderate gasification medium, and ensures thorough mixing of feedstock and bed material. Entrained flow gasifier is capable of handling different types of feedstocks and requires short residence time. Also, temperature is uniform throughout the reactor, and produces syngas with low tar content [144].

Table 5. Gasifiers used in gasification of biomass.

Feedstocks	Gasifier type	Operating temperature (℃)	References
Sawdust	Fixed bed	650–960	[158]
Palm shell		750	[159]
Sewage sludge		800	[160]
Wood		800–900	[161]
Pine woodchips	Fluidised bed	700–900	[154]
Beech wood		750–850	[162]
Wood and bark waste		300–400	[163]
Straw biomass		900	[164]
Bituminous coal and wheat straw	Entrained flow	1300	[165]
Jatropha curcas shell		1000	[166]
Empty oil palm fruits bunch		900	[167]
MSW and plastic solid waste	Plasma	1250–1315	[150]
Biomedical waste		1326	[168]
Hazardous waste from oil and gas		1500	[169]

Plasma gasification is a new gasification process that is suitable for harmful biomass wastes. It is an allothermal method that uses external heat source for heating and maintaining the elevated gasification temperatures. The severe high temperatures used make it suitable for treating both non-hazardous and hazardous biomass waste such as medical waste, infusion kits, bandages, biomedical waste comprising of antibiotics, cytotoxic drugs, and laboratory waste including organisms or biomolecules that are hazardous when released to the environment [168]. It is a non-toxic method to treat hazardous waste and allows easy removal of ash and slag [144]. Plasma gasification generally produces syngas, slug and ash. A study by Mazzoni and Janajreh [150] on plasma co-gasification of

MSW and waste of plastic solid revealed that the process consumes oxygen-rich air as plasma forming gas and give rise to increase in the plant efficiency beyond 26%. Another study by Messerle et al. [168] on plasma gasification of bonny tissue (biomedical waste) and house waste reported the overall concentration of the gas produced to be 69.6% (vol.) and 71.1% (vol.), respectively.

Gasification offers some advantages over direct combustion and pyrolysis. Gasification is reported to be the most efficient process in the production of hydrogen gas from biomass [170]. Biomass gasification is found to be able to recover more energy and higher heat capacity compared with direct combustion and pyrolysis. Conversion of CO and H_2 through pyrolysis and liquefaction is poor because they are greatly dependent on the operating conditions and the presence of secondary reaction resulting from hot solid particles and volatiles [144,157]. The gasification process allows simple conversion by way of the catalytic methanation of CO and CO_2 of syngas to synthetic natural gas [171]. Gasification is a very versatile process as diverse biomass feedstocks can be converted to fuel gas with high efficiency. Also, the fuel gas can be used directly for heat or power applications or upgraded to syngas for biofuel production.

3.5. Hydrothermal processes

Hydrothermal conversion routes utilise biomass that contains high moisture content, which minimise or eliminates the cost of drying or dewatering stage. This means feedstocks containing varying moisture content such as woody biomass, sewage sludge, animal manure, MSW, algal-based biomass, etc are suitable for hydrothermal processes. This section will review the hydrothermal techniques used to covert biomass to bioenergy.

3.5.1. Hydrothermal liquefaction (HTL) technology

Hydrothermal liquefaction (HTL), also called hydrous pyrolysis is a thermochemical process that uses subcritical waster (SCW), whereby the biomass is heated at temperatures between 250–400 °C, very higher pressures (4–25 MPa) [172] and with the application of catalysts (mostly alkali) for a sufficient time to break down biomass biopolymeric structure to predominantly liquid components, producing a liquid fuel called ‘biocrude’ or bio-oil through decomposition and repolymerisation reactions. Biocrude is physically much more viscous, but less dense than bio-oil from pyrolysis [172,173]. The main product of HTL is biocrude, whereas the by-products are gaseous (rich in CO_2), solid and aqueous phases [174,175]. All the products of HTL can be further processed to produce transportation fuel, chemicals, and advanced carbon materials. Unlike bio-oil from pyrolysis, biocrude is more deoxygenated, and that is, have more hydrophobic phase with less dissolved water. Biocrude is comparable to petroleum crude and thus, can be further processed (by hydrotreating) to remove oxygen, to produce petroleum derived products similar to those in the market [176]. The elevated pressure helps to keep water in the liquid state, and the combination of pressure and temperature results in a decrease in the di-electric constant and density, which effect the hydrocarbons to be soluble in water [173]. Like bio-oil from pyrolysis, biocrude or bio-oil produced from HTL cannot be used directly as transportation fuel; hence, requires upgrading before using in transport fuels. Typical bio-oil upgradation techniques have been covered in section 3.3.7. Some recent studies of HTL of biomass is presented in Table 6.

Table 6. Recent studies on HTL of biomass.

Feedstock	Operating conditions	Biocrude yield (wt. %)	Reference
Wet and dry microalgae (*Nannochloropsis sp*)	Fermentation & Ethanol assisted liquefaction Temperature: 265 ℃ Ethanol: 15% (v/v) Ethanol to algae ratio: 2:1	Biodiesel yield Wet microalgae: 14.18% Dy microalgae: 12.48%	[177]
Domestic sewage sludge in high-rate ponds	Temperature: 300 ℃ Reaction time: 15 min Biomass/water ratio: 1/10 (kg/kg)	44.4	[178]
Human faeces	Temperature: 300 ℃ Reaction time: 30 min Total solid content: 25%	24.44	[179]
Jatropha curcas cake	Temperature: 250 ℃ Reaction time: 40 min Catalyst: ChCl-KOH DESs	Energy recovery: 41.48–54.78%	[180]
Microalgae	Temperature: 350 ℃ Reaction time: 15 min	60.0	[181]
Distillers grains	Temperature: 300–400 ℃ Reaction time: 15 min Pressure: 25 MPa	40.0	[182]
Swine manure	Temperature: 275–350 ℃ Reaction time: 5–180 min Pressure 5.5–18 MPa	70.0	[183]
Indonesian biomass Residues	Temperature: 300 ℃ Reaction time: 30 min Pressure: 10 MPa Catalyst: Na_2CO_3	21.0–36.0	[184]

Woody biomass mainly comprises of cellulose (30–50%), hemicellulose (15–36%), and lignin (20–35%) [185–188]. For agricultural residues (e.g., rice straw, coconut husk oak sawdust, etc), the lignocellulosic composition consist of cellulose (18–52%), hemicellulose (6.3–38.8%), and lignin (6–46.4%), whiles that of forest residues (i.e., hardwood and softwood) comprises of cellulose (39.5–46%), hemicellulose (23–36%), and lignin (20–27.5%), and waste materials (e.g., banana peels, orange peels, groundnut shell, etc) contains cellulose (9.7–38.3%), hemicellulose (7.4–32.4%), and lignin (1.3–23.6%) [188]. Hence, this makes them suitable feedstock for HTL. At room temperature, cellulose is a non-polar compound, but it is expected to be soluble as the temperature increases and has the advantage of high degree of polymerisation. Cellulose has strong intramolecular and intermolecular interactions among hydrogen bonds, which is initiated by the glucose monomers produced by hydrolysis of the biomass [189]. Hemicellulose contains weak arrangements and less strong hydrogen bonding that leads to easy disintegration of the molecules. Bio-oil yields obtained from woody biomass are influenced by HTL operation conditions, with or without catalyst and type of solvent, which may vary from 17–68% (wt.) [173].

3.5.1.1. Improved HTL techniques

Other techniques have been studied to improve the HTL process. For instance, Costanzo et al. [190] utilised two stage HTL process to produce biocrude from algae which started with low temperature followed by high temperature coupled with hydrodenitrogenation and hydrodeoxygenation (HDO) catalyst. The biocrude produced from this process was found to be comparable to conventional gasoline. Alhassan et al. [180] used deep eutectic solvents (DESs) as a catalyst in HTL of de-oiled Jatropha cake, recovering about 41.48–54.78% high energy of bio-crude. The DES was used as a substitute of ionic liquid catalyst because of its benefits such as straightforward preparation, economical, low degree of toxicity, and thermal stability. Mateus et al. [191] carried out solvolysis liquefaction at temperatures between 110–160 ℃ under ambient pressure and reported that the extraction process resulted in bio-oil yield with upgraded HHV.

Co-liquefaction has been reported to enhance HTL bio-oil yield and its properties. Co-liquefaction of heavy metal contaminated biomass have been revealed to immobilise the heavy metals because of their extraordinary characteristic of improving bio-oil yield by 20–50% or higher, and improving the properties of bio-oil such as less viscosity and low molecular weight [192–194]. Co-liquefaction has been found to hinder the formation of water and gases such as CO_2, promoting the interaction between free radicals and intermediates of liquefaction leading to an improvement of bio-oil yield [195]. A study by Leng et al. [196] on co-liquefaction of heavy metal contaminated wood sawdust and rice straw with municipal sewage sludge at 300 ℃ using ethanol solvent and reported that bio-oil from liquefaction of wood sawdust, rice straw and sewage sludge were 26.7%, 22.7% and 23.7% respectively. The study found that 10–25% of heavy metals were transferred into the bio-oil during co-liquefaction, compared with only 5% of heavy metals transferred to the bio-oil when liquefaction was done individually. Nazari et al. [192] performed optimisation studies about co-liquefaction of birchwood sawdust and waste activated sludge and reported maximum bio-oil yield of 33.7% at reaction temperature of 310 ℃, 10 min reaction time and 10% (wt.) solids content. It was also found that co-liquefaction enhanced the characteristics of the bio-oil indicated by the presence of lighter components.

HTL of sewage sludge has been studied as it is a readily available waste feedstock. For example, Li et al. [197] performed HTL of sewage sludge and reported that compared to dry sludge, utilising wet sludge was able to decrease energy consumption by 30%. However, the high moisture content (>85%) of dewatered sewage sludge affects the quality of the bio-oil [198]. To improve the quality of the bio-oil, several investigations have been conducted with the aim of reducing the moisture content in sludge such as the utilisation of: (i) biomass-assisted filtration followed by co-liquefaction [194]; (ii) n-hexane to isolate bound water [195]; (iii) supercritical waster (SCW) pre-treatment to break up sludge cells leading to the relief of bound and surface water [199]; (iv) co-conversion with birchwood sawdust [200]; and methanol for extraction of extracellular polymeric substances [201]. Yang et al. [202] investigated the effects of co-pretreatment of cationic surfactant-on-ionic surfactant (fatty alcohol polyoxyethylene ether (AEO_9))-SCW on the HTL of sludge for bio-oil production and found that high amount of bond water is able to be released from the sludge that resulted in high production of bio-oil (up to 47.6%). The application of co-pretreatment of AEO_9-SCW lead to enhancement of the hydrocarbons in the bio-oil and improved its calorific value by 15.5%.

During the HTL process, some of the organics in the feedstock are not converted to bio-oil, which are left in the liquid as post-hydrothermal liquefaction wastewater (PHWW) [203]. About 20% of the carbon in the biomass feedstock is transferred into the PHWW during HTL, which is generally in the form of monosaccharides, oligosaccharides and organic acids such as acetic acids [179]. To improve the economics and effectiveness of the process, it is necessary to recover the remaining organics from the PHWW. An integration of HTL and anaerobic digestion (AD) has been reported to improved energy recovery from the HTL process. In a study by Li et al. [204], AD was used to produce methane and energy recovery of PHWW from *Chlorella* using zeolite adsorption. The study found that addition of zeolite and the HTL-AD merging system enhanced the energy recovery efficiency to 70.5%. Another study by Rahman et al. [177] utilised a green biorefinery concept of integrating fermentation and ethanol assisted liquefaction to produce biofuels from marine microalgae *Nannochloropsis* sp. The pre-treatment and fermentation of the wet microalgae were found to improve the total lipid yield by 40% and 10% of essential solvent for subsequent phase of biofuel production. The study also found that the merging of algae to liquid process increased the production of biodiesel by three-fold contrasting to liquefaction of microalgae.

3.5.1.2. Temperature effect on the HTL process

The yield of bio-oil during HTL process is influenced by the process parameters, namely reaction temperature, residence time, catalyst, solvent type, biomass to solvent ratio, and structural composition of biomass. Among these, temperature is considered as the key parameter for the liquefaction process. During HTL, higher temperatures initially break down the biomass and de-polymerise it to light fragments which are then reorganised through different reactions such as condensation, cyclisation and polymerisation to form new compounds [205]. Increase temperature has been reported to cause a rise in bio-oil yield; however, most of the studies observed particular temperature values for maximising bio-oil yield beyond which there is a decrease in the yield of bio-oil. Sugano et al. [206] conducted HTL of paper industry waste at temperatures from 150 to 350 ℃. The study found that lower temperatures (150–200 ℃) produced high solid yield, formation of liquid products occurred at moderate temperatures (250–350 ℃), whereas higher temperature above 350 ℃ results in gaseous product formation. Zhu et al. [207] studied the effect of temperature on liquefaction product distribution by conducting HTL of barley straw waste with K_2CO_3 at different temperatures (280–400 ℃). It was found that there is a little increase in bio-oil yield when the temperature was increased from 280 to 300 ℃, with a maximum yield of 34.9 %(wt.) obtained at 300 ℃. A further increased in temperature resulted in a reduction in bio-oil yield, but the biocrude oil had better qualities in terms of less oxygen content and higher heating values (HHVs). The decreased in bio-oil above 300 ℃ was due to the cracking of bio-crude oil to gaseous products. Thus, low temperature favoured ionic reactions such as hydrolysis and dehydration reactions, in which case the intermediates decomposition and isomerisation occurred leading to an improved bio-crude oil formation [207]. A study by Zhou et al. [208] reported an increase in bio-oil from 220 to 300 ℃, which was reduced with a further increase in temperature to 320 ℃. Huang et al. [209] on the contrary found maximum bio-oil yield at 320 ℃ liquefaction temperature. Li et al. [210] reported that increasing temperature from 250 to 375 ℃ leads to a rise in bio-oil yield, but a further increase in temperature reduced the bio-oil yield. In a study by Peng et al. [211], temperature above 260 ℃ caused a drop in bio-oil yield. Brand et al. [212] studied liquefaction of pine sawdust and found that bio-oil yield increases from 15.8 to 59.9% (wt.) as the reaction temperature increased from 280 to 400 ℃. These results generally reveal that, during HTL, biomass degradation under both the subcritical and the supercritical conditions likely takes place between 300–350 ℃ [213].

Temperature below the critical conditions favours bio-oil yield formation, while gas formation is improved above the critical conditions [214]. The decreased in residue yield is attributed to the inhibition of the condensation reaction [207]. High temperature causes the secondary breakdown of biomass bonds and supports Bourdard gas reaction, which leads to the formation of gas mixture, resulting in lower yield of bio-oil above the critical conditions [215]. Also, at high temperatures above the critical conditions, free radicals recombine with each other leading to increasing char formation.

3.5.2. Hydrothermal gasification technology

Hydrothermal gasification, also called ‘hydrogasification’ or supercritical water gasification (SCWG) is a thermochemical process in which the biomass is heated in water at temperatures and pressures above 375 ℃ and 22 MPa, respectively (i.e., water at supercritical state) to produce syngas [216]. One of the advantages of hydrothermal gasification over liquefaction is the lower amount of organic carbon found in the water phase after gasification leading to high carbon efficiencies [217]. Unlike traditional or dry gasification, the distinctive properties of water at supercritical state leads to extremely fast kinetics without the formation of char and tar, producing gas of high quality [218]. High solubility of the intermediates in water under supercritical conditions greatly inhibits tar and coke formation; thus, the reactive species from the biomass are diluted by solvation in water, which consequently reduce the reaction rate of polymerisation to unwanted product such as tar and coke leading to high gas yields at comparatively low temperatures [219].

Hydrogasification of biomass can be divided into three main types, depending on the reaction conditions and the main product gases desired. The first type involves aqueous phase reforming in which compounds formed from biomass (e.g., glucose, sorbitol, glycerol, methanol, and glycol) are gasified at about 215–265 ℃ to generate hydrogen as burnable gas and carbon dioxide in the presence of heterogeneous catalyst such as Pt, Pd, Ni, Rh, Ru, and Ir [220–223]. In the second type, the biomass or organic compounds are gasified to largely methane as burnable gas and carbon dioxide in the presence of a heterogeneous catalysts at either about 350 ℃ in the liquid phase or nearly 400 ℃ in the supercritical state [216,223]. Then thirdly, biomass or organic compounds are gasified in supercritical water to mainly hydrogen as burnable gas and carbon dioxide without the addition of a solid catalysis [224], or in the presence of carbon or other solid catalysts [223,225].

Hydrogasification has not been investigated extensively compared to the standard (dry) gasification. Most of the studies have investigated the product gas composition for different feedstock using small-scale laboratory set-ups [225–227]. A few other studies have also focused on the development of a catalysis aiming to reduce the energy needs of the process and increase the selectivity towards hydrogen [228].

Early studies by Xu et al. [229] found that gasification yield decreases at higher glucose concentrations. To overcome this problem, they developed a very effective carbon catalyst. That is, using a coconut shell activated carbon in supercritical water at 600 ℃ and 34.5 MPa, complete conversion of glucose (22% g/g dry matter) to a hydrogen-rich syngas (2.24 mol hydrogen/mol glucose) was achieved at a weight hourly rate of 22.2 h^{-1}. Similarly, coconut shell activated carbon catalyst has been utilised for gasification of digested sewage sludge, corn starch and poplar wood sawdust in supercritical water to produce a hydrogen-rich gas [229,230]. The downside of the process was the accumulation of ash from the biomass and the small amount of coke produced causing plugging of the catalyst solid bed [225,230]. Another study by Nakamura, et al. [231] used carbon-catalysed SCWG for gasification of chicken manure. In their study, the feedstock was mixed with aqueous suspension of activated carbon, and was initially heated in a first heat exchanger before entering a heated liquidising reactor (at 180 ℃, 1.2 MPa, for a reaction time of 26.7 min). The solid biomass was converted to oil at this stage. The mixture was then cooled, compressed by a high-pressure pump and fed to a second heat exchanger. The temperature was increased to the desired value of 600 ℃ in the gasification reactor at a pressure of 25 MPa for a reaction time of 1.7 min. It was found that the gas yield is doubled when using a carbon catalyst. Increasing the carbon catalyst to 5% (g/g) led to complete gasification of the chicken manure (10% g/g).

Elliot et al. [223] reported that an increase of gas yield in the presence of a nickel catalyst (in the reduced form) at temperatures between 350–400 ℃ resulted in high methane yields for the gasification of wet biomass. Alkali salts were added as co-catalyst to avoid poisoning of the heterogeneous catalyst by carbon deposition and to support gas formation. In different studies, Elliot et al. [223,232] successfully conducted continuous gasification of biomass at 350 ℃ and 24 MPa to methane-rich product gas. However, there was some poisoning of the catalyst. Again, there was initial plugging of the catalysts by the biomass, which was solved by a liquefaction step in a CSTR before gasification in the catalyst bed reactor. Kruse and Dinjus [233] investigated the influence of different ingredients of biomass on the gasification process and reported that the alkali salts in the biomass increase the hydrogen yield. The is because of the catalysis of the water-gas shift reaction by alkali salts that increase the hydrogen yield and decrease CO yield. However, unlike alkali salts, other biomass components such as proteins are found to decrease the gas yield [234].

Castello and Fiori [235] developed a non-stoichiometric two-phase equilibrium model for SCWG of biomass with the aim of predicting the process conditions leading to char formation and the energy needs of the process. The study found that char formation only occurs when the carbon content of the biomass feedstock is high, and when processing concentrated streams at low temperatures. The study further reported that at temperatures below 680 ℃ SCWG is weakly exothermic but weakly endothermic above 680 ℃. However, addition of small amount of O_2, makes SCWG exothermic over the entire temperature range (400–1200 ℃) analysed. Onwudili et al. [236] conducted catalytic hydrothermal gasification of algae (*Chlorella vulgaris, Spirulina platensis and Saccharina latissimi*) under SCWG conditions at 500 ℃ and 36 MPa in an Inconel batch reactor for 30 min in the presence/absence of NaOH and/or Ni-Al_2O_3. They reported that hydrogen gas yields were more than doubled in the presence of NaOH than in its absence and tar yields were reduced by up to 71%. The highest hydrogen gas yield of 15.1 mol/kg was obtained from *Saccharina*, a carbohydrate-rich macro-algae.

Salimi et al. [237] studied energy generation from lignocellulosic wastes of canola stalks using novel bimetallic catalysts supported on activated carbon and graphene nano sheets in the hydrothermal gasification process. From the study, the addition of metals such as Nickle (Ni), Rudium (Ru), Copper (Cu) and Cobalt (Co) based catalyst were able to accelerate the reforming reaction that ultimately resulted in improved hydrogen and methane production. It was additionally found that Ni (20%)/activated carbon, and Ni (20%)–Cu (2%)/activated carbon catalysts resulted in greater generation of H_2, CO_2 and CO yields, high catalytic activity and stability. Yakaboylu et al. [238] conducted SCWG of starch (concentration 4.4 %wt.) in a fluidised bed reactor at reaction temperatures of 500, 550 and 600 ℃, and at high mass flow rates of 24.5 kg/h and 35 kg/h. They reported that reactor temperature of 600 ℃ and feed flow rate of 24.5 kg/h gave the highest carbon gasification efficiency of 73.9%, and found that the heating profile in the heat exchanger and the residence time contributed significantly to the conversion efficiencies. Hence, to improve the energy efficiency of the SCWG process, heat exchanger considerations are necessary. There was no clogging problem, but small quantities of char (2.3 %wt. at highest) and oil production (10.4 %wt. % at highest) were observed.

3.5.3. Hydrothermal carbonisation (HTC) technology

The HTC process requires heating biomass submerged in water in a pressurised and oxygen-free reactor at moderate temperatures between 160–260 ℃ for several minutes or a few hours [43,44,239]. The biomass is converted to carbonaceous solids commonly referred to as 'hydrochar' along with aqueous by-products and fewer gases (~1–5%). After HTC, the hydrochar is separated from the liquid phase by filtration as dewaterability of the solids is improved [240]. The difference between HTC and torrefaction as well as pyrolysis is that, in HTC the biomass must be in an aqueous suspension throughout the reaction in a saturated pressure up to 2 MPa resulting in the production of very little gas, whilst most organics remain as or are converted to solids [43,241]. The reaction paths are complex, but the notable ones are dehydration, decarboxylation, polymerisation, and aromatisation [216,239,241]; the detailed nature of these reactions largely depends on the type of biomass feed and reaction temperature [239,241]. Some of the advantages of HTC are that: (i) it is operated in a sealed reactor, so little or no harmful gases are released during the process, and thus contributes to GHG mitigation. (ii) It requires comparably mild reaction conditions, and only takes minutes or hours. (iii) HTC reactors are extremely simple and easily scalable [43,241].

HTC of biomass is an exothermic process [43,239,241,242]. About 20% of the energy contained in the biomass is released as heat during the HTC process [241], whilst about 60–90% of the gross calorific value of the feedstock remains in the hydrochar, which is the main product [243]. The hydrochar is densified and has O/C ratios and improved calorific value comparable to that of a low-rank coal, so it can be used as solid fuel [38,43,44]. Hydrochar also has higher H/C and O/C ratios than biochar produced from pyrolysis [244]. A study by Levine et al. [245] revealed that hydrochar can be used for biofuel production by transesterification. Other studies have reported that hydrochars can be used as feedstock in a standard gasification process for syngas production [246]. These options require different ratios of O/C for optimum conditions, giving rise to different reaction temperatures and time requirements during HTC. As shown in Table 7, there has been extensive studies into HTC of biomass to investigate the energy value of the hydrochar. The higher heating values (HHV) ranks the hydrochars as an alternative coal fuel.

The aqueous by-product is reported to contain organic compounds such as furans, phenol, acetic acid, levulinic acid, aromatics, aldehydes, other soluble organic compounds [38,247]. Methane production from wastewater substrates following biomass HTC has been reported by few studies [248,249] and has gain research interests in recent times. This has been found to improve the energy efficiency of the HTC process [242].

The HTC process is influenced by the following operation parameters, namely, reaction temperature, residence time, pressure, biomass solid content, catalyst and pH used. Among these, temperature is found to be the key parameter that influences product characteristics the most, whilst residence time and biomass solid content also affect product characteristics to some extent.

Table 7. Calorific values of hydrochars derived from HTC of different biomass feedstock.

Biomass feedstock	Temperature (°C)	Time	HHV (~MJ/kg)	Reference
Primary sewage sludge	140–200	15–240 min	16.7–18.7	[38]
Primary sewage sludge	140–200	4 h	21.5–23.1	[44]
Algae	NR	NR	20.6–28.4	[245]
Loblolly pine	200–260	5 min	21.1–26.6	[250]
Microalgae	203	2 h	30.5–31.6	[251]
AD waste	250	20 h	13.7 [a]	[252]
Food waste	250	20 h	29.1 [a]	[252]
Mixed MSW	250	20 h	20.0 [a]	[252]
Waste paper	250	20	23.9 [a]	[252]
Anaerobic digested maize silage	190–270	2–10 h	25.4–35.7	[253]
Wood	210	4	22.9–30.1	[254]
Wood	200–260	5	21.6–26.4	[255]
Loblolly pine	200–230	1–5	21.4–22.4	[256]
Barley straw	280–400	15	26.8–35.5	[257]
Dewatered activated sludge	180–240	15–45 min	18.3–20.2	[258]

[a] unit in dry basis (db). NR = not reported.

3.5.3.1. Effect of temperature on HTC

Temperature influences the rate of hydrolysis of biomass fragments during HTC [259,260]. Hydrolysis of hemicellulose occurs at temperatures between 180 °C and 200 °C, hydrolysis of lignin occurs in the range of 200 °C and 220 °C, and that of cellulose occurs above 220 °C [261]. The rate of polymerisation also depends on temperature. The glucose content in the water-soluble component increases with a rise in temperature, which further decomposes at higher temperatures to produce 5-(hydroxymethyl) furfural (5-HMF) [262]. The amount of colloidal carbon particles increases with increasing temperature; but less structural features of the original biomass feedstock remain [241].

Reaction temperature has a significant effect on the produced hydrochar characteristics. Temperature shows nearly a linear relationship with carbon content, but hydrochar yield decreases as temperature increases [44,253]. Increasing temperature from 140 to 200 °C has been reported to increase the calorific value or HHV of the hydrochar derived from sewage sludge from 16.7 to 23.1 MJ/kg as well as energy densification [38,44]. Volatile matter content in hydrochars decreases as reaction temperature increases, while ash content increases with rise in temperature due to excess loss of volatile matter and minerals retained in the hydrochars [38].

3.5.3.2. Effect of residence time on HTC

Reaction time has been reported by various studies to influence the HTC process and products characteristics. It has been reported that HTC at higher temperature (200 °C) and shorter reaction times (15–60 min) favours dehydration reaction (evident by lower H/C), whilst longer reaction time (120–240 min) is predominated by dehydration and decarboxylation reactions (lower H/C and O/C). Carbonisation at longer reaction times (240 min) and lower temperatures (140 °C) are mainly dehydration reactions, and those at relatively moderate temperatures (160 °C) and times (60–120 min) are primarily governed by decarboxylation reactions, whilst at longer times (240 min) both dehydration and decarboxylation occurred [38].

Hydrochar produced from HTC of carbohydrates at low residence times is observed to contain higher amounts of furan groups at low residence times and low temperatures (below 200 °C), whilst longer residence time and higher temperatures (above 200 °C) result in an arene-rich content, which resulted from either condensed polycyclic aromatic hydrocarbon (PAH) groups or from three-membered furanic units [263]. Increasing reaction time has been found to increased fixed carbon content and decreased volatile matter content in the hydrochar derived from sewage sludge, as well as gradually increasing the fuel ratio from 0.02 to 0.18 after 10 h residence time. Longer reaction times between above 30 min and higher temperatures (above 180 °C) lead to liquid products containing products of Maillard reaction such as aldehydes, furans, pyrroles, pyrazines, and pyridines [38]. A longer reaction time has been observed to decrease hydrochar yield [38,44,239,264]. However, a study by Heilmann et al. [251] observed that reaction time has no significant effect on HTC, and suggested the possibility of using shorter reaction times (<30 min) for continuous HTC processes.

3.5.3.3. Effect of feedstock solids content on HTC

Feedstock solids content affects HTC conversion efficiency, extent of carbonisation and product characteristics. A study by Danso-Boateng et al. [44] at different feedstock solid content (10%, 15%, and 25%) at 200 °C for varying reaction time (15–240 min) reported that moisture content affects the HTC process; feedstocks with higher initial moisture content (lower solid content) resulted in lower hydrochar yield, whilst feedstock with lower moisture content (i.e., higher solid content) led to more carbonised hydrochar, indicated by higher HHV values. The lower hydrochar yields obtained from feedstocks with lower solid content is due to carbon loss per unit mass of feedstock to the liquid phase [43,44], which also leads to the liquid by-products containing higher content of chemical oxygen demand (COD) [38,43]. The HTC reaction is also found to be faster at lower solid contents (or higher moisture content), especially after 30 min, resulting in lesser hydrochar yield [44]. The practical implications of HTC solid loading should range in excess of 15–20% (wt.) as feedstocks with higher moisture content will require high cost of heating the material to the required temperature, and will cause heat loses, which will make the process uneconomical [38,264].

The various biofuel and bioenergy production methods via thermochemical conversion have been compared and their pros and cons are provided in Table 8.

Table 8. Comparison of pros and cons of thermochemical biomass conversion routes for bioenergy.

Process	Advantages	Disadvantages
Combustion	• Simple and available technology. • Low running costs. • Simple biomass pre-treatment. • Up to 90% volume reduction.	• Feasible for biomass with low moisture content. • High costs for pre-drying high moisture content biomass, as high moisture decreases efficiency. • Requires feedstock pre-treatment. • Adverse environmental effect caused by generation of by-products such as soot, dust, ash, NOx, CO, and CO$_2$. • Flue gas cleaning. • Low efficiency at small-scale.
Torrefaction	• Zero waste process. • Improves the combustion behaviour of biomass.	• High costs for pre-drying high moisture content biomass. • Ash in the torrefied biomass causes corrosive deposits on boiler tube.
Pyrolysis	• Flexible to changes in feedstock composition. • It is scalable, can be operated as a batch process. • Produces a variety of valuable products: biochar, bio-oil, syngas. • Produces hydrogen directly. • Up to 90% volume reduction. • Low pressure process requires minimal feedstock pre-treatment. • MAP ensures efficient heat transfer and process large size biomass.	• High costs for pre-drying high moisture content biomass. • High char abrasion and erosion to equipment. • Extensive gas cleaning of the syngas. • High investment costs. • Fast pyrolysis requires feedstock with low moisture content, high heating rates and high temperature. • Flash pyrolysis requires feedstock with small particle size to obtain high heating and heat transfer rates. • Catalyst deactivation due to char in catalytic pyrolysis. • MAP requires high operating costs.

Continued on next page

Process	Advantages	Disadvantages
Direct gasification	• Maximum conversion can be obtained. • Syngas and biochar production • High hydrogen yield can be obtained. • Reduced emissions. • High efficiency at small-scale. • Flexible in capacity. • Versatile, can process diverse biomass feedstocks to fuel gas with high efficiency.	• Feasible for biomass with low moisture content. • High costs for pre-drying high moisture content biomass, as high moisture decreases thermal efficiency. • Complex technology. • High investment and operating costs. • Extensive gas cleaning of the syngas to remove tar, char, ash and dust. • Incomplete carbon burnout results in reduced energy efficiency. • Feedstock such as sewage sludge and manure emit sulphur in the form of H_2S, requiring a gas cleaning system.
Hydrothermal liquefaction	• Suitable for all biomass types including those with high moisture content. • In addition to the bio-oil, it produces a variety of useful chemicals, although feedstock dependant. • The water by-product can be recycled.	• High cost resulting from high energy demand to reach the reaction temperature, heat exchanger and reactor costs. • To avoid reactor clogging, a high-pressure pump is required to pump highly concentrated biomass feedstock. • High temperature and pressure may cause fracture, rupture or burst of pipeline or reactor is not properly engineered. • Hot compressed water may lead to electrochemical corrosion due to exposure of reactor walls and pipeline to alkali salts. • Catalyst deactivation reduces product yield and quality. • Large-scale applications are limited.
Hydrothermal gasification	• Suitable for all biomass types including those with high moisture content. • Produces high-quality syngas free from char and tar at low temperatures. • Syngas with high carbon efficiency, as liquid phase contains less of organic carbon.	• High cost resulting from high energy demand to reach the reaction temperature, heat exchanger and reactor costs. • Complications due to high energy requirements. • High temperature and pressure and the chemical substances will cause corrosion of the reactor. • Coke and tar will form in parts of the biomass that is not gasified.
Hydrothermal carbonisation	• Suitable for all biomass types including those with high moisture content. • Simple and easily scalable reactors. • Low energy requirements. • Releases little or no harmful gases during operation, contributing to GHG mitigation.	• Post-treatment of the liquid by-product or process water may be required. • Continuous process required feeding against high reactor pressure.

4. Process integration

The integration of one or more thermochemical technologies has gain recent research focus as a means to increase the yields and quality of the desired products, improve efficiency of the process and reduce environmental effects, and greenhouse gas emissions.

4.1. Combustion integration with torrefaction and HTC

4.1.1. Combustion integration with HTC

Pre-treating the biomass using HTC has been found to reduce inorganics present in the feedstock, as a larger amount of the inorganics are transferred to the liquid by-products during HTC [38,265], reducing the ash content. HTC also improves the fuel properties and stability of the biomass [29,30,266]. HTC removes 60% of nitrogen and sulphur contents in the sewage sludge feedstock producing a cleaner hydrochar (or solid fuel) containing lower amount of nitrogen and sulphur, as the 60% is released into gases and liquid phase [265]. HTC improved the removal of N, S and Cl from hydrochars derived from food waste, which consequently reduced pollutants emissions (HCl, SO_2, and NO) from the hydrochar combustion. However, hydrochar produced above 220 ℃ led to increase NO emission, which was likely caused by the formation of more stable nitrogen groups such as pyridine-N and quaternary-N. Hydrochar is also found to have reduced slagging and fouling indexes in boilers compared to raw biomass [267]. This means using hydrochar as a feedstock for combustion will improve the energy efficiency and reduce the potential risk of generating harmful chemicals such as NO_x, SO_x, HCl and smoke producing compounds.

The combustion behaviours of hydrochars are distinct from raw biomass, with increased maximum weight loss rate, higher ignition temperature, wide combustion ranges, lower burnout temperature, especially at higher temperatures [29,266,267]. Also, temperature of maximum mass loss rate of hydrochar is higher than raw biomass, which significantly increase with temperature, suggesting a longer combustion time was needed for the hydrochar to reach the maximum weight loss rate expected, while producing a more stable flame [265–267]. Hydrochar produced from poultry litter at 250 ℃ had combustion properties similar to coal, while the combustion behaviour of hydrochar produced at temperatures up to 220 ℃ was similar to that of the original litter. Pollutant emissions during hydrochar combustion were reduced as HTC production temperature increased, especially for CH_4 and NH_3 [268]. Hydrochar derived from aquatic biomass (water hyacinth and cattail leaves) have higher fuel quality with increasing HTC temperature [266]. Addition of carbohydrates to food waste during HTC was found to enhance the homogeneousness and thermal stability of the hydrochar, because carbohydrates were the most active reactants contributing to hydrochar formation. When the content of carbohydrates or proteins increased, hydrochar burned less violent, which is beneficial for stable combustion in the furnace. By increasing the proportion of lipid in the feedstock, its derived hydrochar exhibited a higher volatile content (74.51%) and HHV (29.17 MJ/kg), lower activation energy (101.1 kJ/mol), and more violent combustion process of the hydrochar [269]. These studies show that HTC temperature and feedstock type influence the combustion characteristics of the hydrochars. Hence, more research works are need to better understand the impact of HTC on the combustion behaviour of a variety of biomass, especially those of more complex feedstock origin.

4.1.2. Combustion integration with torrefaction

Torrefaction improves the combustion behaviour of biomass. Lasek et al. [270] studied the combustion of torrefied willow in a bubbling fluidised-bed combustor and found low SO_2 emissions (the measurements were based on a 6% O_2 concentration) level (2 ppm) during the combustion of the torrefied biomass. This was mainly attributed to the comparatively low sulfur content in the torrefied biomass. Net CO_2 emissions could fall significantly by consuming torrefied biomass in co-firing systems. Ohlemüller et al. [271] studied a 1 MWth pilot plant coupled with chemical looping combustion (CLC) of hard coal and torrefied biomass. Co-combustion (coal: torrefied biomass = 50/50), resulted in a total carbon capture efficiency (ηCC) of reach 66%, leading to a 122% CO_2 reduction, which corresponds to negative CO_2 emissions compared to a conventional coal-fired power plant.

4.2. Gasification integration with torrefaction and HTC

Traditional biomass gasification technologies lead to low-quality product gas, because it is contaminated by impurities like tar, char, ash and dust. Hence, expensive purification operations are required to clean the gas to achieve the require quality standard [272] before it can be used in engines. In addition, incomplete carbon burnout results in lesser energy efficiency [273]. Torrefied biomass and hydrochars have improved gasification characteristic than gasification of raw biomass.

4.2.1. Gasification of torrefied biomass

Torrefied biomass could improve gasification in terms of both energy efficiency and syngas quality because of the removal of oxygenated volatile compounds from torrefied biomass leading to a reduced amount of tar formation [274,275]. Co-gasification of wet sewage sludge and torrefied birch for syngas production revealed that the use of torrefied birch under high torrefaction severity led to high H_2 and CH_4 production, and gave rise to the decrease in CO_2 and CO formation. The maximum yield of H_2 from wet sewage sludge and torrefied birch co-gasification was 32.17 mol/kg at 827 ℃ (1100 K) [276]. However, more work is required in this area to investigate scaleup effects and study the energy integration in a commercial system.

4.2.2. Gasification of hydrochar

A study of the gasification behaviour of hydrochar derived from sewage sludge observed that compared to the raw material, the hydrothermally treated sewage sludge had improved gasification characteristics in terms of hydrogen-rich syngas production [277]. The study by Gai et al. [277] further reported that HTC pre-treatment combined with subsequent gasification had a lower energy recovery efficiency of the entire process. Utilising steam gasification of the hydrochar (produced at 220 ℃, 1 h) resulted in higher hydrogen concentration and yield (76.70 g H_2/kg biochar) as well as higher heating value, and improved gasification efficiency. The excellent gasification characteristics was due to the higher content of nickel, iron, alkali and alkaline earth metals and nitrogen containing functional groups on the surface of the hydrochar. The same result was not observed for steam gasification of sewage sludge-derived biochar obtained from pyrolysis at 220 ℃, 1 h. This is because, the more porous structure of the hydrochar enabled diffusion and transport of condensable hydrogen molecules during the gasification process. One advantage of HTC-gasification integration is that most of the organics that results in tar formation during direct gasification are transferred to the HTC water. Steurer and Ardissonea [278] reported that the utilisation of hydrochar as a feedstock for gasification has the advantage of a clean gasification process with a very low level of ash and dust pollution. However, further studies into these areas are required for a variety of biomass feedstock to understand the process mechanisms, kinetics, product composition, energy balance, large-scale potential, and so on.

4.3. Pyrolysis integration with torrefaction

Torrefaction is recently considered as an efficient pre-treatment method for improving pyrolysis-derived bio-oil quality and production [279]. Pyrolysis-derived bio-oils from torrefied biomass comparatively contain lower organic acids, furfural, and aldehydes as well as higher hydrocarbons, phenols, furans, ketones, aromatic, anhydrous sugars, aliphatic groups, and carbonaceous residues [279]. Fast pyrolysis of torrefied hardwood showed that the bio-oil yield significantly decreased from 44% (wt) for the raw material) to 31 %(wt) for the torrefied material, but the bio-oil obtained from the torrefied biomass had higher quality in terms of oxygen content, decreasing from 45.7 to 37.2%(wt), and HHV, increasing from 19.1 to 23.1 MJ/kg, when compared with the bio-oil from the virgin biomass [280]. In a study into co-pyrolysis of low-density polyethylene (LDPE) and torrefied rice straw by microwave heating, it was revealed that the bio-oils from the torrefied biomass had a lower water content, and the main compositions in the bio-oil were phenols, ketones, hydrocarbons, esters, and alcohols [281]. Chen et al. [282] conducted a two-stage thermodegradation of hemicelluloses, cellulose, and lignin to investigate the effect of torrefaction on pyrolytic products. They found that inherent pentose units and O-acetyl of hemicelluloses were decomposed into furfural and acetic acid during torrefaction; hence, the pyrolysis bio-oil of torrefied hemicelluloses contained lower acetic acid and furfural contents. In the case of lignin, a noticeable influence on its pyrolysis was observed when torrefaction at 300 ℃ was applied, resulting in an increase in aromatic compounds in the course of pyrolysis. On the contrary, the effect of torrefaction upon cellulose was insignificant, due to the high thermal stability of the crystalline structure in the cellulose. However, torrefaction pre-treatment of biomass to pyrolysis oil production has not been applied to various biomass feedstock, especially those with complex compositions such as food waste, sewage sludge, MSW, animal waste, etc. to understand the process mechanisms and large-scale potential application.

5. Technological challenges and perspectives

Thermochemical waste-to-energy technologies have become fast-developed techniques to convert biomass to bioenergy or biofuels, as discussed above, due to the ability of these technologies to handling a variety of biomass materials. However, the utilisation of the current technologies for the production of bioenergy from waste is relatively not as competitive as fossil fuels. Some of the major technological challenges in biofuels production are: (i) efficient utilisation of biomass as a renewable energy source; (ii) economical and safe utilisation of waste such as sludges, manure and MSW due to their high moisture and ash contents; (iii) minimisation of environmental effects, air pollution, and GHG emissions (even though lover than those for fossil fuels); (iv) scale of production; (v) high energy input for instance, for setting up the plant equipment, waste pre-treatment, reactor operation and maintenance, and purification of the biofuels; (vi) process and energy efficiency. These could limit their commercialisation as waste to bioenergy technologies. To increase the energy efficiency, the conversion technology should be efficient and economical whilst considering a high scale of production. This requires process optimisation to increase the yields of the desired products and process efficiency.

5.1. Combustion challenges and perspective

The drawbacks with combustion are that biomass containing higher moisture (>10%) requires pre-drying as dry fuels are the best for combustion. Higher moisture content could lead to low thermal efficiency during combustion [283]. Moisture interferes with effective oxidation of biomass, especially in small capacity combustion systems, resulting in high emissions of carbon monoxide and non-combusted hydrocarbons. Wood biomass has low ash, nitrogen and sulphur in comparison to coal, which rarely causes problems in boilers during combustion. However, certain biomass sources such as sewage sludge, animal manure and MSW contains high fractions of ash, sulphur and nitrogen (Table 1). Hence, industrial combustion of such biomass is associated with various operational problems such as deposition, fouling, and corrosion due the presence of inorganics such as K, Na, Cl, S, and P [284,285], and requires high cost [286]. Even with the use of advanced combustion technology, combustion produces more indoor and outdoor air pollution, releasing CO_2 into the atmosphere causing global warming, as well the generation of NO_x and SO_x (for feedstocks such as sewage sludge, MSW and manure). It produces and creates carbon monoxide poisoning. These have resulted in many governments to look for alternative and more environmental-friendly means of producing energy from such biomass feedstocks.

Combustion of biomass with high ash content such as sewage sludge, MSW and animal manure can lead to formation of lumps of slag that can block grates and cause erosion and jamming of ash augers, deposit on heat exchanger surfaces causing problems in boiler tubes. Besides moisture and ash, the amount of heat released during biomass combustion will also depend on the properties of the fuel such as carbon, hydrogen and oxygen contents. Current research has focused on pre-treatment of biomass using torrefaction and HTC to improve the combustion behaviour of biomass (discussed previously). HTC reduces the inorganic and ash content in the produced hydrochar, which consequently reduced pollutant emission [267], while torrefaction reduced the moisture in the biomass and decreases the sulphur content in the torrefied biomass [270]. However, future research needs to focus on process optimisation and scale-up of the process towards industrial scale applications.

5.1.1. Post-combustion CO_2 capture

The development of adsorption-based technologies for CO_2 capture in the post-combustion process has gain research attention in recent times as a means of reducing GHG global emissions [287,280]. Based on the BLUE Map Scenario of the International Energy Agency (IEA), Carbon Capture and Storage (CCS) technologies are capable of reducing CO_2 emissions of up to 19% from fixed industrial sources by 2050 [289]. Activated carbons are the most promising adsorbents for CO_2 capture, as these adsorbents require less energy for regeneration in a desorption process [290], because of the weaker physical interaction of the activated carbons with the CO_2 molecules and the lower heat of adsorption involved [291]. Karimi et al. [292] studied CO_2 capture using chemically and thermally modified commercial activated carbon (Notrit ROX 0.8). Their study showed that chemical modification with nitric acid and urea, and thermal calcination improved the CO_2 uptake capacity, and that the later partially influences the CO_2 capture capacity, whose increment increases CO_2 capture and the breakthrough time. In a recent study by Karimi et al. [66,67], activated carbons derived from MSW were utilised for CO_2 capture. The highest CO_2 uptake capacity was obtained from MSW treated with sulphuric acid and activated at the highest temperature (800 °C) as these conditions resulted in an improved surface chemistry of the adsorbent with more active sites for CO_2 adsorption.

These studies have revealed than biomass-based adsorbents can be employed for CO_2 capture; however, this area still requires more efforts to improve the energy consumption of the adsorbent production process as extremely high temperatures are required. Future directions should consider metal-doped bio-based adsorbents for CO_2 capture as the surface functionalities of such materials can be tailored to open new directions for several applications in pollutant control. There are several varieties of biomass feedstocks, which can be considered as potential sources for future developments of adsorbents for CO_2 capture in biomass post-combustion systems.

5.2. Torrefaction challenges and perspectives

As explained earlier, torrefaction has been applied in combustion to improve the combustion behaviour of biomass and reduced the emissions of SO_2 and CO_2 [270,271]. Also, application of torrefaction in gasification is found to improve energy efficiency and syngas quality [274,275], whiles the yield and quality of bio-oil are enhanced in the pyrolysis of torrefied biomass [293]. However, at the torrefaction temperature range of 200–350 °C, there is formation of persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) [294]. POPs formation is reported to occur primarily through heterogeneous reactions of a precursor pathway and de novo synthesis from a carbonaceous matrix [295].

Torrefaction requires pre-drying of the biomass to remove, especially, the free water if the moisture content is above 20% (wt.); as this affects the thermal degradation of the biomass. Also, torrefaction increases the ash content in the torrefied biomass, which limits the utilisation in combustion and gasification [31] due to the formation of alkali-induced slagging, silicate melt-induced slagging, and corrosion occurring in biomass-fired furnaces [296]. Hence, torrefaction of biomass sources such as sewage sludge, animal manure and MSW will be problematic. Pre-treatment by washing the biomass before torrefaction could remove chemical substances such as Na, K, Ca, Fe, Mg, Cl, P, and S from biomass, which will reduce the emission of pollutants [297,298]. Another critical challenge with biomass torrefaction is the formation of tar and liquid by-products (comprising about 10–40%), depending on feedstock type and torrefaction severity [299,300]. The tar produced creates problems in industrial systems, such as in pipelines, torrefaction reactor, and facility management [30]. As a result, future work should look into technologies for the post-treatment of produced tar from biomass torrefaction. Another area for further research is to consider how washing pre-treatment could improve the quality of boil-oil produced from pyrolysis of torrefied biomass.

5.3. Gasification challenges and perspectives

The updraft fixed bed gasifier is not suitable for the gasification of biomass with high volatile content due to high tar production rate in the gasifier [301], which still remains a challenge to date.

With the fluidised bed gasifier, biomass feedstocks with high ash/alkali content will lead to agglomeration and sintering, causing the formation of a thin sticky substance around the bed particles with an instant loss of bed fluidisation (defluidisation). The use of advanced artificial bed materials such as alumina and magnesite are a solution to the defluidisation problem; however, the high process cost in relation to the use of these materials is a major drawback [302]. Gasification of high ash biomass using the high-pressure entrained flow gasifier results in the production of molten ash. The molten ash forms deposits on the walls of the gasifier, which depending on the operations solidify, triggering plugging and the blockage of critical parts of the gasifier, which hinders efficiency of the process [302]. Hence, further investigations are needed to study the feedstock conversion and gasifier hydrodynamics, especially when high ash biomass feedstock such as MSW, sludges, manures, and some agricultural residues are used in fluidised bed and high-pressure entrained flow gasifiers. Such studies should take into consideration char gasification, devolatilisation kinetics and gas composition regarding particle agglomeration and sintering (in the case of fluidised bed gasifier). As discussed earlier, torrefaction and HTC pre-treatment of biomass reduces the ash content in the biomass, and thus improve gasification performance. Hence, such areas also need further investigation in relation to the application in fluidised bed and entrained flow gasifiers. Papa et al. [303] developed a combined system involving fluidised bed gasification, HTC, and solid oxide fuel cell (SOFC) technologies using ASPEN Plus simulation software and revealed that the combined system improved syngas composition and yield and plant efficiency. Mutlu and Zeng [304] also detailed the challenges and opportunities of modelling the gasification technology using Aspen Plus, who referred to the problems of the gasification technology as impeding the widespread commercialisation of the technology. Therefore, future studies should focus on large-scale biomass gasification regarding integration of biomass feedstocks, development of cost-efficient gas upgrading processes, integration of the process in complete biofuel production designs.

5.4. Pyrolysis challenges and perspectives

High moisture content affects biomass waste conversion into biofuel [305], by directly or indirectly affecting the bio-refining operations and feedstock supply chain [4]. Moisture content could lead to a decrease in bio-oil quality [96]. High volatiles in the biomass can lower the bio-oil stability and energy content [306]. Hence, future work should focus on pre-treating the biomass feedstock using, for example torrefaction, as explained earlier or washing and drying and optimising the pre-treatment conditions to achieved the most improved bio-oil yield and quality.

The bio-oils produced using microwave-assisted pyrolysis give fewer hazardous compounds and produce more useful chemicals of industrial interest than those obtained under conventional pyrolysis. Also, the gas fraction produces higher yields of hydrogen or syngas, which is equally beneficial and advantageous. However, it is difficult to predict the process and products by only relying on the feedstock characteristics due to the variations in feedstock properties. Therefore, there might be the need to optimise the reaction conditions governing this process to improve bio-oil yield and at the same time maintaining its quality. This would allow the suitable process parameters to be defined, which will be beneficial in the scale-up of the MAP process and assist the commercialisation of the process. Other areas that need future work include studying the reaction kinetics, improving catalyst selectivity, and pre-treatment of the biomass feedstock to achieve homogeneity; for example, torrefied the biomass before MAP.

Coking or coke deposition is a major challenge in catalytic fast pyrolysis of biomass, which lead to both carbon loss and catalyst deactivation [34,307], which is caused by the decomposition of the oxygenates derived from biomass pyrolysis and the re-polymerisation of phenolic oxygenates [307]. Several attempts have been made to investigate the zeolite catalyst regeneration [33,308,309]. Although the thermal coke can be removed by regeneration, its presence blocks the access of small molecules to the active sites of the catalyst. Luna-Murillo et al. [35] observed that there are irreversible chemical changes in the catalyst structure (e.g., decrease in the aluminum content) after catalyst regeneration, causing a loss of activity even after a single reaction/regeneration cycle. Their study revealed that the Lewis acid sites of the alumina binder also showed catalytic activity; so, future studies should investigate binder selection in catalytic pyrolysis. Excessive metal loading decreases both acidity and physical properties of ZSM-5. This consequently reduces the diffusivity of reactants and catalytic activity. Also, a high amount of mesoporous fraction increases the coke formation and catalysts deactivation [310]. Therefore, it is necessary to find out the optimal loading of mesoporous template and metals for ZSM-5. The shape selectivity of metal modified ZSM-5 catalysts mostly depends on the properties of the metal, but the type of metal which is effective for modifying ZSM-5 for catalytic pyrolysis is not well understood [310]. Therefore, a comparative study is required in this area in the future. Catalyst coking is influenced by the constituents of the biomass feedstock, as different biomass constituents coke differently. This means that the catalytic fast pyrolysis process seems to be governed by the feed-dependent interaction of mass transfer limitations and the pyrolysis chemistry [35]. Therefore, future work should take this complexity into consideration when designing a zeolite-based catalyst for efficient conversion of biomass to the desired products in catalytic fast pyrolysis.

5.5. Hydrothermal liquefaction challenges and perspectives

The general challenges of biomass HTL are that, the acidic and oxidising conditions can cause rapid corrosion, which can be even more serious at subcritical conditions than at supercritical conditions as subcritical water is comparatively dense and polar. Also, biomass containing very high minerals could cause salt deposition in the reactor, which could lead to reactor clogging [218]; so, future work should investigate how biomass pre-treatment could improve biomass HTL in this regard.

As discussed earlier, the integration of HTL with other biofuels production techniques such as HTL and AD, and HTL and fermentation improves the economics and efficiency of the process to recover the unconverted organics transferred into the liquid as post-hydrothermal liquefaction wastewater (PHWW) [125,220]. However, these have been used on only limited biomass feedstocks, for instance, *Chlorella* and microalgae *Nannochloropsis* sp. Therefore, future studies should focus on using lignocellulosic biomass and biomass feedstock with complex composition such as sludges, manure and MSW in HTL, and should look into the optimal conditions to produce high bio-oil yield with high quality.

5.6. Hydrothermal gasification challenges and perspectives

One of the challenges of biomass hydrothermal gasification is that so much water has to be heated up. In the temperature range of 700–900 ^{o}C, the isothermal SCWG process is weakly endothermic or neutral energetically, and when the feedstock solid content is between 10–20%, which are most practical conditions for a good application of the process whereby no char is produced at equilibrium [235]. The heat required to reach, for example, 700 ◦C may exceed the energy content of the biomass at a water content higher than 80% (g/g). This means that a heat exchanger is required to transfer the sensible heat from the process stream to the feed stream. Hence, the efficiency of this heat exchanger is crucial to the overall energy efficiency of the process [219,235]. Another major downside is the high investment costs needed because of the high pressure, mainly for supercritical water gasification that requires the use of special materials because of the combination of high pressure and temperatures above 600 ℃ [235]. Hence, design and optimisation of the SCWG process is necessary to established the ideal conditions for efficient conversion of variable feedstock to a clean syngas as different types of application may be needed for different SCWG processes.

In the dry gasification process, the presence of inorganic compounds like chloride in the gas phase leads to severe corrosion problems, which is important to the process. In hydrothermal gasification, inorganic compounds are found in the aqueous product phase. This means less cleaning and less corrosion problems with the product gases during further processing. Conversely, the problem to be to be addressed in further studies is how to isolate these inorganic compounds in an economical way, which can be used as a fertiliser to close the nutrition cycle of biomass [219].

There are process challenges to overcome before SCWG of biomass process can be industrialised. Some of the problems include pumping of slurry, low conversion, energy efficiency, char and tar formation, and clogging problems due to salt precipitation. Some of these challenges can be eliminated by having long residence times, high heating rates and application of fluidised bed reactors [221]. However, the major challenge that requires investigation in the future is the designing and operation of clogging free fluidised bed reactors at large scales to establish their suitability of achieving higher heat and mass transfer rates to enhance the gasification efficiency during SCWG of biomass.

5.7. Hydrothermal carbonisation challenges and perspectives

HTC offers several advantages for converting both dry and wet feedstock to hydrochar, which is a clean solid fuel. The energy characteristics of the hydrochar improves as the reaction severity increases (high temperatures and long residence times). However, at this higher reaction severity there are more mass transfers from the feedstock towards the liquid phase [38], even though dewaterability is improved at such conditions [240]. Also, at higher reaction severity, formation of difficult to treat coloured liquid products formed through Maillard reaction between amino acids and reducing sugars are observed [183]. In order to decrease water footprint and maximise energy recovery, research have focused on two approaches: (i) anaerobic digestion of the liquid by-products (or process water) after HTC [39,40,311]; and (ii) recirculation of the process water during HTC [312]. HTC-AD enhances biogas production; however, the biogas production is feedstock and process conditions dependent [40,311]. However, there are only few studies that have dealt with AD of HTC process water; so, future research should focus on utilisation of different biomass feedstock, especially lignocellulosic, manures and MSW, and optimisation of the HTC-AD conditions. Process water recirculation results in increased hydrochar yield and significant improvement in energy properties, especially at a lower HTC temperature [312]. However, not many research in the literature have carried out HTC process water recirculation. Also, the optimisation of process parameters is a major challenge of process water recirculation during HTC; hence, further investigations are needed in this area, especially, to study the influence of process water valorisation by recirculation on its macro-constituents at different temperatures, residence times, and solid loads for different biomass feedstock. Comprehensive studies are also required to investigate how process water recirculation during HTC influences the combustion and gasification characteristics of the produced hydrochar for different biomasses. Future studies should also focus on the kinetic and heat transfer models and scale-up for continuous and large-scale applications.

There are few industrial scale HTC plants, namely ANTACO [313], SUNCOAL [314], and INGELIA [315]. However, real data on industrial scale HTC process seems difficult to find; hence, there are considerable gaps in economic evaluation of industrial scale HTC systems. Another challenge in industrial or continuous HTC plant is pumping of the feed and water mixture against high pressure of the reactor pressure. Therefore, future studies should focus on designing continuous pilot-scale HTC reactors than could enable scale-up of the process to an industrial scale.

6. Conclusions

This review addressed the recent progress and challenges related to biofuel and bioenergy production from various biomass feedstocks via thermochemical technologies. The review has shown that abundant biomass residues and waste are generated from different sources worldwide, which could be potential feedstocks for bioenergy if efficient and economical techniques are utilised. However, biomass feedstock characteristics significantly influence the conversion efficiency and characteristics of the products. The thermochemical conversion processes can process diverse feedstocks for the production of a variety of bioenergy sources such as heat energy, solid, liquid and gaseous biofuels. The feedstocks and the desired end product determine the choice of process technology. However, most of these technologies are affected by operational constraints that hinder their large-scale applications, such as low conversion and energy efficiency, high capital and operation costs, and environmental concerns owing to the release of harmful emissions. Indeed, biomass feedstock such as sewage sludge, manure and municipal solid waste (MSW) are readily available waste, but they seem to produce biofuels containing high amounts of impurities such as inorganics, ash and tar that cause corrosion, salt deposition and clogging in reactors, catalyst coking and deactivation, as well as generation of NOx, SOx and HCl. Feedstock pre-treatment by utilising torrefaction and hydrothermal carbonisation (HTC) by means of technology integration would reduce the inorganics and ash contents, improving product yield and quality, whilst minimising the production of harmful chemicals such as HCl, NOx and SOx and air pollution. Hence, this area must be studied or developed further to enhance biofuel production by optimising the conditions of the integrated processes for efficient utilisation of a variety of biomass feedstock, reduce operational costs and improve process efficiency, prevent catalyst deactivation, and reduce environmental pollution and greenhouse gas (GHG) emissions. Further research should also focus on scale-up of the integrated processes towards industrial scale applications.

Conflict of interest

All authors declare no conflicts of interest in this paper.

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