Review

Opportunities and Challenges of High-Pressure Fast Pyrolysis of Biomass: A Review

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Abstract: Most pyrolysis reactors require small sizes of biomass particles to achieve high-quality products. Moreover, understanding the usefulness of high-pressure systems in pyrolysis is important, given the operational challenges they exhibit specific to various biomass materials. To actualize these aspects, the authors first checked previous reviews involving pyrolysis on different biomass and different conditions/situations with their respective objectives and subsections. From these already existing reviews, the team found that there has not been much emphasis on high-pressure fast pyrolysis and its potential in biomass conversion, showing that it is a novel direction in the pyrolysis technology development. Therefore, this review aims to shed more light on high-pressure fast pyrolysis, drawing from (a) classification of pyrolysis; (b) reactors used in fast pyrolysis; (c) heat transfer in pyrolysis feedstock; (d) fast pyrolysis parameters; (e) properties/yields of fast pyrolysis products; (f) high pressure on pyrolysis process; (g) catalyst types and their application; and (h) problems to overcome in the pyrolysis process. This review increases the understanding regarding high-pressure fast pyrolysis. An attempt has been made to demonstrate how high-pressure fast pyrolysis can bring about high-quality biomass conversion into new products. It has been shown that fluidized bed (bubbling and circulating) reactors are most suitable and profitable in terms of product yield. The high-pressure, especially combined with the fast-heating rate, may be more efficient and beneficial than working under ambient pressure. However, the challenges of pyrolysis on a technical scale appear to be associated with obtaining high product quality and yield. The direction of future work should focus on the design of high-pressure process reactors and material types that might have greater biomass promise, as well understanding the impact of pyrolysis technology on the various output products, especially those with lower energy demands. We propose that the increase of process pressure and biomass particle size decrease should be considered as variables for optimization.

Keywords: feedstock; temperature; pressure; pyrolysis process; reactors; liquid fraction; heat transfer; biochar; catalysts; biorefineries

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1. Introduction

Energy demand concerns and environmental problems have increased the global attention on renewable energy pathways to replace coal, oil, and natural gas [1]. Since biomass feedstock has been recognized worldwide as promising in its conversion to biofuel and other energy sources, energy continues to be generated by developing technologies

known to be capable of converting waste materials (in particular biomass), all of which soon require environmental consideration [1–3]. As the first step in gasification, pyrolysis is key in exploiting biomass energy, even in other thermochemical conversion processes [1]. On this premise, the pyrolysis conversion process using a suitable (pyrolytic) reactor has become attractive for converting waste, which has been seen as an alternative renewable energy source over the last decade [4]. Essentially, this process provides a suitable and sustainable approach to transform low-value biomass residues into energy and upcycled products. Additionally, biomass is believed to bring about insignificant greenhouse gas emissions, for example, methane and carbon dioxide [5]. The CO₂ emission from fossil fuels, such as coal, is a major contributor to global warming. Therefore, CO₂ recycling via biomass gasification and pyrolysis technology has a high promise to reduce the negative impact of global warming [6]. Imperatively, there is a need for pragmatic efforts by governments and organizations responsible for environmental protection to ensure that legislations/regulations are robust to reduce the CO₂ emission from fossil fuels (coal, etc.) [7]. Over the recent decade, there has been increased pressure on environmental protection, which has particularly revamped many companies to become eager to embrace new technologies that favor green production [8].

From a technical standpoint, among the challenges of pyrolysis that remain of great concern is how to obtain high product quality and yield [9,10]. Another challenge of pyrolysis, which is of greater concern, is how to completely pyrolyze biomass particles, given the nature of rapid heat transfer specifically from the heating medium. Most pyrolysis reactors require small sizes of biomass particles to achieve high-quality products [8,10,11]. The data generated by, for example, high-pressure gasification and pyrolysis processes in terms of the product yields are underscored by biomass conversion, and its corresponding thermal effects [1]. Over the years, the applications associated with the reactor's structure have significantly increased, specifically in terms of design and testing. To actualize better product yield, for instance, such applications have aimed to maximize energy transfer and mass concerns. This is largely because many of the reactors, like those involved in a high degree of heat exchange given by exothermic reactions, have to avoid catalyst deactivation to obtain strong performance [12]. Nonetheless, high-pressure pyrolytic reactors for biomass transformation to biochar, bio-oil, and pyrolytic gas production have several benefits, such as product quality, lower operating costs, higher product yields, increased reaction rate, and reduced required heat of reaction [1]. Therefore, it is important to understand the usefulness of high-pressure systems in pyrolysis, given the operational challenges they exhibit specific to various biomasses.

Previous reviews involving pyrolysis on different biomasses and different conditions/situations with their respective objectives and subsections captured are shown in Table 1. Besides the acquisition of the knowledge regarding how catalysts function in the biorefinery industry [13], the context of pyrolysis technology (i.e., determination of operating parameters of pyrolysis) and reactor types has been based on the desired characteristics of the product (biochar, bio-oil, and pyrolytic gas) [14], as well as on the field of biomass pyrolysis and upgrading [10]. Feedstock properties, the reactor type, product characteristics and upgrading options [15], biochar catalysts for fuel production [16], and the properties of the bio-oil [5] are among key areas demonstrated as synthesized literature with relevant information. It is important to note that some conducted reviews have looked at systematic approaches for mapping biomass resources to conversion pathways, forming the basis for biomass valuation and informing when biomass pre-processing is needed to ensure feedstocks are conversion-ready [17]. These reviews have also considered the fundamental process mechanisms of slow pyrolysis and hydrothermal carbonization processes by identifying research needs and summarizing the characteristics of products as a useful potential for industrial applications [18]. It is clear from these reviews that not much emphasis has been on the high-pressure fast pyrolysis and its potential in biomass conversion. Therefore, the objective of this review is to throw more light on high-pressure fast pyrolysis, drawing from (a) classification of pyrolysis; (b) reactors used in fast pyrolysis;

(c) heat transfer in pyrolysis feedstock; (d) fast pyrolysis parameters; (e) properties/yields of fast pyrolysis products; (f) high pressure on pyrolysis process; (g) catalyst types and their application; and (h) problems to overcome in the pyrolysis process.

Table 1. Previously conducted reviews involving pyrolysis on different biomasses and different conditions/situations, with their respective objectives and subsections captured.

Objective	Subsections Captured	Years	References
To harness deep insights into how catalysts perform in the production of carbohydrates from biomass.	Depolymerization; Chemo-catalytic reaction pathways in the conversions of carbohydrates; Epimerization; Retro-aldol reactions; Oxidation/Reduction Catalytic; Dehydration/hydration; Cascade catalysis of cellulose; Isomerization	2019	[13]
To identify how the pyrolysis technology pathways/routes perform, i.e., how operating parameters of pyrolysis are selected, and reactor types based on the desired product characteristics (biochar, bio-oil, or pyrolytic gas).	Pyrolysis principles; Pyrolysis classification; Slow pyrolysis; Fast pyrolysis; Flash pyrolysis; Biomass feedstock; Biomass composition; Physical, chemical biomass characteristics; Pyrolysis reactor types like fixed bed, fluidized bed, bubbling fluidized bed, circulating fluidized bed, and ablative; Pyrolysis process include feed preparation and biomass heating; Pyrolysis products	2012	[14]
To create a systematic approach for mapping biomass resources to conversion pathways, forming the basis for biomass valuation, and informing when biomass pre-processing is needed to ensure feedstocks are conversion ready.	A biomass grading system for biofuels; Management approach; Technical accomplishments; and Relevance	2017	[17]
Review update of the slow pyrolysis basics and process mechanisms, hydrothermal carbonization processes, spot out research gaps, and briefs about the characteristics of biochars for potential industrial use.	Biochar and hydrochar production; chemical process mechanisms underscoring biochar and hydrochar production; Biochar and hydrochar characterization; potential applications/benefits associated with biochar and hydrochar industrial use	2019	[18]
Field of biomass pyrolysis and upgrading	Conceptual design; Catalysis; Bio-oil characterization; Mechanisms and thermal kinetics; Modeling; Economic viability; Environmental performance; Supply chain	2019	[10]
Characterization of the biomass; type of reactors dedicated for fast/slow pyrolysis, the composition of products/upgrading.	Feedstock characterization; Reactor types; Products formation; Biomass upgrading	2012	[15]
Highlighting the reason why biochar catalysts are key elements for production of fuel and their merits	Biochar production techniques; Biochar composition; Catalysts produced from biochar; Biochar-based catalyst utilized to produce fuel	2021	[16]
Review of the characteristics of pyrolysis oil derived from different types of biomasses under different technological conditions used so far.	Review the pyrolysis oil characteristics, such as acidity and pH, alkali elements, ash content, density, heating value, oxygen content, solids, viscosity, and content of water.	2015	[5]

2. Pyrolysis and Its Technological Challenges

Pyrolysis refers to the irreversible chemical change brought about by heat without the involvement of oxygen [1,2]. It is considered one of the technologies of waste recycling, resulting in the production of pyrolysis of bio-oil, biochar, pyrolytic gas, and tar as the main products. One of the technological solutions is the application of fast pyrolysis for bio-oil production with high mass yield [19–22]. One of the identified technological problems is the effective transport of heat, both in the reactor and the substrate itself so that the feedstock reaches the set temperature in the shortest possible time [7,14]. In traditional

externally heated reactors, heat transport occurs through conduction [22]. The introduction of mixing and the flow of hot gases inside the reactor allows the acceleration of feedstock heating through convection [1,5,6,23–25]. Additional fragmentation of the feedstock to a very small size results in shortening the time required to reach the process temperature within the volume of the entire feedstock [25]. However, when striving to further reduce the feedstock's heating time and at the same time increase the efficiency energy of the pyrolysis, the proposal would be to run the process under high-pressure conditions.

The application of the high-pressure fast pyrolysis may reduce the energy demand, which has the potential to shift the process from endo- to exothermic. Notably, the energy demand depicts the energy necessary to increase the temperature of pyrolysis to the target level, which is influenced by biomass moisture and process temperature. There is a general agreement that there is a linear increase in the heat capacity of biomass with the increase of temperature. Hence, an increase from 5 to 423 K would depend on the intended purpose of the pyrolysis study [26]. Additionally, the processes of biomass decomposition and volatilization may give some thermal effects [27]. Basile et al. [1] performed an experiment using four different types of biomass samples, such as corn stalks and poplar, as well as switchgrass types, “Alamo” or “Trailblazer”. By analyzing the influence of high pressure in each biomass type, these workers understood that pressure increases would decrease the energy demand for the pyrolysis in the case of studied materials. For instance, Trailblazer changed noticeably to affect a shift from endo- to exothermic. Pressure increases between 0.1 and 4 MPa can shift the total energy that the pyrolysis requires between −50 and −272 J/g for corn stalks, 29 and −283 J/g for poplar, 37 and −199 J/g for Alamo, and 92 and −210 J/g for Trailblazer, wherein the values with a negative sign (−) express exothermic processes [1].

3. Classification of Pyrolysis

Pyrolysis usually begins with temperature ranges of between 250 and 300 °C, as the volatiles in the absence of oxygen are rapidly released at between 750 °C and 800 °C [28–39]. Largely, this occurrence anchors on the pyrolysis types and the purpose of any given (pyrolysis-based) project [40–70]. The characteristics of the identified types of pyrolysis have been summarized in the Table 2 [15,49,71–75]. Generally, pyrolysis comprises four (diverse) process types, namely: conventional (also called ‘slow’), flash, fast, and slow [28]. These types could also be classified based on operational conditions. In addition, processing the pyrolysis heat at a very high rate, such as 10,000 K/s, and short duration, such as 20–500 ms, helps to classify the pyrolysis as ultra-rapid [28].

Table 2. The technological parameters and product yield typically linked to pyrolysis [15,49,71–75].

Pyrolysis Type	Rate of Heating, K/s	Size of Particle, mm	Process Duration, s	Temperature, °C	* Product Yields, %		
					Bio-Oil	Biochar	Gas
Flash	>1000	<0.2	<0.5	550–1000	75	12	13
Fast	10–200	<1	0.5–10	400–550	50	20	30
Slow	0.1–1	5–50	450–550	300–400	30	35	35

* Approximate and/or expected product yield.

3.1. Slow Pyrolysis

Slow pyrolysis takes place at low temperatures at a range of 300–400 °C, with a heating rate from 0.1 to 1 K/s and duration between 5–30 min. These conditions yield good quality charcoal of around 35% biomass quantity normally obtained in this process, while the bio-oil is rather slightly lower. A longer duration of the process can bring about reduced yield of bio-oil production due to further cracking. However, the process has some technical limitations compared to other processes, such as extra energy input demand due to a lengthened duration and a reduced transfer of heat rate within the process [13,15,72].

3.2. Fast Pyrolysis

In the progress of the fast pyrolysis process, the biomass usually reaches the temperature of around 500 to 600 °C, using a higher heating rate of 10–200 K/s, with a short duration of 0.5–10 s. The fast pyrolysis would produce up to 50% of the bio-oil, 20% of biochar, and 30% pyrolytic gas, respectively. The process usually occurs under a small vapor retention time, and high bio-oil yield is always achieved for the turbine, engine, boiler, and power supply for industrial applications due to its technical advantages [73–75].

3.3. Flash Pyrolysis

The biomass flash pyrolysis can produce biochar, pyrolytic, bio-oil, and gases with respective share(s) of 12%, 13%, and 75% of initial biomass weight. Particles are usually heated for a very short time of about <0.5 s and with a very high rate of heating, greater than 1000 K/s, with a high-temperature level in this process between 550 and 1000 °C. However, the process is not thermally stable. Despite the catalytic activity of the biochar, which affects the oil making, it can become viscous to contain some solid particles [2,31]. This process still provides a high potential of good quality bio-oil at minimum water content [36].

4. Reactors for Fast Pyrolysis

4.1. Classification of Reactors

The reactor is one of the most significant design parameters that influence the fast pyrolysis product yield. The pyrolysis reaction occurs in the reactor. The production quality of the target products depends on the heat transfer method [37]. There are various fast pyrolysis reactor types designed to pyrolyze a variety of biomass into three main products, for instance, bio-oil, biochar, and pyrolytic gas. The pyrolysis reactor properties is shown in Table 3 [62–66]. Besides, the production yield depends on the reactor design and operation processes. The classes of the reactor are as follows: rotating cone reactor (RCR), fluidized bed reactor (FBR), entrained flow reactor (EFR), circulating fluidized bed reactor (CFBR), ablative reactor (AbR), and auger reactor (AuR) [55–57].

Table 3. The pyrolysis reactor properties [62–66].

Reactor Type	Capacity, kg/h	Temperature, °C	Pressure, Bar	Method of Heat Transfer	Residence Time, s	Particle Size, mm	Products Yield, %		
							Oil	Gas	Char
Rotating cone	10	500	0.8	Conduction	0.3–0.5	<0.5	49	15–20	10–15
Fluidized bed	500	450–560	0.01	90% Conduction	0.5–2	2–3	50–80	10	10–15
Entrained flow	50	400–550	5–20	Convection	0.5–1	0.5	60	30	10
Circulating fluid bed	30	500	1	Conduction	0.5–1	1–2	39–70	25	10–15
Ablative	2.5	450–600	1	Conduction	0.5	5	70	10–20	10–15
Auger	1–6	450–550	1	Conduction	2	<5	30–50	20–35	20–30

4.2. Description of the Reactors

4.2.1. Rotating Cone Reactors (RCR)

These types of reactors are comparable to CFBR reactors. Typically, hot sand with a biomass particles mixture is utilized in this reactor as the reaction medium. The way in which the particles move removes the rationale for a carrier gas, which must be achieved by centrifugal force within RCR. During the pyrolysis process, both biomass and sand must be introduced into this reactor type (that is, RCR), particularly from the bottom of the cone. When the biomass particles move up to the lip of the cone to become subject to pyrolysis reactions, the sand and char are, at that point, transferred to the combustor, condensing the

vapors, thereby separating the bio-oil. According to Mahdi et al., the bio-oil yield product of this reactor is up to 70% (Table 3) [10].

4.2.2. Fluidized Bed Reactor (FBR)

Advances in the bubbling FBR have been attributed to the Dynamotive Energy System, a reactor type that is globally widespread given its simple process operation. Frequently made of sand, the bed media being supported on a perforated plate has the inert gas typically fluidized, such that, from the reactor bottom, it flows upward. By developing a model of this reactor type, Felice et al. determined the physical and chemical properties of output products under-thigh temperature of about 425 °C, where the product yield of the gaseous component is higher than that of liquid [40]. Generally, the bio-oil yield associated with this reactor type ranged between 70% and 75% (Table 3), which is very high in comparison to the other reactors. Additionally, this reactor is of the feedstock input type and continuously produces bio-oil [15,25].

4.2.3. Circulating Fluidized Bed Reactor (CFBR)

The CFBR resembles bubbling FBR, especially where the gas transports the hot sand (that is, with a sand/feed proportion from 20% to 25%). Biochar, together with the sand, then gets separated from other products by the cyclone. The burning of unreacted particles empowers heat supply relevant to the endothermic pyrolysis process, which in turn, facilitates the drawbacks associated with the scale up of circulating FBR. A short residence time is required for char and sand in this type of reactor (0.5–1 s) (Table 3) compared to the bubbling FBR, for which small particle sizes are required because of the high residence time at a range of 2–3 s [25,59].

4.2.4. Entrained Flow Reactor (EFR)

EFR is motivated by the technologies associated with the gasification process. A preheated inert gas stream can entrain the biomass particles in this reactor. Typically, the reactor temperature can exit at 500 °C. If the production of bio-oil yield is about 50%, the char yield could be between 20% and 30% (Table 3) [10]. Such a reactor type has demerits, such as the lack of heat transfer between the biomass particles and gas, which usually is of high process temperature and results in increased gas flow rate and challenges associated with scaling-up [42].

4.2.5. Ablative Reactor (AbR)

In the heat transfer linked with AbR, the biomass during the pyrolysis reactions is driven against a hot plate (reactor wall). The process resembles the standard method of melting butter in the frying pan. This reactor accepts a bigger feedstock particle size (20 mm) relative to other reactor types. However, the main disadvantages are linked to heat supply and the low reaction rate.

An experiment was performed in an AbR that involved the National Renewable Energy Laboratory (NREL) facility, which aimed to scale up a reactor from a small private firm that designed a reactor capacity of 35 tons per day. The feedstock particles, transported with superheated steam with a velocity of 200 m/s, were tangentially fed at 625 °C to the reactor. Via the heat transfer rate at the level of 1000 W/cm² high, up to 70% (Table 3) of bio-oil yield was achieved [6,61].

4.2.6. Auger Reactor (AuR)

Another reactor design type utilized for biomass feedstock is the auger. This AuR allows the biomass feedstock to be moved via a heated cylinder. Further, the process is such that the tube creates a passage through which the feedstock is raised to achieve a desirable pyrolysis temperature range between 400 and 800 °C (Table 3). Additionally, it is this temperature range that allows which feedstock to devolatilize and gasify. The output product includes char and associated gases, which can be condensed as bio-oil. There could also be other non-condensable vapor, which can be collected as syngas (also synthesis gas). Notably, the AuR's design would allow for process duration to be modified, which could take place by applying changes within the heated zone. Through this approach, the vapor can pass through the system before entry into the condenser train [14]. The basic properties of the above-mentioned pyrolysis reactors are demonstrated in Table 3.

5. Heat Transfer Pyrolysis

The heat transfer methods are divided into two parts according to the type of reactor. The heat can be transferred by the method of conduction using an external device to the reactor or convection method, which means that heat can be generated within the reactor. By assessing the high heat transfer rate to the biomass particles, Sharifzadeh et al. [10] found that the initial products are being removed quickly. Hence, the biomass feed composition is a very key parameter within the fast pyrolysis, able to produce reduced char with increased bio-oil product yield [10]. Two major components to consider before heat transfer in fast pyrolysis reactors include heat transfer to the reactor wall and heat transfer from the reactor wall to the biomass particles. Lødeng et al. [48] believed that the fast pyrolysis warrants an increased heat transfer rate that rapidly makes the biomass particles but sufficiently arrives at a target temperature level for the reaction to be optimal. There are these two different ways to heat the biomass particles under the fast pyrolysis process: solid-solid or gas-solid, depending on the type of operating reactor. Generally, heating rates are between 1 and 1000 C/s; however, the high (local) heating rates may reach 10,000 C/s [48]. The heat transfer methods within the pyrolysis process vary with reactor operating conditions, which are presented in Table 4 [14]

Table 4. The common methods of heating applicable to different types of reactors [14].

Reactor Type	Heating Method
AuR	Fire tube
AbR	Wall heating
CFBR	Sand and wall heating
EFR	Heating (Electric) elements
FBR	Solar radiation
RCR	Gasification of biochar on heat sand

6. Pyrolysis Feedstock

Feedstock can be categorized into different types in the pyrolysis process, including lignocellulosic biomass, municipal solid waste, and refuse-derived fuel. Promising as a bio-renewable resource, the lignocellulosic biomass as a focus [49] has often replaced fossil fuel resources, particularly in the biorefinery industries [12,13]. The biomass comprises three main components: cellulose, hemicellulose, and lignin. The percentage covered by the individual biomass components is presented in Table 5 [14–18].

Table 5. Cellulose, hemicellulose, and lignin content of some selected biomasses [14–18].

Biomass Type	Lignin, %	Cellulose, %	Hemicellulose, %
Wheat straw	15–20	33–40	20–25
Rice straw	18	32.1	24
Tobacco stalk	27	42.4	28.2
Softwood stem	25–35	45–50	25–35
Corn stover	16–21	28	35
Switch grass	5–20	30–50	10–40
Olive husk	48.4	24	23.6
Hazelnut shell	42.9	28.8	30.4
Tea waste	40	30.20	19.9
Hardwood stem	18–25	40–55	24–40
Walnut shell	52.3	25.6	22.7
Sunflower shell	17	48.4	34.6
Nutshell	30–40	25–30	25–30
Cottonseed hairs	0	80–95	5–20
Oat straw	16–19	31–37	24–29
Bamboo	21–31	26–43	15–26
Banana waste	14	13.2	14.8
Sugarcane bagasse	23–32	19–24	32–48

Biomass Properties Affecting the Pyrolysis Process

The properties of biomass affecting the process of pyrolysis are the thermal degradability of biomass components, calorific value, elemental composition, and specific heat capacity. The structure of biomass comprises three main bio-macromolecules, such as hemicellulose, cellulose, and lignin, along with some minerals such as ash [19,20]. The above-mentioned layers of lignocellulosic biomass are pyrolyzed at different temperature levels during the pyrolysis reaction, where bio-oil, biochar, pyrolytic-gas, and tar are produced as the main target products. The hydrophobicity of cellulose is normally considered moderate, and it has a high heating value between 17 and 18 MJkg^{−1} [55]. Hemicellulose is thermally stable in comparison to other structural biomass components due to its amorphous shape. Hydrolysis of hemicellulose takes place at approximately 200–300 °C. The hydrophobicity is short lived, and the calorific value is between 17 and 18 MJkg^{−1} [55]. Biomass degradation of lignin takes place at around 600 °C. The hydrophobicity (23.3–26.6 MJkg^{−1}) is high compared to other biomass structures [55]. The decomposition rates of three biomass components with pyrolysis temperatures are shown in Figure 1 [14]. The water mass loss rate pyrolysis temperature below 100 °C appears to be minimal. Besides water, the mass loss rates of hemicellulose and cellulose noticeably differ at respective pyrolysis temperatures of 325 and 375 °C. Additionally, there appears to be no distinct mass loss rate difference in the case of lignin from pyrolysis temperatures between 250 and 500 °C.

Understanding the decomposition behavior of the main biomass requires useful knowledge about its properties and structure, particularly in the context of moisture status and the specific temperature points in obtaining different pyrolysis products. To throw more light on this, the rate of thermal decomposition involving cellulose, hemicellulose, and lignin with moisture/water operating within pyrolysis temperature is shown in Figure 2 [31]. The temperature ranges within the pyrolysis process reflect different layers of biomass structure. Given that these three main layers are understood to pyrolyze at different temperature ranges, the emergent products would be achieved at specific temperature levels. Previous studies involving approximate and ultimate analyses have shown the fundamental fuel trademark to be among effective ways that relate to general properties of biomass composition, particularly with regards to ash, carbon, hydrogen, oxygen, nitrogen, sulfur, moisture, and volatile matter [56]. Volatiles and ash presence might affect the pyrolysis reaction, and, therefore, it would result in a considerable effect on the quality and bio-oil yield [16,22]. When the volatile content is higher, it is subjected to

high volatility, and this could change the characteristics desired of bio-oil production [56]. However, the ash content lowers the calorific value of the feedstock and subsequently impacts the production of bio-oil. A higher water content results in an increase of the aqueous phase under the pyrolysis process, which will cause a reduction of calorific values of the biomass-derived bio-oil. Furthermore, the carbon burn rate is considerably lower during the process [22,24].

Figure 1. The rate of thermal decomposition of cellulose, hemicellulose, and lignin with moisture/water operating within pyrolysis temperature. Adapted with slight modifications from [14].

Figure 2. The decomposition processes and products of biomass components under different temperatures of pyrolysis. Modified from [31].

7. Fast Pyrolysis Parameters

7.1. Temperature Effects

Numerous parameters influence fast pyrolysis product yields and properties. Key parameters are commonly temperature, pressure, reactor type, residence time, particle size, and energy demand effect. Variable product yield from fast pyrolysis with ranging temperatures is shown in Figure 3 [29]. To measure a specific temperature demand for pyrolysis, the biomass particles (specific to the fast pyrolysis process) are very sensitive. This is because it can be measured by either the reaction or reactor temperatures [42,53–55]. Given the heat loss during the heat transfer from the reactor side wall to biomass particles, the temperature of the reactor usually appears higher than the reaction temperature, which can result in a paucity of completely pyrolyzed biomass particles. Therefore, any changes in reactor temperature would affect the reaction temperature. For instance, the temperature of the reactor would correspondingly rise with the temperature of the process. Hence, authors of such scientific experiments should specify where the temperature was measured [42,53–55]. Typically, increases in temperature within the pyrolysis process occur with gas production yield and with a corresponding lowering of the biochar production. However, the maximum pyrolytic oil production can be achieved at the desired temperature range (480 to 550 °C). Additionally, the water content would be decreasing at 550 °C operating temperature (Figure 3) [42,53–55].

Figure 3. Variable product yield from fast pyrolysis at different temperatures; adapted from the International Energy Agency [29].

The way in which temperature impacts bio-oil production appears to be more complex. This is because the bio-oil yield suggests the gross of organics/water yields. Hence, the best way to achieve that is to look at the yields of water and organic liquids independently. Mostly when the pyrolysis process is operating at a range between 400 and 600 °C temperature level, the yield of the organic liquids tends to achieve a peak value under specific temperature, but it depends on the feedstock type. In the case of wood feedstock, usually, the maximum temperature is 500 °C. The influence of temperature on bio-oil qualitative characteristics was investigated by Elliot [62], who characterized a fast pyrolysis process with a short residence time. In that study, the chemical composition showed a direct association with the process temperature [62]. Despite this, the temperature increase would feasibly decrease the released oxygen content [55]. Additionally, the pyrolytic gas increases with temperature but decreases in bio-oil, biochar, and water [29].

7.2. Pressure Effects

Pressure is a significant factor in the fast pyrolysis of biomass, given its influence on product yield. Generally, critical parameters involved in fast pyrolysis include a high rate of heat exchange to the biomass and a speedy removal of initial biomass feed composition/products, which results in an increase in liquids yields and a reduction of biochar yield. Many studies have shown that increasing pyrolysis pressure would result in proportionally more oil with decreased gas yield. Higher pressure would lower the obtained gas product yield [63]. By using three different pressure values, 5, 10, and 20 bar, to generate char samples without change in temperature condition, the pyrolysis pressure would have a demonstrated impact on the shape and size of particles, through the proportional rise in the void and reduction in thickness of a cell wall. Most swelling occurs at pressures with low values, whereas an increase of the pressure of pyrolysis would lead to bubbles forming with the increased size of biochar particles [64]. Another study that used four types of biomasses, namely poplar, switchgrass Alamo, switchgrass Trailblazer, and corn stalks, evaluated the relationship between heat and high-pressure values of pyrolysis by proximate analysis equation, and the resultant outputs are shown in Figure 4 [1]. The process pressure would noticeably affect the biochar yield. This is governed by pressure rising from 1 bar to 5 bars, which resulted in increased biochar yields from 23.8% to 28.3%, from 17.3% to 30.7%, from 15.2% to 27.3%, and from 19.1% to 28.5%, for corn stalk, poplar, Alamo, and Trailblazer, respectively. An increase in pressure in all biomass samples would shift the process from an endothermic to an exothermic reaction [1].

Figure 4. The influence of pressure on heat of pyrolysis for (a) corn stalks (with biomass weight of volatiles = 77.7%, fixed carbon = 16.0%, and ash = 6.3%); (b) poplar (with biomass weight of volatiles = 81.8%, fixed carbon = 14.8%, and ash = 8.4%); (c) switchgrass Alamo (with biomass weight of volatiles = 79.3%, fixed carbon = 12.1% and ash = 2.1%); and (d) switchgrass Trailblazer (with biomass weight of volatiles = 64.1%, fixed carbon = 8.6%, and ash = 27.3%) [1].

7.3. Reactor Type Effects

The reactor is among the parameters that influence the fast pyrolysis yield products. Nonetheless, different reactor types vary with operating processes, which would eventually impact the energy demand/transfer, gas emission, particle size, product quality, and reactor capacity. Indeed, the reactor is at the heart of the pyrolysis process, influencing product quality, even when compared to various pyrolytic reactor types, corresponding operating procedures, and product yield. The fluidized beds (bubbling and circulating) are suitable,

more profitable among others in terms of product yield because those mentioned types could produce bio-oil of about 75% [7,58,59].

7.4. The Process Duration Effects

The process duration (residence time of the feedstock under desired conditions) refers to the total time it takes to pyrolysis within the hot environment to achieve the point of condensation, and fast pyrolysis needs a short residence time. Generally, the fast pyrolysis vapor residence time is usually <2 s [25], typically to decrease the secondary reaction, such as recondensation, thermal cracking, repolymerization, and formation of biochar, which results in a decrease of liquids yields, while the yield of permanent gas and biochar increases.

7.5. Particle Size Effects

The feedstock particle size is a key parameter that impacts the production yield and overall energy requirement in fast pyrolysis. The size of the biomass particle is related to reactor type. The biomass particle size impacts biomass composition. The increment in particle dimensions leads to a decreased content of ash, with an increase in the content of fixed carbon and volatile solids. However, the ash content usually increases when the biomass particle size is too small (typically <0.1 mm). However, biomass ash is influenced by increasing the reactivity of the pyrolyzing biomass, which results in the generation of non-condensable gasses, such as CO, CO₂, and H₂ [11,67]. According to Vinu et al. [8], an experiment was performed to observe trends of biomass particle size in yields of the biochar from fast and slow pyrolysis, and the findings of this specific study appeared to be consistent with previous literature. Onay et al. [68] investigated the influence of the heating rate and particle size on rapeseed pyrolysis products yields [68]. They revealed that under the fast pyrolysis conditions at 400 °C, 300 °C min⁻¹, with 0.425–1.25 mm dimensions, a higher biochar yield was obtained, reaching ~30 mass%, relative to that under slow pyrolysis (30 °C min⁻¹), not exceeding 25 mass%. However, at an increased temperature from 500 to 550 °C, the biochar yield was lower: ~10–15 mass% in the case of fast pyrolysis and ~17–20 mass% in the case of slow pyrolysis. This points to the fact that results might differ from the literature as the fast mode of this process appeared to be on the lower side. Additionally, a comparison of the final biochar yield obtained under 750 and 800 °C in the case of slow pyrolysis with fast pyrolysis (500 °C) indicates significant variations in biochar yields [11,67].

7.6. Energy Demand Effects

The energy demand in fast pyrolysis processes is among the essential parameters impacting pyrolysis product yields. This depends on biomass properties and the operating reactor [11,67]. Understanding how the kinetics of pyrolysis function is essential, particularly for energy demand evaluations. This is because, for instance, the kinetics of pyrolysis are underpinned by parameters such as heating rate, as well as the size of feedstock particles. These two parameters are believed to influence the overall energy requirement for the process. On the other hand, the size of the particles can also influence biomass composition [11,67]. It is also believed that decreases in ash content would increase volatile matter, fixed carbon, and biomass particle size. Notwithstanding that a very small particle size makes the ash content more evident (typically <100 µm), the critical size would equally depend on the biomass type, for instance, in the situations of agro residues functioning against woody biomass [11,67].

8. Quantitative and Qualitative Characteristics of Products from Fast Pyrolysis

8.1. Bio-Oil

Fast pyrolysis of biomass has attracted high interest worldwide given its product advantages. Fast pyrolysis involves a biomass-to-energy conversion process, which results in the three primary products, char, pyrolytic gas, and liquid, known as bio-oil or biofuel,

but also with some by-products, such as tar, whose gasses usually condense at low temperature. Generally, bio-oil is the liquid oil obtained via the pyrolysis of biomass. Heavily colored (often dark red, brown, or black) and viscous, the bio-oil comprises a mixture of many compounds, which vary both in their content, proportion, and physical properties depending on feedstock type, production method, and age of the sample [21,25]. Bio-oil maximum yield production usually occurs at temperatures between 450 and 500 °C [26,28]. Michailof et al. [72] considered bio-oil properties determination among the greater challenges that hinders achieving consistent production. Additionally, mixing or upgrading of bio-oils may be difficult [72]. A proper analysis of bio-oil property behavior is essential given that the quality of the product would anchor on both chemical and physical properties. This helps to identify a suitable potential application of the bio-oil, as shown in Table 6 [5,24,25,29,31].

Table 6. Properties and common measurement methods of bio-oil [24,25,29,31].

Property	Unit	Analytical Method	Range of Values
Heating value	MJ/kg	Calorimetry (ASTM D 4809)	16.5–19
Moisture	Wt.%	ASTM E871	-
Water	Wt.%	Karl-Fisher (ASTM D 1744)	15–35
Volatile matter	Wt.%	EN15148-2009	-
Ash	Wt.%	DIN EN 7	0.01–0.2
Carbon	Wt.%	ASTM E 777	50–64
Hydrogen	Wt.%	ASTM E 777	5–7
Nitrogen	Wt.%	ASTM D 5291	0.05–0.4
Oxygen	Wt.%	EN 15296:2011	35–40
Sulfur	Wt.%	XRF (ASTM D 4294)	0–0.05
Density	kg/dm ³	Densimeter (ASTM D 4052)	1.10–1.30 (at 15 °C)
Copper corrosion test	-	ASTM D 130	1A–1B
Acidity	pH	E70	2–3

The physicochemical properties of bio-oils are influenced by the conditions associated with feedstock, production, and reactor type. Major challenges can include the increase of acidity, oxygen, and water, which affects the supplementary scale up of bio-oil usage, given that the miscibility with fossil fuels is to be obstructed, with decreased calorific value, etc. Additionally, the instability of bio-oil, attributed to polymerization, characterizes the bio-oils, and this phenomenon has been associated with either the phenols undergoing oxidative coupling or when some components failed to saturate [72]. The potential applications of bio-oil, as demonstrated by relevant literature, could be seen as an alternative candidate to fossil fuel [12,19,25,34,51,52]. The applications involving the areas of fuel, chemistry, power, and heat are summarized in Figure 5 [55].

8.2. Biochar

Biochar is a solid pyrolysis product that is commonly produced under low temperature, typically consisting of 0.5–5% ash, 50–90% fixed carbon, 1–15% moisture, and 0–40% volatiles solids. However, the mentioned proportions depend on the feedstock type and technological parameters of the process [74]. Typically, biochar pyrolysis is at a temperature between 200 and 900 °C [75]. Biochar can serve, for example, as energy fuel or soil amendment. The quantity and quality of biochar derived from the fast pyrolysis process depend on the reactor type, feedstock, and temperature of pyrolysis, which have a considerable effect on product composition/yield [76–80]. The release of gases, while it changes with different temperatures, would decrease in biochar yield with temperature increase. Temperature decrease would bring about a higher amount of biochar. However, the char heating rate would increase with temperature increase [32,34–36,81–84]. Normally, the separation of char is achieved by a cyclone, removing it from the vapor stream. The main component of biochar is carbon, but it contains a small amount of hydrogen and oxygen as well. Furthermore, it may contain high proportions of inorganics [32,34–36,81–84].

Figure 5. The potential applications of pyrolysis-based bio-oils adapted from [55] with modifications.

The biochar characteristics at different temperatures and selected feedstock types are presented in Table 7 [37–42]. The feedstock type, pyrolysis temperature, and production conditions have a role to play towards these (physicochemical) properties.

Table 7. Biochar characteristics at different temperatures and feedstock types [37–42].

Feedstock	Temperature, °C	Product Yield, %	Specific Surface Area, M ² /G	Ash Content, %	pH (-)	Volatile Solids, %	Carbon, %
Rice straw	300	50.1	-	25.4	9.3	48.4	72.5
Corn stover	300	66.2	3.2	5.7	7.7	54	45.5
Cottonseed hull	350	36.8	4.7	5.7	7.0	34.9	77.0
Oakwood	450	-	1.9	64.5	-	15.6	71.3
Corn cobs	500	18.9	0	13.3	7.8	-	77.6
Soybean stover	700	29.6	420.3	17.2	11.3	14.7	82.0
Vine pruning	350	64.6	8.1	8.3	10.3	30.2	64.7
Orange pomace	350	71.9	1.2	11.3	9.9	32.3	56.8
Fescue straw	100	99.9	1.8	6.9		69.6	48.6
Sugarcane bagasse	750	26.9	-	2.2	9.7	7.7	90.5

The potential application of the pyrolytic biochar may involve the following:

- Soil amendment and carbon sequestration;
- The use of biochar to generate heat energy because it contains a high heat value of about 23 MJ/kg;
- The use of biochar in hydrogen or syngas production, which could be useful due to thermal cracking or steam reforming;
- Application of biochar as a solid fuel [31,42,43].

8.3. Pyrolytic Gas

When fast pyrolysis involves biomass, the non-condensable gases mainly constitute CO₂, CO, C₂H₆, C₂H₄, H₂, CH₄, C₃H₈, and C₃H₆ [25]. Furthermore, the liquid collection unit must be highly effective to avoid the presence of some light volatiles in the gaseous stream, for example, acetaldehyde, benzene, pentane, toluene, and xylenes. The pyrolysis temperature impacts the composition and product yield of pyrolytic gas, and the relative gas changes with different temperatures. An increase in temperature correlates with a higher pyrolytic gas yield [10]. The pyrolysis gas could serve as a fuel because it has reasonable quantities of CO, alongside CH₄ and several other flammable gases. The most

suitable application for pyrolytic gas is its use as a carrier gas or fluidized gas. It may be utilized within plants providing cycle heat [83]. The operating temperature increases with the gas production yield, whereas bio-oil and biochar decrease [84].

8.4. Tar

Biomass is a significant essential fuel source and an environmentally-friendly power source. Pyrolysis delivers biochar, liquid fraction, and valuable fuel gases, but some by-products, such as fly ash, NO_x, SO₂, and tar, are associated with it. Generally, tar condenses at low temperatures and causes obstruction or blockage in fuel lines, piping, filters, engines, and other devices. Additionally, if tar is present in the pyrolytic gas, it may cause a reduction in biomass usage efficiency. Hence, the removal of tar from pyrolytic gases is crucial for its use as a fuel. The tar removal methods have been assessed in literature [85]. They can be categorized into five different groups based on their characteristics: catalyst cracking, mechanism methods, plasma methods, self-modification, and thermal cracking. Tar separation is of more concern in pyrolysis product quality assessments. The methods and effective reduction efficiencies of tar in pyrolysis processes are presented in Table 8 [85].

Table 8. Methods of tar reduction [85].

Methods	Tar Removal Efficiency, %
Fabric filters	0–50
Fixed bed adsorbers	50
Rotational particle separators	30–70
Sand bed filters	50–97
Venturi scrubbers	50–90

9. Impact of High Pressure on Emergent Products

The pressure level is crucial in fast pyrolysis, which influences production yield. Pressure influences the reduction of volatile yield at a range of 10–14 bars and affects the fluidity of the metaplast, swelling, and char morphology. The swelling problem rises with pressure up to 5–10 bar, and as such, the reduction occurs as the pressure increases [86]. The pressure increase can significantly impact some gas yields under the fast pyrolysis process. This reaction increases the products of CO₂ and methane, while propene and H₂ decrease, but have fewer impacts on the CO yield because it is constant [87].

An experiment carried out at a range between 0 and 5 bars indicated that pressure had a significant impact on the quality and characteristics of the product. Pressure improves both dehydrogenation and deoxygenation reactions of bio-oil, resulting in increases of CH₄, H₂, and CO₂ in the gas. Despite the unrestored combustible features of biochar, high pressure increases the biochar surface compactness and structure [88].

10. Catalyst Types and Their Application

The catalyst's low cost with high effectiveness under the fast pyrolysis process needs to be seen as an economically sustainable strategy, able to effectively compete within the existing energy market. Areas of interest in this subject area include foundation catalysts, such as MgO. Another that is considered attractive and emerging is calcium-based materials, which some consider to be relatively economical catalysts, able to deliver catalytic pyrolysis. The fast catalytic pyrolysis could also involve the commercial lignocellulosic biomass, which, at a specific scale, would be performed by the CFBR facility. The latter is understood to involve both MgO catalysts and commercial zeolites. Ketonization and aldol condensation reactions would, therefore, be promoted by the foundation sites of MgO, which would bring about sufficient hydrogen bio-oil [89].

10.1. Classification of Deoxygenation Catalysts

Catalytic cracking is another way of upgrading the bio-oil production, aiming for low oxygen content by solid acid catalysts, for instance, zeolites at an ambient pressure where

hydrogen is not required. Although the process would bring forth low-grade products, which include benzene and toluene, as well as small chain alkanes, it is very important to undergo further refining. Generally, the catalytic cracking process usually produces a low carbon yield due to its high formation of coke that leads to a reduced short lifetime of the catalyst [90,91].

The application of hydro-treating is very effective in the fast pyrolysis, in which the production of bio-oil would be the main target intending to achieve good product quality. It is a hydrogenation process to eliminate contaminating molecules from the product in the range of 90%, such as nitrogen, sulfur, oxygen, and metals from bio-oil products to improve the qualities. This process is very widely used as the quality of the product is of very high grade [85,86,91].

10.2. Catalysts' Influence on the Products of Pyrolysis

Catalyst processing is a high potential upgrading processes used in the fast pyrolysis reaction of biomass to increase the product quality/yield [89]. However, to scale up the catalytic process, careful development of the catalyst is needed. Good knowledge of process design must be employed if a premature deactivation of the catalyst is to be avoided. In the context of the fast pyrolysis reaction of biomass, the catalyst upgrading process considers two different routes when bio-oil is among the main target products during bio-oil pyrolysis vapor upgrading [25].

11. Concluding Remarks and Prospects

Over the last decade, advances in fast pyrolysis (particularly of bio-oil and biochar) and pyrolytic gas production have gained increased research attention. This is largely because fast pyrolysis processes have been providing appropriate pathways to transform low-value biomass residues into value-added energy-based products. However, the challenges of pyrolysis on a technical scale include the requirement to obtain high product quality and yield, such as rapid heat transport from the source onto the particles of biomass to completely pyrolyze. Most of the pyrolysis reactors require very small sizes of biomass particles to achieve good quality products, which could be considered as another challenge.

This review has reflected on the high-pressure fast pyrolysis as a novel solution to challenges related to heat transfer, as well as product quantity and quality. The authors have attempted to demonstrate that high-pressure fast pyrolysis can bring about high-quality biomass conversion into new products. It has been shown that fluidized beds (bubbling and circulating) are more suitable and profitable among others in terms of product yield because those mentioned types could produce improved bio-oil quality and quantity. In recent years, the pyrolysis technologies of biomass conversion to energy production have gained more attention and are increasingly attaining advances, given their production environment considerations specific to emission and waste management. Therefore, and from an economic point of view, there is a need for future research to focus more on optimization processes. Moreover, it is important to mention that high-pressure pyrolytic reactors for biomass conversion into bio-oil and biochar, together with pyrolytic gas, presents several benefits, such as better product quality, lower operating costs, higher liquid product yield, increased reaction rates, and decreases in the required heat of reaction. High pressure, especially combined with a fast-heating rate, is more efficient and beneficial than working under ambient pressure.

The challenges of pyrolysis on a technical scale have been associated with obtaining high product quality and yield. Of greater concern is the rapid heat transport from the heating source to the feedstock to pyrolyze completely. A scale up of the pyrolytic reactors specific to high-pressure processes to achieve good quality products continues to be a great concern. The increase of process pressure and biomass particle size decrease should be considered as variables to be optimized. This suggests that there is a need for future studies to investigate the designs of high-pressure process reactors and material types that might have greater biomass promise such that there could be a way to achieve an improved

quality product. Future studies should also seek to understand the impact of pyrolysis technology on the various output products, which are bio-oil, biochar, and syngas, having lower energy demands.

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Abbreviations

Rotating cone reactor (RCR), fluidized bed reactor (FBR), entrained flow reactor (EFR), circulating fluid-bed reactor (CFBR), ablative reactor (AbR), and auger reactor (AuR)

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