

Review

An Overview of Recent Developments in Biomass Pyrolysis Technologies

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Abstract: Biomass is a promising sustainable and renewable energy source, due to its high diversity of sources, and as it is profusely obtainable everywhere in the world. It is the third most important fuel source used to generate electricity and for thermal applications, as 50% of the global population depends on biomass. The increase in availability and technological developments of recent years allow the use of biomass as a renewable energy source with low levels of emissions and environmental impacts. Biomass energy can be in the forms of biogas, bio-liquid, and bio-solid fuels. It can be used to replace fossil fuels in the power and transportation sectors. This paper critically reviews the facts and prospects of biomass, the pyrolysis process to obtain bio-oil, the impact of different pyrolysis technology (for example, temperature and speed of pyrolysis process), and the impact of various reactors. The paper also discusses different pyrolysis products, their yields, and factors affecting biomass products, including the present status of the pyrolysis process and future challenges. This study concluded that the characteristics of pyrolysis products depend on the biomass used, and what the pyrolysis product, such as bio-oil, can contribute to the local economy. Finally, more research, along with government subsidies and technology transfer, is needed to tackle the future challenges of the development of pyrolysis technology.

Keywords: renewable energy; biofuel; environment; technology development

1. Introduction

Nowadays, energy usage is prodigious, and a significant key factor for the advancement of a nation, and the scarcity of energy has become an economic threat for the development of nations around the world [1,2]. It is said that “Energy is a critical component of our lives. Without energy, we can’t even dream of economic growth. But despite its central role, not everyone has access to modern energy services” [3,4]. Today’s energy requirement is increasing in trend, due to population

growth and ongoing economic and technological advancement around the world [4]. Currently, fossil fuels are the main source of energy because of their high calorific values, good anti-knocking properties, and high heating values; meanwhile, reserves are limited. Therefore, the development of alternative energy resources can lower the depletion of fossil fuel by reducing their consumption [5–7]. On the other hand, the world's heating condition is increasing every day. The atmospheric CO₂ level has crossed the risky level that was forecast to happen in another 10 years [8]. Furthermore, the depletion of fossil fuels and extreme change of climate have driven the search for alternative energies and renewable energy sources that can meet the world's energy demand, reduce greenhouse gas emissions, curb pollution, and maintain the planet's temperature at a stable level [9–11].

Among the alternative energy sources, biomass can become a promising sustainable energy source, due to its high diversity and availability [12]. Biomass can be defined as all biodegradable organic material derived from animals, plants, or microorganisms. This definition also includes products, by-products, waste originating in agricultural activities, as well as non-fossil organic waste produced by industrial and municipal waste [13]. Biomass is the third most important source used to generate electricity and thermal applications [14,15]. The most common biomass feedstocks are banana peel, rice and coffee husks, sugarcane bagasse, palm oil processing residues, and the waste of animals [16,17]. Biomass can be considered as a blend of organic resources and minor amounts of minerals, which also contains carbon, oxygen, hydrogen, nitrogen, sulphur, and chlorine [18].

Different types of energy can be produced through the thermal conversion of biomass, such as combustion, pyrolysis, gasification, fermentation, and anaerobic decomposition. Combustion is a thermochemical process used for the production of heat, which consists of a chemical reaction in which a fuel is oxidised, and a large amount of energy is released in the form of heat (exothermic reaction). Pyrolysis is a thermal decomposition process which takes place in the absence of oxygen [19,20]. In combustion and gasification processes, the first step is pyrolysis, followed by total or partial oxidation of primary products. Gasification is the process of generating electricity by applying heat to organic material in the presence of less oxygen. In the fermentation process, organic materials are used to produce alcohol, with the help of yeast, to generate power in automobiles. Anaerobic decomposition is the process of producing biogas, and generates electricity.

Among all the conversion techniques of biomass conversion, the pyrolysis process offers a number of benefits, including less emissions and that all the by-products can be reused. In addition, during the process, pyrolysis produces solid or carbonised products, liquid products (bio-oils, tars, and water) and a gas mixture composed mainly of CO₂, CO, H₂, and CH₄ [21–23]. The oil resulting from the pyrolysis of biomass, usually referred to as bio-oil, is a renewable liquid fuel, which is the main advantage over petroleum products. It can be used for the production of various chemical substances [24]. The pyrolysis process has three stages: the dosing and feeding of the raw material, the transformation of the organic mass and, finally, the obtaining and separation of the products (coke, bio-oil, and gas). The factors that influence the distribution of the products are the heating rate, final temperature, composition of the raw material, and pressure [25].

The pyrolysis process has great market potential; in this process, biomass is used as raw material in order to produce energy. Therefore, intense research is taking place around the world to improve this method of energy production. Among the technologies, such as digestion, fermentation, and mechanical conversion, thermo-conversion for producing energy from biomass is relatively newer from a commercial perspective, and gaining more attention because of its technical and strategical advantages. In addition, the production of waste is constantly increasing, and the economic activity linked to it is becoming increasingly important. The elimination or attenuation of environmental problems and obtaining profitability in the process of managing them is a very favourable step. Therefore, pyrolysis could be an alternative means of energy recovery, obtaining different fractions that are also recoverable not only from the energy point of view.

Though the research into pyrolysis technology indicated that pyrolysis is a more promising option to the sustainable development, pyrolysis technology still needs further improvement, and several

challenges need to be tackled to gain its full potential benefits. Furthermore, several types of research have been carried out recently, focusing on the use of pyrolysis technology, but only a few papers have been analysed and reviewed by the researchers. Thus, the main aims of this study are to present a brief review of the development of pyrolysis technology, including their present status and future challenges, to provide information to the researchers who are interested in pyrolysis technology. A number of studies from highly rated journals in scientific indexes are reviewed, including the most recent publications.

2. Biomass Pyrolysis

Biomass is a renewable source for the production of energy, and it is profusely obtainable everywhere in the world [26,27]. The sustainable use of biomass energy is an alternative to partially replace the use of fossil fuels and nuclear energy. Rural people in developing countries, representing about 50% of the global population, depend on biomass energy [9]. Biomass assists the world in meeting greenhouse gas reduction goals [9,28,29]. The increase in availability and technological developments of recent years allow the use of biomass as a renewable energy source with low levels of emissions and environmental impacts. Biomass energy can be in the forms of biogas, bio-liquid, and bio-solid fuels. It can be used to replace fossil fuels in power and transportation. It is considered as a renewable energy source because the energy mainly comes from the sun and, also, it needs a short time period to re-grow.

Pyrolysis process is mainly characterised by solid fuel thermal degradation, which involves the rupture of carbon–carbon bonds and the formation of carbon–oxygen bonds. Pyrolysis requires temperatures of up to 400–550 °C, although it can be done at temperatures even higher [30–33]. Figure 1 shows the percentage yield during the pyrolysis of biomass.

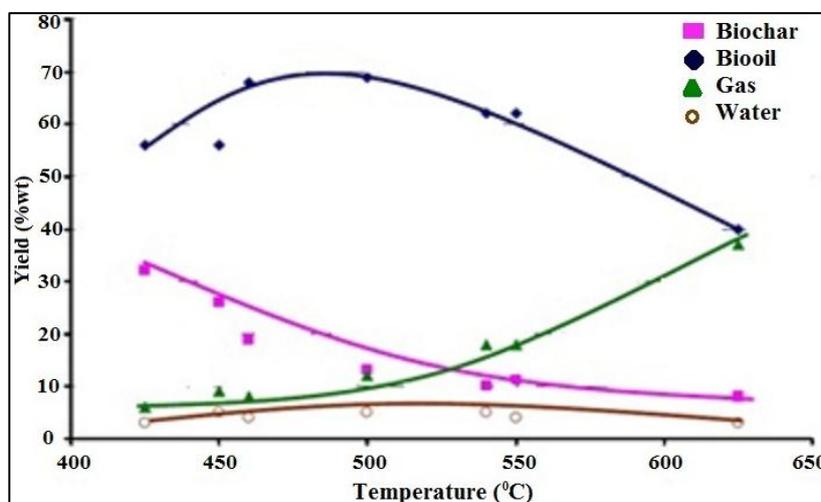


Figure 1. The % yield of the end products the pyrolysis of biomass [9].

One part of the biomass is reduced to carbon, while the remaining part is oxidised and hydrolysed to carbohydrates, phenols, aldehydes, ketones, alcohols, and carboxylic acids, which combine to form more complex molecules such as esters, polymer products, and others [34–36]. Pyrolysis can be achieved by the complete absence of the oxidising agent. The practice of using air to perform pyrolysis is achieved by feeding air in an amount below stoichiometric; combustion occurs in only a small part of the biomass and, thus, the heat released in the combustion is used to keep the temperature of the reactor constant, while processing the reactions related to pyrolysis [37].

The products formed during pyrolysis, namely, coal fines, gases, acid extract, and bio-oil, have high calorific value, and have had several applications in both the chemical and power generation industries. In ancient Egyptian times, the pyrolysis process was used to generate tar for sealing

boats [16], and the ancient Egyptians performed wood decontamination by assembling tars and pyrolignous acid for use in their mummifying industry [38,39]. Pyrolysis has gained more attention as an effective and practical method in converting biomass into bio-fuel recent years [40]. Pyrolysis is not only part of the combustion and gasification processes, but it is also the first stage of both of these processes. The gas is composed of carbon monoxide, carbon dioxide, and light hydrocarbons. This dark-coloured liquid is called bio-oil and charcoal solid. The yields and quality of the products are influenced by the operating conditions. Pyrolysis receives different denominations depending on the conditions used. In slow pyrolysis or carbonisation, low temperatures and long residence times are employed, favouring the production of charcoal. High temperatures and long residence times favour the formation of gases. Whereas moderate temperatures and low residence time of the gases favour the production of liquids (bio-oil). Figure 2 shows the chemical reaction during the pyrolysis process.

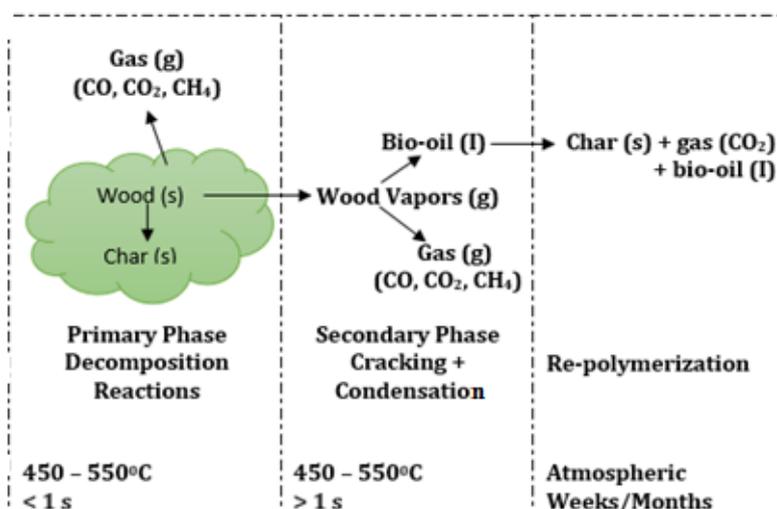


Figure 2. Representation of the reaction paths for wood pyrolysis [41].

3. Mechanism of Pyrolysis Process

The biomass pyrolysis can be divided into two categories, such as primary and secondary mechanisms [41]. Figure 3 shows the detailed mechanism of the pyrolysis process. In the primary mechanism, volatile compounds are released, while the chemical bonds within the polymers are broken during biomass heating process [42,43]. Furthermore, rearrangement reactions within the matrix of the residue take place. Some of the volatile compounds which are unstable further undergo additional reactions, which are defined as a secondary mechanism.

The primary mechanism can be described using three different approaches, namely char formation, depolymerisation, and fragmentation. In the char formation process, initially, benzene rings are formed, and these rings combine into a solid residue known as char, which is an aromatic polycyclic structure [44]. During this process, water or incondensable gas is also released [45,46]. In the depolymerisation process, the polymers are broken into monomer units, which reduce the degree of polymerisation. This process continues until the volatile molecules are produced [47]. Finally, in fragmentation, incondensable gas and small chain organic compounds are formed through the linkage of many covalent bonds of the polymer, even within the monomer units [42].

The secondary mechanism consists of cracking, recombination, and others [42,48]. In cracking, lower molecular weight molecules are formed by breaking volatile compounds [49]. By contrast, in the recombination process, volatile compounds combine into high molecular weight compounds, which may or may not be volatile [43,50]. In some cases, a secondary mechanism leads to the formation of secondary char [48,51].

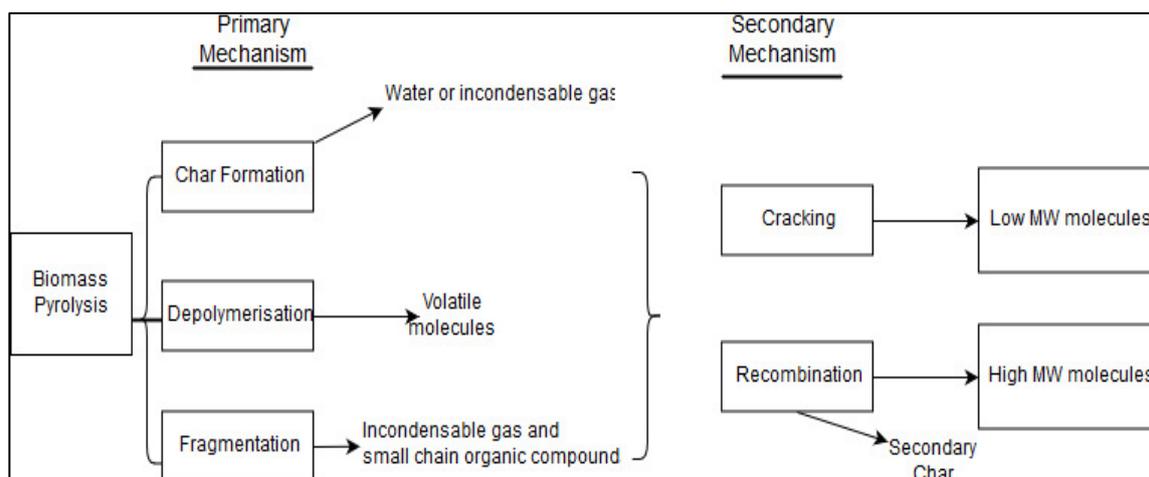


Figure 3. The detailed mechanism of the pyrolysis process.

4. Sources of Biomass and Their Properties

Biomass energy is currently recognised as the third largest global energy source. In many developing countries which have significantly large forest and agricultural land, 40–50% of energy usage is based on biomass. Green plants can directly/indirectly produce biomass using the photosynthesis process, by transforming sunlight into plant material [29,52]. The resources of biomass include various natural and derived materials, such as agricultural crops and residues, forest wood and leaf residues, municipal solid wastes (MSW), forest and mill residues, animal residues, and sewage. Agricultural crops and wastage (sugarcane, cassava, and corn) provide carbohydrate and starch. Roughly, the biomass species contain woody biomass, straw, beech wood, seedcakes, bagasse, and municipal solid waste (MSW) [53–59]. The available sources of biomass are shown in Figure 4.

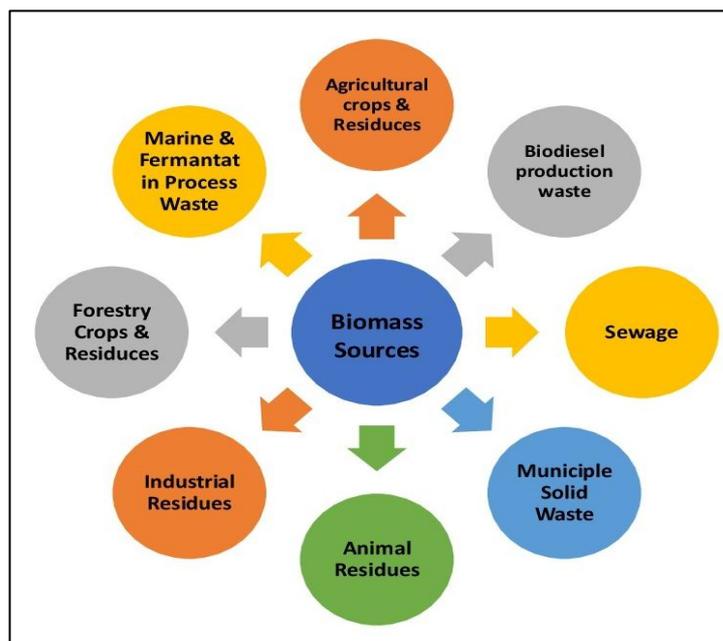
Biomass is a very versatile feedstock in its morphology and physical characteristics. It can be quite wet or dry dense or fluffy, high or low ash containing, small in shape or large, homogeneous or inhomogeneous, and so on. This makes the use of biomass fuels in dedicated gasifier reactors quite difficult and, in most cases, some pre-treatment of the biomass is needed. The feedstocks used for pyrolysis and their physical and chemical properties are more important. The highest bio-char yields are achieved when feedstocks with high lignin content are pyrolysed at moderate temperatures (approx. 500 °C). Furthermore, some other indicators of pyrolysis product yields are the ratios of fixed carbon, moisture, volatile matter, and ash content. Generally, biomass containing significant volatile matter offers a large amount of syngas and bio-oil, while fixed carbon raises the production of biochar. Moisture content in biomass influences the heat transfer process, as well as significantly affects product distribution. Tables 1 and 2 show the physical and chemical properties of biomass. Biomass consists of elements such as carbon, hydrogen, oxygen, and nitrogen. Sulphur is present in smaller proportions, and some types of biomass also contain significant portions in inorganic species. The chemicals obtained from co-products and residues can improve the biomass production chains, due to the strategic participation of the chemical industry in the supply of inputs and final products to various economic sectors, for example, agribusiness, petrochemical, automotive, pharmaceutical, cosmetics, civil construction, and so on [60].

Table 1. Physical characteristics of biomass [9].

Feedstock	Density (kg/m ³)	Moisture Content (%)	Ash Content (%)	Volatile Matter (%)	Fixed Carbon (%)
Wood	380	20	0.4–1	82	17
Bituminous coal	700	11	8–11	35	45
Wheat straw	18	16	4	59	21
Barley straw	210	30	6	46	18
Pine	124	17	0.03	-	16
Polar	120	16.8	0.007	-	-
Switchgrass	108	13–15	4.5–5.8	-	-

Table 2. Chemical characteristics of biomass [9].

Feedstock	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)	Ash (%)
Wood	51.6	6.3	41.5	0.1	1
Bituminous coal	73.1	5.5	8.7	1.4	9
Wheat straw	48.5	5.5	3.9	0.3	4
Barley straw	45.7	6.1	38.3	0.4	6
Pine	45.7	7	47	0.1	0.03
Polar	48.1	5.30	46.10	0.14	0.007
Switchgrass	44.77	5.79	49.13	0.31	4.30

**Figure 4.** Available sources of biomass [61].

5. Pyrolysis Technology

Pyrolysis technology is the decomposition of heated organic matter in the absence of atmospheric oxygen, where heating is controlled by temperature ranges and provides the energy needed to break down the structures of the macromolecules present in biomass [62]. In the process of pyrolysis, biomass degradation occurs through heating, in which the formation of three products occurs: coal, oil, and pyrolytic gas, and, depending on the conditions in the reactor, one of these products can be maximised [63,64]. Currently, there are basically three pyrolysis processes in the world: slow pyrolysis, fast pyrolysis, and ultrafast pyrolysis. Biomass is first put into the reactor feed system, usually an endless screw. Then, the biomass enters the reactor and undergoes thermal degradation. Any gas that

does not condense and has no energetic ends returns to the process and is used as entrainment gas in the reactor.

5.1. Slow Pyrolysis

Slow or conventional pyrolysis consists of systems known as “charcoal” or continuous systems, with slow biomass heating above 400 °C in the absence of oxygen [65]. In this process, the biomass is pyrolysed with low heating rates, around 5 to 7 °C/minimum, where the liquid and gaseous products are minimal, and the coal production is maximised [66,67]. Slow pyrolysis of wood, with a 24 h endurance, was a very common technology in industries until the early 1900s, where coal, acetic acid, methanol, and ethanol were obtained from wood [68,69]. Slow pyrolysis is characterised by small heating rates and a maximum temperature range of around 600 °C, and the biomass time in the reactor is between 5 and 30 min. The main products are bio-oil, coal, and gases [68].

5.2. Rapid Pyrolysis

Rapid pyrolysis is a promising method for conversion of biomass into a liquid product. The produced pyrolysis oil (bio-oil) is an intermediate dense energy fuel, which is possible to upgrade to hydrocarbons in diesel and gasoline [70]. In rapid pyrolysis, the biomass decomposes very quickly, generating mainly vapours and aerosols, and a small amount of coal and gas. After cooling and condensation, a homogeneous mobile dark brown liquid is formed, which has a calorific value corresponding to half of the conventional fuel oil [71]. Rapid pyrolysis technology is used globally, in large scale, for the production of liquids (bio-oils), and there is a lot of interest regarding this technology among biofuel researchers. Several reactors are used in the rapid pyrolysis process. Among them are the dragged-flow reactor, vacuum furnace reactor, vortex reactor, rotary reactor, bubbling fluidised bed reactor, and others; many researchers have contributed in the field of pyrolysis using one of these reactors [67].

5.3. Ultrafast Pyrolysis

The ultrafast pyrolysis has, as its main characteristics, very high heating rates and very low residence time of the biomass in the reactor. These characteristics favour the production of vapours, and make the process very similar to gasification. Due to the high heating rate, where biomass residence times are only a few seconds, reactors are needed to meet these heating needs [67]. These reactors have a fluidised bed and are flow-dragged. The fluidised bed reactor is used in the execution of multiphase chemical reactions, where a catalyst, usually sand, is used, working the same as with a fluid inside [72,73]. According to Laird et al. [65], ultrafast pyrolysis for coal production involves heating the biomass, under moderate to high pressure, in a reactor. In this particular case, the coal yield reaches 60%, and is volatile (bio-oil and synthesis gas) to 40%; this technology is more likely to use heat recovery equipment. Table 3, below, demonstrates some operating parameters of the three types of pyrolysis process [72,73].

Table 3. Operating parameters of different pyrolysis processes.

Process	Time (s)	Rate (K/s)	Size (mm)	Temp. (K)	Oil Yield	Char Yield	Gas Yield
Slow	450–550	0.1–1	5–50	550–950	30	35	35
Fast	0.5–10	10–200	<1	850–1250	50	20	30
Flash	<0.5	>1000	<0.2	1050–1300	75	12	13

5.4. Flash Pyrolysis

This process is also known as fast pyrolysis, due to the high speed of the process. However, in this process, not only kinetics play an important role, but heat and mass transfer processes, such as phase

change phenomena, are also important. In this process, the biomass decomposes to generate mainly vapours, aerosols, and a certain amount of coke. After cooling and condensation, a dark brown liquid (bio-oil) is formed, with a calorific value that is half the value corresponding to that of diesel. Unlike traditional processes, this is an advanced process with carefully controlled parameters to obtain high liquid yields [74]. In order to carry out this process, the following must be observed: (a) subjecting the biomass particles to an optimum temperature so that they react, and (b) minimising their exposure to low intermediate temperatures that stimulate coke formation. One method to achieve these objectives is to use small particles, for example, those that are present in fluidised bed processes (a fluidised bed is a packed bed with a fine-grained solid). Another possibility is to transfer heat quickly, only to the surface of the particles that are in contact with the heat source, which is applied in ablation processes [75,76].

6. The Products of Pyrolysis Process

The pyrolysis of biomass produces three primary products, namely char, permanent gases, and vapours which condense to a viscous liquid (dark brown in colour) at ambient temperature. Biomass pyrolysis product yields can be improved as follows: (1) charcoal—less temperature and lower heating rate procedure, (2) liquid products—lower temperature but higher heating rate procedure, and (3) fuel gas—higher temperature and lower heating rate procedure. Table 4 shows the pyrolysis processes at different temperatures.

Table 4. Pyrolysis processes at different temperature.

Condition	Processes	Products
<350 °C	Free radical formation, water elimination, and depolymerisation	Formation of carbonyl and carboxyl, the evolution of CO and CO ₂ , and mainly a charred residue
350–450 °C	The split of glycosidic connections of polysaccharide by substitution	A combination of levoglucosan, anhydrides, and oligosaccharides as a tar segment
450–500 °C	Dehydration, rearrangement, and fission of sugar units	Formation of carbonyl compounds
>500 °C	A combination of all the above processes	A combination of all the above products
Condensation	Unsaturated products shrink and split to the char	A highly reactive char remainder comprising trapped free radicals

6.1. Bio-Oil

Bio-oil, also known as pyrolysis oil, crude bio-oil, pyrolytic tar, pyrolignous tar, pyrolignous liquor, wood liquid, wood oil, smoke condensate, and distilled from wood, is a dark brown-coloured liquid, almost black, with a characteristic odour of smoke, and an elemental composition similar to the biomass. It is a complex mixture, containing oxygenated compounds and a high volume of water, which originates from the moisture of the biomass and the reactions. It might also contain some amount of coal particles and dissolved alkali metals from the ash. The composition of the total mixture depends on the type of biomass, process conditions, equipment, and the efficiency in the separation of the coal and the condensation.

The bio-oil can be considered as a micro emulsion, in which the continuous phase is an aqueous solution of the products of cellulose and hemicellulose fragmentation which stabilises the discontinuous phase of the pyrolytic lignin macromolecules [71]. There is a very current and praising demand to convert biomass into liquid fuels in order to use in ships, trains, and aeroplanes, to substitute petrol and diesel [77,78].

Bio-oil is the main product from the pyrolysis process. Several types of research around the world, in order to maximise and improve the quantity and quality of bio-oil produced, are currently

being carried out. Reactor designs are the primary target of researchers to achieve a better-quality bio-oil. As shown in Figure 5, the bio-oil product has a number of applications: it can be improved to be used as a transport fuel or used as a chemical, and it can also be used in turbines and electric power generation engines, or in boilers to generate heat. In summary, the bio-oil product has many applications and deserves large investments in research.

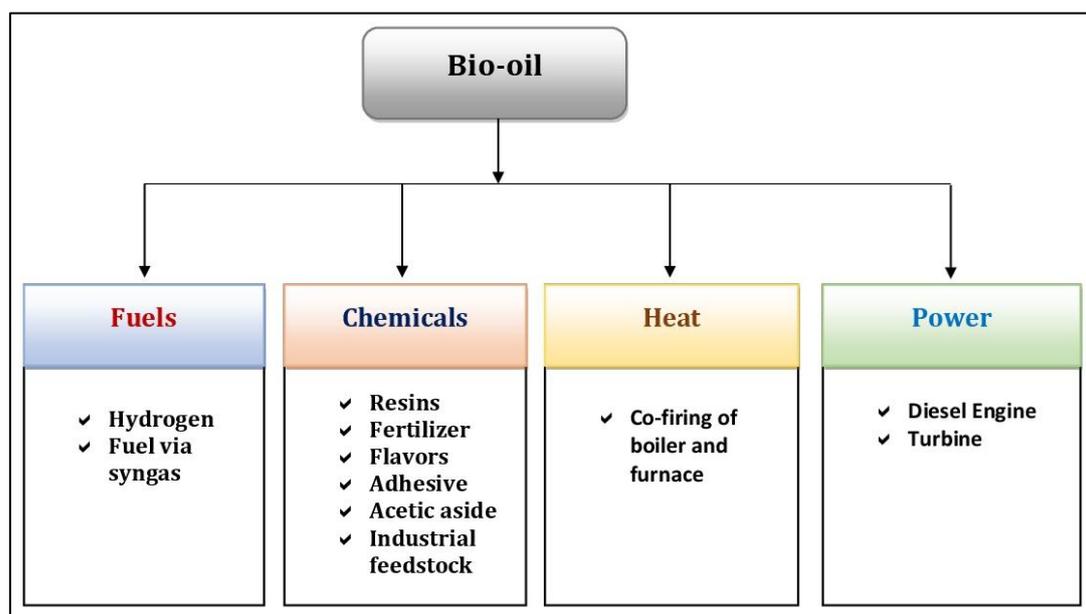


Figure 5. Various applications of pyrolysis bio-oil [77,78].

6.2. Biochar

The production of biochar is an emerging technology which can improve countries' food security and mitigate climate change [79]. In the literature, the potential benefits of applying biochar as soil enrichment have been highlighted heavily, addressing issues such as waste management, bioenergy production, increased soil fertility through alteration of soil pH, retention of nutrients through cation adsorption, reduction of emissions of nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2), adsorption of organic pollutants, and improvements in productivity [80]. As a promising modifier to soil, biochar attracts the attention of policymakers in developed countries, such as the United States, Japan, Europe, and some developing countries. Sustainable biochar is one of the few technologies that is relatively cheap, widely applicable, and rapidly scalable. These benefits are confirmed by many investigations [79,81,82], including:

- Reduced nitrogen leaching in groundwater
- Possible reduced emissions of nitrous oxide
- Increased cation exchange capacity resulting in better soil fertility
- Moderation of soil acidity
- Greater water retention
- Increase in the number of beneficial soil microbes

6.3. Syngas

In slow pyrolysis processes, around 10–35% of biogas is produced which is similar to char. Syngas produced from biomass pyrolysis can be used as an alternative renewable source of fuel for industrial combustion processes, as well as for internal combustion (IC) engines. In power generation, transportation, and other sectors, gaseous fuel can be used in converted commercial petrol and diesel engines [83], which was quite common between 1901 and 1920 and, after that, due to the availability of

cheap liquid fuels, the usage of gaseous fuels in IC engines. However, in recent years, as the focus has moved towards renewable fuels for engines, the use of syngas in IC engines has, once again, gained interest [84].

Syngas yield is highly influenced by the pyrolysis temperature, and it is possible to achieve a higher yield in flash pyrolysis with high temperatures. He et al. [85] investigated syngas production in a bench-scale downstream fixed-bed reactor from pyrolysis of MSW over a temperature range of 750–900 °C [86]. The researchers used calcined dolomite as a catalyst, and reported a 78.87% gas yield at 900 °C. In another study, Tang and Huang reported 76.64% syngas yield in a radio frequency plasma pyrolysis reactor [87].

Another factor that greatly influences pyrolysis processes and the resulting product distribution is the reactor temperature. With the increase of pyrolysis temperature, the inner moisture of the biomass evaporates first, followed by thermal degradation and devolatilisation of the dried particle portion. Simultaneously, tar is produced, and volatile species are slowly released from the particles' surface, which then undergoes a series of secondary reactions, such as decarboxylation, dehydrogenation, deoxygenation, and cracking, to form components of syngas. Thus, higher temperatures favour tar decomposition and the thermal cracking of tar to increase the proportion of syngas, which reduces oil and char yields [85]. Some researchers have also reported that when the reactor temperature is increased, the syngas flow rate also increases; however, this lasts for a short time, and then dramatically reduces [88].

Syngas mainly consists of hydrogen (H_2) and carbon monoxide (CO). It may also contain a small volume of nitrogen (N_2), water, carbon dioxide (CO_2), hydrocarbons such as C_2H_4 , CH_4 , C_2H_6 , ash, tar, and so on, which depend on biomass feedstock and pyrolysis conditions [89]. These components are obtained during several endothermic reactions at high pyrolysis temperatures.

7. Reactors Employed in the Pyrolysis Process

The heart of the pyrolysis process is the reactor. This is the place where all reactions occur [90–93]. However, to perform flash pyrolysis, it is necessary to have special reactors. For this process, an oxygen-free atmosphere is required in the reactor, and a temperature range between 475 and 550 °C. When the gas flows through the bed, the solid behaves like a liquid [94,95].

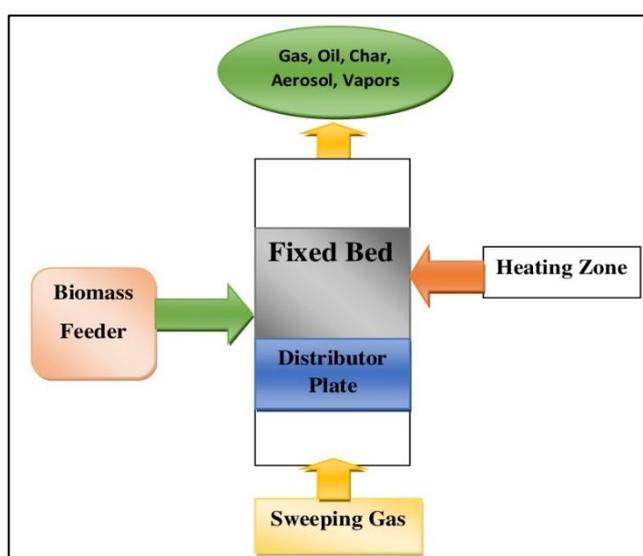
The reactor is at the core of any sort of pyrolysis procedure that has been the content of invention, significant research, and advancement, to expand the indispensable physiognomies [96–98]. In the beginning, the developers of the pyrolysis reactor presumed that a minor biomass particle size and very short residence time could obtain prominent bio-oil yields, but further research has found divergent consequences. Component part size and vapour residence time have a slight impact on bio-oil yield, while the parameters significantly trace bio-oil composition [99,100]. The pyrolytic reactor is undoubtedly the most important equipment in the pyrolysis process. Currently, several types of reactors have been designed, most with the aim of maximising the main product of pyrolysis, the bio-oil. There are many pyrolytic reactors used lately, the main ones being those of fluidised bed (bubbling and circulating). Besides these, we also find the fixed bed, jet bed, rotary cylinder, cyclonic reactor, rotary cone, and others. The reactors can be classified into two general systems, either a batch system or a continuous system (continuous flow of biomass occurs, and continuous collection of the products generated). Table 5 shows the comparison of different pyrolysis reactors. The summary of previous research using different reactors and outcomes is listed in Table 6.

Table 5. Comparison of various biomass pyrolysis reactors based on overall performance and efficiency [96].

Pyrolyser	Status (units)	Bio-Oil Yield (wt %)	Operational Complexity	Particle Size	Biomass Variability	Scale-Up	The Inert Gas Flow Rate
Fixed bed	Pilot (single), lab (multiple)	75	Medium	Large	High	Hard	Low
Fluidised bed	Demo (multiple), lab (multiple)	75	Medium	Small	Low	Easy	High
Recirculating bed	Pilot (multiple), lab (multiple)	75	High	Medium	Low	Hard	High
Rotating cone	Demo (single)	70	Medium	Medium	High	Medium	Low
Ablative	Pilot (single), lab (multiple)	75	High	Large	High	Hard	Low
Screw/auger reactor	Pilot (multiple), lab (multiple)	70	Low	Medium	High	Easy	Low
Vacuum	Pilot (single), lab (few)	60	High	Large	Medium	Hard	Low

7.1. Fixed Bed Reactor

The fixed bed pyrolysis system is simple, reliable, and proven for fuels that are relatively uniform in size and have a low content of coal fines which consist of a reactor with a gas cooling and cleaning system, and it was customarily used to produce charcoal [101,102]. The fixed bed reactors generally function with high carbon preservation, low gas velocity, and low residue conveyed over a long solid residence time. A major problem of fixed bed reactors is the formation of tar, although the recent evolution in thermal and catalytic conversion of tar has given feasible opportunities for confiscating tar [103,104]. Figure 6 shows the fixed bed reactor, which is considered simple, and includes the following basic units: drying, granulation, heating, and cooling. In the fixed bed pyrolysis process, the “temperature” ensures that the variables, such as temperature program, heating rates, and residence time in the temperatures, remain within the limits established by the operator and final pyrolysis temperatures between 450 and 750 °C, with heating rates fluctuating between 5 and 100 °C min/min [105].

**Figure 6.** Fixed bed reactor.

7.2. Fluidised Bed Reactor

The fluidised bed reactors (bubbling and circulating) have a well-known technology, and they have a series of industrial applications, where they present themselves as advantageous on a commercial scale, unlike other technologies that are still in the process of improvement [106]. There are several reactors that employ the principle of the fluidised bed, among them, the vortex reactor and the abrasive reactor [105]. Fluidised bed reactors are used in many projects to maximise the liquid product (bio-oil) produced, and several projects demonstrate their real ability to produce good quality bio-oil. As biomass has a very low density, it is common in fluidised bed reactors to use an inert element, usually sand, to give fluid dynamic stability to the process and help biomass heating [107].

The fluidised bed reactor comprises a fluid–solid blend that shows similar properties to the fluid [108]. Fluidised bed reactors seem to be widespread and popular because they offer rapid reaction and heat transfer, a wide and high shallow area of contact between the fluid and solid, and high comparative velocity [108,109]. Different types of fluidised bed reactors are available include bubbling fluidised bed reactors and circulating fluidised bed reactors.

7.2.1. Bubbling Fluidised Beds

Bubbling fluidised bed gasifier is categorised as having high reaction rates, well-understood technology, simple construction and operation, virtuous temperature control, efficient heat transfer to biomass particles, and it has superior lenience to particle size range [110,111]. It is very prevalent, since it generates high quality bio-oil from a dry source. A significant feature of bubble fluidising bed reactors is they require small biomass particle sizes to attain high biomass heating rates [112].

7.2.2. Circulating Fluidised Bed (CFB) Reactors

CFB reactors are comparable with bubbling fluidised bed reactors, and this type of reactor is suitable for large quantities [113]. There are two types of CFB reactors: single circulating and double circulating. The CFB gasifier is considered by all features of the bubbling fluidised bed reactors, along with a higher charge at a lower volume. The CFB pyrolyser is notable for a decent temperature regulator in the reactor [114,115]. Figure 7 shows the circulating fluidised bed reactor.

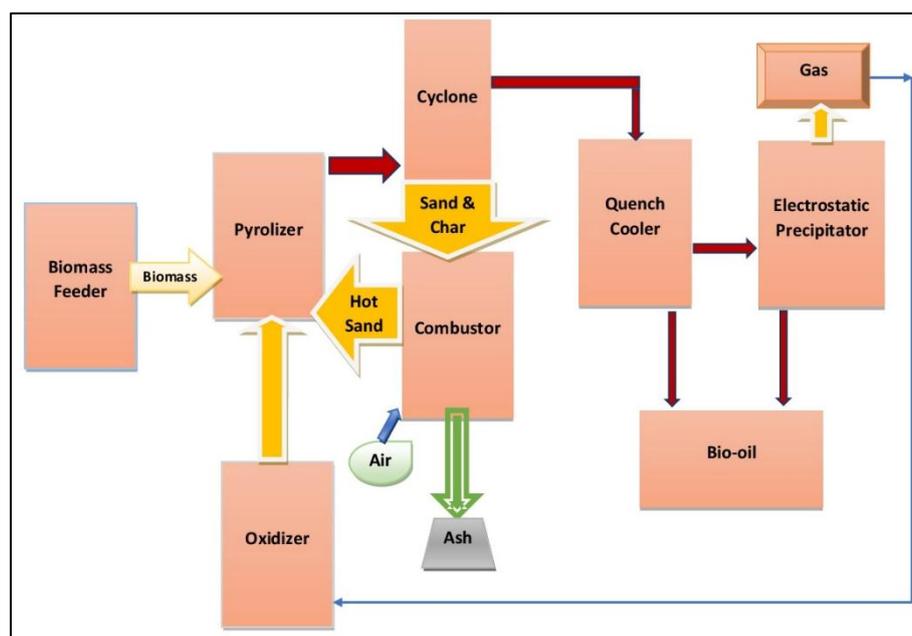


Figure 7. Circulating fluid bed reactor.

7.3. Ablative Reactor

Ablative pyrolysis is primarily dissimilar from fluid bed procedures in the absence of a fluidising gas. Material connected to the wall fundamentally melts, and the residual oil evaporates as pyrolysis vapours. The ablative pyrolysis reactors have good heat transfer with high heating rates and a relatively small contact surface. They also have high energy and cost efficiency, as no heating and cooling of fluidising gases is required, furthermore, they tolerate fixing of condensation units with a small volume in requiring less space at lower costs [116–118].

7.4. Vacuum Pyrolysis Reactor

Vacuum reactors represent a sluggish pyrolysis process with lower heat transfer rates conveyed with the fluidised bed technologies. An induction and burner heater is used with molten salts [80]. For this reactor, the vapours formed are quickly detached from the vacuum. This reactor is categorised by lengthier residence time; it is known to produce larger particles than most fast pyrolysis reactors. There is also no requirement for carrier gas, and the process is mechanically complicated; it needs high investment costs. Consistent operation of vacuum pyrolyser entails a superior feedstock input apparatus which discourages latent investors [116–118].

7.5. Rotating Cone Reactor

The rotating cone reactor is an innovative reactor for flash pyrolysis with tiny char formation. Biomass ingredients, like rice husks, wood, palm kernel, coffee husk, and so on, can be milled in the rotating cone reactor. There is no big scale of commercial implementation for a rotating cone reactor. Nonetheless, high-speed rotation provokes dynamic mixing of biomass that sequentially proceeds to fast heat transfer [114,115,119]. Figure 8 shows the rotating cone reactor.

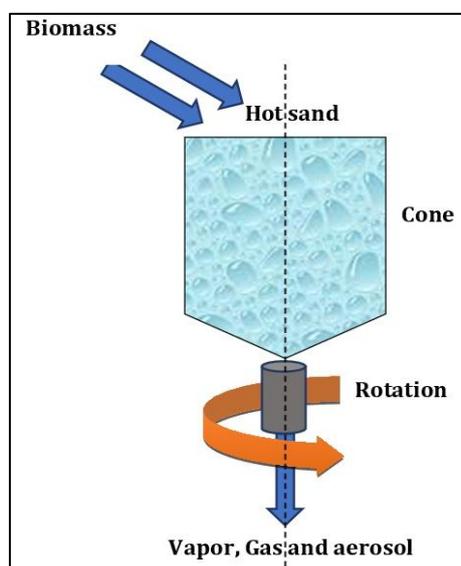


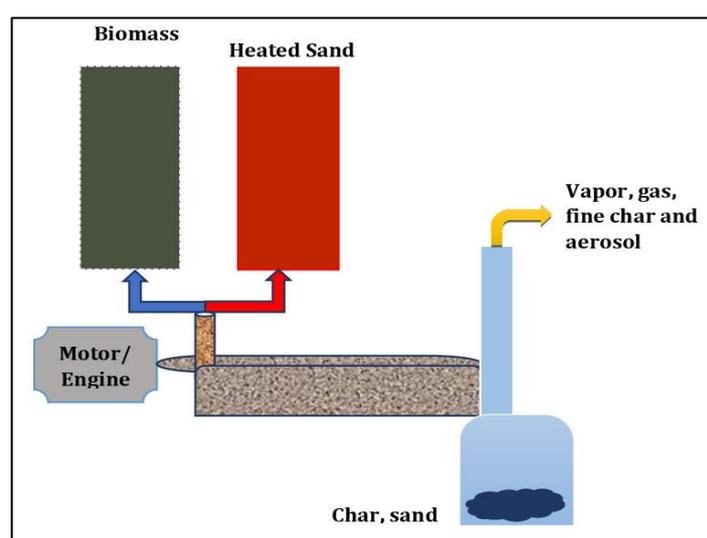
Figure 8. Rotating cone reactor.

Table 6. Summary of previous researches on biomass conversion.

Feedstock	Reactor Type	Temperature (°C)	Yields (wt %)			References
			Char	Bio-Oil	Gas	
Corn stover	Fluidised bed	450–600	28–46	35–50	11–14	[120]
Rice husk	Fluidised bed	450	29	56	15	[121]
Corn cob	Fluidised bed	500	20	62	17	[121]
Sugarcane bagasse	Fluidised bed	500	23	73	4	[122]
Switchgrass	Fluidised bed	480	13	61	11	[123]
Miscanthus	Fluidised bed	505	29	51	12	[124]
Wheat straw	Fluidised bed	550	24	54	24	[125]
Sunflower hulls	Fluidised bed	500	23	57	20	[125]
Rice husk	Fixed bed	100–500	42–48	28–35	-	[126]
Sugarcane bagasse	Vacuum	530	26	51	22	[127]
Rice straw	Vacuum	500	35	47	18	[128]
Douglas fir	Fixed bed	500	22	66	8	[129]
Pine	Vacuum	500	20	50	30	[130]
Wood	Ablative	650	6	60	34	[131]
Barley straw	Ablative	549	32	50	12	[128]
Rice straw	Auger	500	45	26	13	[120]
Hardwood	Auger	500	15	66	18	[132]
Eucalyptus	Conical spouted	500	18	75	6	[133]
Rice husk	Conical spouted	450	26	70	4	[134]
Pine chips	Fixed bed	500	31	15	18	[135]
Softwood	Auger	500	15	69	16	[132]
Olive stone	Rotary kilns	500	26	38	55	[136]

7.6. Auger Reactor

Auger reactors are used to interchange biomass feedstock over an oxygen-free cylindrical tube. In this reactor, vapour residence time could be altered by fluctuating the heated zone. Auger reactors are getting more consideration from many mid-size industries. Challenges for the auger reactor include stirring parts in the hot precinct and temperature transmission on a large scale [114,115]. Figure 9 shows the Auger pyrolysis reactor.

**Figure 9.** Auger pyrolysis reactor [96].

8. Current Status of Pyrolysis Technology

The deteriorating reserves of fossil fuels have posed a great threat and challenge to the quality of life, the world economy, and the environment [137–139]. Biomass pyrolysis possibly will help reduce CO₂ and the world's dependence on oil production [137,140,141]. These bio-oils have the potential to

lower CO₂ discharges; they are derived from plants which use CO₂ for growing. An amalgamation of technologies is required to assimilate reactor design and operational procedure to recover the efficiency of biomass [142,143]. Fast pyrolysis systems process small elements to maximise bio-oil yield, whereas low pyrolysis technologies use wood to produce char chunks [138,139,141]. The recognition of the environmental matters are allied with the use of carbonisation technologies and the technical difficulties of operating fast pyrolysis reactors. Intermediate pyrolysis reactors propose prospects for the extensive balanced production of bio-oil and char [144,145]. Presently, the foremost interests in pyrolysis technology are for CO₂ mitigation, electricity generation from biomass, and energy independence. The pyrolysis technologies can be considered as slow, intermediate, fast, and flash pyrolysis [146–149] but, then again, the most frequently used systems, meanwhile, are the fast and slow pyrolysis processes. Biochar is the key product of the slow pyrolysis, and transpires with moderate temperature, longer residence time, and small heating system rate [150]. Dissimilarly, bio-oil is the key product of fast pyrolysis which formed with a fast heating rate within short residence time [151,152].

Fast pyrolysis produces a higher quality and quantity of bio-oil than the slow pyrolysis [76,153]. It is expected that environmental and economic performance will increase the effectiveness of the pyrolysis process. Various actions are needed to overcome the technical challenges, including plummeting parasitic energy losses, improving pyrolysis reactor outlines, improving feedstock logistics, and enhancing biomass heating rate [9]. Biomass feedstocks are most important to increase the pyrolysis products on a large scale [154,155]. This can be attained by producing energy-condensed products from biomass. Accumulation of metal and ash in reactor bed materials impedes pyrolysis which can reduce bio-oil yields [156,157]. Controlling pyrolysis temperature and heating rate, and using smaller particle sizes can reduce accumulation [158–160]. Recently, a study revealed that an ablative reactor can convert entire wood chips and produce more energy [161,162]. To conclude, cohesive pyrolysis systems that associate gasification or fast pyrolysis are one more important approach for making pyrolysis commercially viable and improving environmental performance [163–167]. Table 7 shows the available pyrolysis plants worldwide.

Table 7. Current pyrolysis plants worldwide [9,168–174].

Reactor Technology	Organisation/Location	Capacity (kg/h)	Desired Product
Fixed bed	Bio-alternative, USA	2000	Char
	THEE	500	Gas
Bubbling fluidised bed	Dyna Motive, Canada	400	Oil
	BEST Energy, Australia	300	Oil
	Wellman, UK	250	Oil
	Union Fenosa, Spain	200	Oil
	Zhejiang University, China	20	Oil
	RTI, Canada	20	Oil
	Waterloo University	3	Oil
	Zhejiang University, China	3	Oil
Circulating fluidised bed	Red Arrow, WI; Ensyn	1700	Chemicals
	Red Arrow, WI; Ensyn	1500	Chemicals
	Ensyn Engineering	30	Oil
	VTT, Finland, Ensyn	20	Oil
Rotating cone	BTG, Netherlands	200	Oil
	University Twente	10	Oil
Vacuum	Pyrovac, Canada	350	Oil
	Laval University	30	Oil
Ablative	PYTEC, Germany	250	Oil
	BBC, Canada	10–15	Char
	PYTEC, Germany	15	Oil
Vortex	Solar energy research Ins.	30	Oil
Another type	Fortum, Finland	350	Oil
	University Zaragoza	100	Gas
	Georgia Tech. Research Ins.	50	Oil

9. Future Challenges

To gain the full potential of biomass pyrolysis technology, such as to enable improved understanding and successful commercialisation, additional research and development are needed. In addition, a couple of issues must be overcome, including the lack of markets for pyrolysis oils and lack of biochar-derived products with well-defined performance characteristics. Also, it is recommended to speed up the improvement and deployment of bio-oil refineries. The improvement of flexible designs for pyrolysis units for producing higher yields of the product is a technical challenge. This review clearly indicates that different pyrolysis technologies have different ranges of product yields. Thus, the selection of pyrolysis technologies, feedstocks, and their operating parameters should be based on the economic trade-offs. However, in addition to the fundamental challenges, a few more important challenges for future biomass pyrolysis research are listed below:

- Understanding the proper working of pyrolysis reactors and processes
- Development of a new reactor that is cost-effective and highly efficient
- Development of catalysts for bio-oil upgrading
- Development of proper solar system reactors
- Post-pyrolysis processing to improve product bio-oil properties
- Understanding the limitations and potential for improvements of the quality of products obtained by biomass pyrolysis
- Development of both fast pyrolysis and bio-oil upgrading, ensuring these are focused on delivering useful and valuable products

For the full implementation of pyrolysis technology, more research is needed to determine designs that will remove oxygen in the gas phase from pyrolysis oil. Pyrolysis technology has the potential to be applied in a vast diversity of situations and, through this process, diversity of products can be obtained. Hence, it is quite difficult to explore a sustainable design for all prospective applications. In addition, balanced financial investments to create new knowledge, technology, and markets for the purpose of building a united vision for the utilisation of pyrolysis technologies is crucial.

10. Conclusions

Biomass is a renewable source for the production of energy which is profusely obtainable globally. The sustainable use of biomass energy can be a supplement for fossil fuels and nuclear energy. Biomass consists of elements, such as carbon, hydrogen, oxygen, and nitrogen. Sulphur is present in smaller proportions, and some types of biomass also contain significant portions of inorganic species. There are several types of pyrolysis processes, namely slow, rapid, ultrafast, and flash pyrolysis which can be used to convert the biomass, which depends upon the process used and also depends on the temperature of the pyrolysis. The main products of the pyrolysis of biomass are bio-oil, biochar, and syngas. The physical and chemical properties of these pyrolysis products depend on the quality of biomass. The bio-oil product has a number of applications; it can be improved to be used as a transport fuel or used as a chemical. Reactor designs are the primary target of researchers to achieve a better-quality bio-oil. For example, fluidised bed reactors are used in many projects to maximise the liquid product (bio-oil) produced, and several projects demonstrate their real ability to produce good quality bio-oil. Auger reactors have the potential to be used in small-scale production. Bio-char is considered as a promising addition to the soil. It can be concluded that the development of biomass pyrolysis technology offers more sustainable products compared to the other available technologies. Finally, in order to gain the full potential of biomass pyrolysis technology and address future challenges, additional research and development are needed.

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