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Review

Progress of the Pyrolyzer Reactors and Advanced Technologies for Biomass Pyrolysis Processing

Mohsin Raza [1,†], Abrar Inayat [2,*], Ashfaq Ahmed [3,4,5,†], Farrukh Jamil [3], Chaouki Ghenai [2], Salman R. Naqvi [6], Abdallah Shanableh [7], Muhammad Ayoub [8], Ammara Waris [9] and Young-Kwon Park [4,*]

[1] Department of Chemical & Petroleum Engineering, United Arab Emirates University (UAEU), Al-Ain 15551, United Arab Emirates; mohsin.morha@gmail.com
[2] Department of Sustainable and Renewable Energy Engineering, University of Sharjah, Sharjah 27272, United Arab Emirates; cghenai@sharjah.ac.ae
[3] Department of Chemical Engineering, Lahore Campus, COMSATS University Islamabad, Raiwind Road, Lahore 54000, Pakistan; ashfaqengr97@gmail.com (A.A.); fjamil@cuilahore.edu.pk (F.J.)
[4] School of Environmental Engineering, University of Seoul, Seoul 02504, Korea
[5] Institute for Sustainable Industries and Liveable Cities, Victoria University, PO Box 14428, Melbourne 8001, Australia
[6] School of Chemical and Material Engineering, National University of Science and Technology, Islamabad 44000, Pakistan; salman.raza@scme.nust.edu.pk
[7] Department of Civil and Environmental Engineering, University of Sharjah, Sharjah 27272, United Arab Emirates; shanableh@sharjah.ac.ae
[8] Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskander 31750, Malaysia; muhammad.ayoub@utp.edu.my
[9] Department of Zoology, Lahore College for Women University, Lahore 54000, Pakistan; ammara.suleri@gmail.com
* Correspondence: ainayat@sharjah.ac.ae (A.I.); catalica@uos.ac.kr (Y.-K.P.)
† First coauthors with equal contributions.

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Abstract: In the future, renewable energy technologies will have a significant role in catering to energy security concerns and a safe environment. Among the various renewable energy sources available, biomass has high accessibility and is considered a carbon-neutral source. Pyrolysis technology is a thermo-chemical route for converting biomass to many useful products (biochar, bio-oil, and combustible pyrolysis gases). The composition and relative product yield depend on the pyrolysis technology adopted. The present review paper evaluates various types of biomass pyrolysis. Fast pyrolysis, slow pyrolysis, and advanced pyrolysis techniques concerning different pyrolyzer reactors have been reviewed from the literature and are presented to broaden the scope of its selection and application for future studies and research. Slow pyrolysis can deliver superior ecological welfare because it provides additional bio-char yield using auger and rotary kiln reactors. Fast pyrolysis can produce bio-oil, primarily via bubbling and circulating fluidized bed reactors. Advanced pyrolysis processes have good potential to provide high prosperity for specific applications. The success of pyrolysis depends strongly on the selection of a specific reactor as a pyrolyzer based on the desired product and feedstock specifications.

Keywords: pyrolysis; pyrolyzers; fast pyrolysis; slow pyrolysis; advanced pyrolysis

1. Introduction

A dependable, clean, and economical energy provision is of paramount significance for the economy, environment, and society, and will continue to be cutting-edge for the 21st century [1]. Over the past few decades, CO_2 emissions have increased, and many other environmental pollutants are responsible for the greenhouse effect, causing global warming to planet Earth [2]. Other than carbon emissions and environmental issues, the energy from fossil fuels has sustainability issues [3]. To solve this issue, international organizations have made many efforts to meet energy demands without affecting the environment using renewable and carbon-neutral sources. In this scenario, the focus of many countries is now on renewable and green energy technologies and the implementation of policies for reducing carbon emissions [4].

Among the various renewable energy technologies, biomass is the most profuse and low carbon emission bioenergy resource. Biomass releases the same amount of CO_2 consumed during photosynthesis for its growth and works on the principle of a carbon fixation process [5]. Therefore, biomass is a carbon-neutral fuel by eliminating the increased CO_2 levels and landfill methane emissions. Hence, landfilling and dumping will decrease steadily [6]. Biomass has clear environmental advantages and reduces the risks that various carbon emissions are causing to the ecological balance [7]. According to the World Energy Assessment report, approximately 65% of the total energy supply by renewable energies comes from biomass [8]. This will meet approximately 11–12% of the world's total energy consumption [9]. Other advantages of biomass include a stable supply for sustainable energy, very low sulfur content, economic availability of biomass as a feedstock, and syngas production for many poly-generation purposes [10].

Biomass consists of a wide range of renewable biological resources, such as crop residues, wood and forestry residues, municipal solid wastes, spent coffee grounds, and other energy crops for biohydrogen and biofuels recovery [11]. The exploitation of biomass for energy production meets the dual goals of fuel security and a reduction in CO_2 emissions [12]. Biomass stores solar energy as chemical energy that is extracted by the breakdown of bonds [13]. The energy in biomass can be recovered as biofuels via thermochemical conversion and biochemical conversion processes. Biochemical conversion implies fermentation and anaerobic digestion to transform biomass into liquid and combustible gaseous fuels [14]. Recently, membrane-integrated processes have emerged as a potential alternative to recover and separate biofuels, biogas, biohydrogen, waste gases (e.g., CO_2 during waste streams), and biomass processing, such as wastewater and gases [15]. The thermochemical process adopts pyrolysis, combustion, and gasification technologies to convert biomass into multiple poly-generation purposes [16].

Pyrolysis is an established thermochemical process for converting biomass materials into bio-oil, gaseous products, and liquid fuel. The process can be categorized into slow, fast, and flash pyrolysis [17]. Each pyrolysis type has different products and their corresponding compositions [18].

Pyrolysis occurs in an inert atmosphere by applying thermal heat to change biomass into numerous fuels, such as char, gas, and liquid oils. The liquid fuel is a combination of dozens of oxygenated organic compounds [19]. Multiple products are formed depending on the various operation conditions, such as the rate of heating, operating temperature, residence time, and biomass particle size [20]. The amounts of lignin, cellulose, and hemicellulose, which are leading polymers of biomass, also contribute to the composition of the final products [21]. Compared to thermochemical conversion processes, such as combustion and gasification, pyrolysis occurs at moderately lower temperatures (400–600 °C) and is generally preferable because the pyrolysis products, mainly char and liquid fuels, are easy to store and transport [22].

Considerable research has been conducted into the pyrolysis of different materials, including biomass and, most recently, e-waste materials such as electronics scrap components. Pyrolysis has numerous advantages as compared to other thermochemical conversion processes, such as [23]:

1. It is a simpler and relatively cheaper conversion process.
2. Pyrolysis is suitable for a wider variety of feedstock.
3. It reduces the landfill requirements and greenhouse gas (GHG) emissions.
4. It has very little water pollution potential.
5. Pyrolysis reactor construction is relatively rapid process.

Pyrolysis efficiency is the thermal efficiency obtained as the ratio of the difference between the overall heating values of the pyrolytic products and the total thermal energy utilized for processing the sample. Pyrolysis is a well-known process of producing high energy-density biofuels and chemicals [24]. Wang et al. [25] presented a comprehensive overview of the pyrolysis mechanisms of three biopolymers in biomass materials and highlighted the complexities in their structure. Sharma et al. [26] conducted a critical review of pyrolysis modeling to highlight the gaps in the technology and explore new opportunities for integrating biomass pyrolysis models of disparate scales. Kan et al. [27] published a comprehensive review of the pyrolysis product properties and effects of pyrolysis parameters. They reported that the heating rate and temperature are the main influential parameters affecting the pyrolysis yield and quality. Dai et al. [28] published a review on understanding the chemistry of non-catalytic and catalytic pyrolysis processes. They introduced recent progress on producing value-added hydrocarbons, phenols, anhydrosugars, and nitrogen-containing compounds from the catalytic pyrolysis of biomass over zeolites and metal oxides via different reaction pathways. The pyrolyzer reactor in the biomass pyrolysis process is the primary component used to convert biomass into valuable products. Several review papers on the biomass pyrolysis process are available, but the authors found few studies on the scope of biomass pyrolyzers. Most review papers on biomass pyrolysis presented experimental and modeling studies in general. Few articles explained the characterization of the products (bio-oil and bio-char). There are also review papers available on the pyrolysis process parameters, the catalyst used in the reactions, and the upgradation of products. Garcia-Nunez [29] presented a study of different reactors used in biomass pyrolysis, but the review paper presented the pyrolysis technologies from a historical perspective. This review follows these former summaries and many others. Where suitable, particular topics previously sufficiently covered in earlier reviews are summarized or the corresponding review paper is referenced. This review provides a detailed evaluation of biomass pyrolysis technology, which includes the selection of biomass feedstock, treatment of biomass material, choice of required pyrolysis process, and finally, pyrolysis in a suitable reactor. This review paper comprehensively discussed biomass pyrolysis technology covering all the aforementioned biomass pyrolysis stages from feed selection to final product formation; special emphasis is made on biomass pyrolysis reactors. Biomass pyrolysis processes are categorized with respect to (w.r.t) reactor type. This review paper is the first to highlight the research on biomass pyrolysis processes in terms of the different pyrolyzer reactors and advanced pyrolyzers. This review article will be of significant interest to researchers in this field. Furthermore, the current review paper will help in the research and development of biomass pyrolysis processes. The review paper also highlights the advanced pyrolyzer technologies and reactors that further enhance the renewability of the pyrolysis process. The review paper contributes significantly to the field of research by critically analyzing fast pyrolysis, slow pyrolysis, and advanced pyrolysis processes.

2. Conversion Mechanism of Biomass by Pyrolysis

As the biomass material is heated, the chemical structure of the polymers inside the matrix of its residue changes. The heating and rearrangement reactions release volatile compounds [30]. After these primary reactions, some unstable, volatile compounds are further converted. Hence, biomass conversion reactions can be categorized as primary and secondary reactions [31].

2.1. *Pyrolysis Primary Conversion Mechanisms*

Lignin, cellulose, and hemicellulose, commonly known as biopolymers, are the core ingredients in biomass. The conversion reaction of these compounds presents the foremost characteristics. The pathways for breaking the various chemical bonds can be described by the following three pathways [32].

2.1.1. Mechanism of Char Formation

The solid residue left after the anaerobic thermal heating of biomass is called char. The char has a polycyclic aromatic structure [33]. The route is dominated by the inter and intramolecular reorganization of the molecular structure, which results in higher thermal stability and filigree of residue [34]. The formation of benzene rings and the grouping of rings is the main mechanism in this pathway. These rearrangements result in the release of incondensable gases and moisture within the biomass material [35].

2.1.2. Mechanism of Depolymerization

The depolymerization phenomenon in this pathway involves the breakdown of biopolymers (lignin, cellulose, and hemicellulose) into separate units called monomers [36]. The degree of polymerization is reduced until the molecules formed become volatile. The molecules condensing at room temperature are found as a liquid fraction [37].

2.1.3. Mechanism of Fragmentation

Fragmentation entails polymer covalent bonds. The linkages also occur between various monomers of the polymer [38]. This pathway is responsible for releasing many incondensable gases and various small chained organic compounds condensing at room temperature [39].

2.2. Pyrolysis Secondary Conversion Mechanisms

The reactor temperature is essential in the second conversion mechanism of biomass. When the reactor temperature causes the release of unstable, volatile compounds, these volatile compounds can undergo further secondary reactions, such as cracking or recombination. Cracking constitutes the breakdown of volatile compounds into lower-molecular-weight compounds [40]. There is some resemblance between the products obtained from cracking and fragmentation because the breaking of the same chemical bonds can occur inside the polymer or within the volatile compounds [41]. Recombination or recondensation is the reverse of cracking and involves the formation of higher molecular weight compounds. The newly formed compounds are mostly non-volatile in the reactor conditions. This pathway is also responsible for the generation of additional secondary char [42].

2.3. Principle of Pyrolysis and Product Distribution

Biomass feedstock is thermally degraded in the absence of oxygen. This phenomenon is a combination of several complex reactions in the reaction zone. Volatile biomolecules of the biomass material are released by heating, which are then transformed into bio-oil by condensation. The inert atmosphere heats the biomass above its thermal stability limit, bringing more stable products and solid residue. The main advantage of the inert medium is that biomass materials are heated without combustion [43]. As explained in detail above, the pyrolysis process consists of two stages: primary pyrolysis and secondary pyrolysis. Primary pyrolysis involves the formation of different carbonyl, carboxyl, and hydroxyl groups as the biomass material splits up and devolatilizes into different constituents. In the devolatilization process, biomass material is decarboxylated, dehydrated, and dehydrogenated [44]. The main conversion process occurs in secondary pyrolysis, where heavy compounds are cracked into char and gases (CH_2, CO_2, CO, and CH_4). Subsequently, the volatile gases are condensed into bio-oil. The proposition of these solid and liquid products depends on the pyrolysis conditions, such as temperature, residence time, and heating rate [45]. The general pyrolysis reaction is as follows [46]:

$$(C_6H_6O_6)n \rightarrow (H_2 + CO + CH_4 + \ldots. + C_5H_{12}) + (H_2O + CH_3OH + CH_3COOH + \ldots.) + C$$

The first part of the product side ($H_2 + CO + CH_4 + \ldots. + C_5H_{12}$) is a mixture of various combustible gases known as synthesis gas; the second part ($H_2O + CH_3OH + CH_3COOH + \ldots.$) is a mixture of different liquids that form bio-oil, and finally a solid yield (char). Pyrolysis processes significantly affect the product distribution according to their operating parameters. The product distribution is based on the temperature, heating rate, residence, particle size, and pressure. Based on these operating parameters, the pyrolysis technology is classified into different sub-categories. Figure 1 provides an overview of the pyrolysis process based on these parameters.

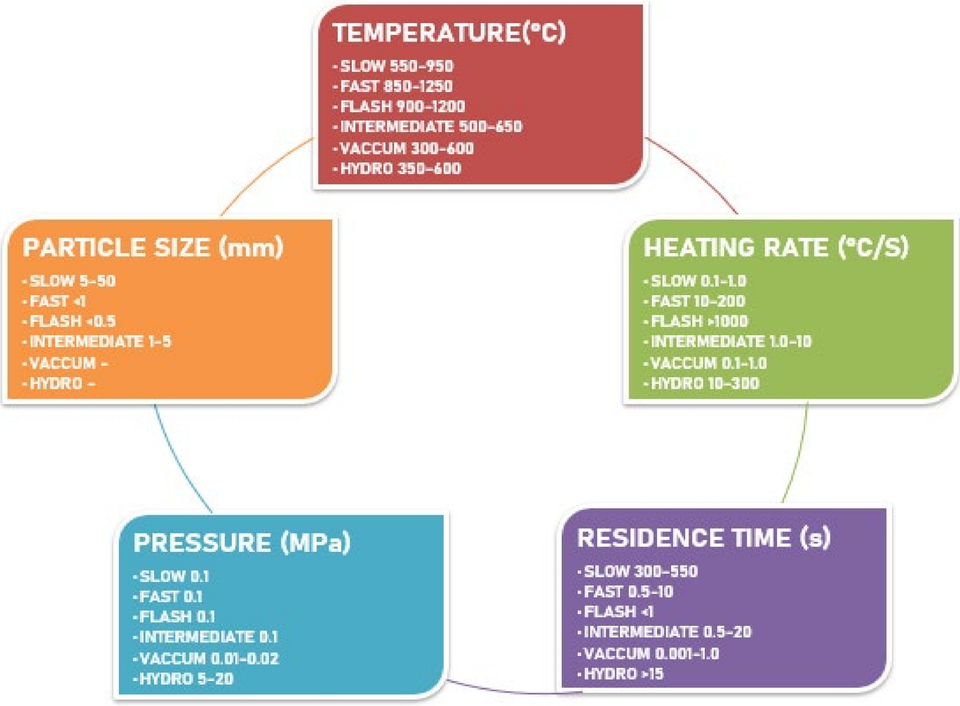

Figure 1. Overview of different pyrolysis process parameters.

Slow pyrolysis has a slow heating rate (0.1–1 °C/s), prolonged residence time (5–30 min), and moderate temperature (400–500 °C). Charcoal or char is the main product of the slow pyrolysis of biomass. Under these conditions, the pyrolysis conversion reaction leans towards the maximum yield of solid product char. On the other hand, bio-oil and synthesis gas are also produced, albeit in comparatively smaller quantities. The mechanism of a more solid product in slow pyrolysis is that the long residence time and lower heating rate promote the secondary reactions to completion. A longer vapor residence time allows the elimination of vapors produced during secondary reactions heading towards a higher char yield [47].

Fast pyrolysis has a higher operating temperature range (800–1250 °C), a higher heating rate (10–200 °C), and a very short residence time (1–10 s). These conditions favor the biomass pyrolysis reaction mechanism towards producing more liquid fuel. The main product of the fast pyrolysis process is bio-oil (65–75%), with smaller amounts of biochar (10–25%) and non-condensable gases (10–20%). The aim is to exceed the temperature such that decomposition is not favored over char formation. The very high heating rate converts the biomass material to condensable vapors before it can form char. A higher heating value (HHV) of the bio-oil produced is half the HHV of crude oil [48].

Flash pyrolysis is an advanced form of fast pyrolysis. The conditions that distinguish it from the fast pyrolysis process are the extremely high heating rate of 1000 °C/s. The operating temperature is kept between 900–1200 °C, and the biomass feedstock is exposed to these conditions for very small residence times (0.1–1 s). Compared to fast pyrolysis, the bio-oil yield further increased in flash pyrolysis (>75%) with significantly smaller amounts of solid and gaseous products. The operating parameters required for flash pyrolysis are also hindrances in industrial-scale applications [49].

The intermediate pyrolysis process is adopted to make a balance between liquid, solid, and gaseous products. The operating conditions for pyrolysis are kept between slow and fast pyrolysis processes so that a balance should be drawn in the ratio of the product. The typical intermediate pyrolysis conditions are 500–650 °C, 0.1–10 °C/s, and 300–1000 s residence time. Intermediate pyrolysis leans more towards fast pyrolysis with bio-oil yield (40–60%), biochar (15–25%), and non-condensable gases (20–30%). An advantage of bio-oil produced by the intermediate pyrolysis process is that it has a lower tar content and can be used directly for thermal heat generation [50].

Hydropyrolysis is a new emerging technology to produce high-quality bio-oil from a biomass feedstock. The operating temperature is the same as fast pyrolysis with the addition that biomass feedstock is operated at elevated pressures (5–20 MPa) and mixed with hydrogen or hydrogen-based material. The presence of hydrogen at high pressures and temperatures reduces the oxygen content in the bio-oil produced and hinders the formation of solid char [51].

Vacuum pyrolysis is the conversion of biomass feedstock under low-pressure conditions (0.05–0.20 MPa), and all other conditions for the slow pyrolysis process are maintained. On the other hand, the difference between the two processes is the procedure for eliminating vapors from the reaction region. The vacuum is used for vapor removal instead of a purge gas, which is used mainly in other pyrolysis techniques. Another advantage of vacuum/low pressure is that the biomass components are decomposed at relatively lower temperatures. The rapid removal of vapors during the primary pyrolysis mechanism allows a better bio-oil yield. The bio-oil yield is improved with vacuum pyrolysis, and the biochar produced has high porosity [52].

In biomass pyrolysis, the end products depend on the reaction parameters. The reaction parameters determine the yield and quality of the products. Biomass pyrolysis is used mainly to obtain a specific type of product. The following operating parameters affect the end product in the biomass pyrolysis conversion processes [53]:

1. Effect of the biomass particle size
2. Effect of the operating temperature
3. Effect of the heating rate
4. Effect of the residence time
5. Effect of pressure
6. Effect of the catalyst
7. Effect of the pyrolysis bed-height
8. Effect of the carrier gas flow rate

The coarser particle size of the biomass feedstock supports char formation. The heat must travel long distances from the material surface to its core; this higher temperature difference favors solid char production. Furthermore, the vapors formed must travel a longer distance through the char layer, which increases char formation. On the other hand, smaller and refined particles are recommended for producing condensable gases that form bio-oil [54]. Siyi Luo et al. [55] performed the pyrolysis of three different biomass materials (garbage, wood, and plastic) and investigated the effect of particle size on the pyrolysis process. The outcomes from the investigation showed that for all the biomasses, particle size affects pyrolysis product yields and composition: smaller particle size results in higher gas yield with lower tar and char; the decrease in particle size can increase the hydrogen and carbon monoxide contents of gas, as well as the ash and carbon element contents in the char. An increase in temperature favors the formation of more bio-oil and non-condensable gases and results in char formation. Elevated temperatures accelerate the thermal cracking of higher hydrocarbons heading towards the formation of more liquid and gaseous products [56]. Feedstock heating rates greatly influence the nature and composition of the pyrolysis products. Lower heating rates ensure the reduction in secondary pyrolysis reactions. This favors the formation of more solid char. In contrast, a high heating rate supports the fragmentation and rapid thermal degradation of the biomass feedstock, resulting in more gaseous and liquid end-products [57]. Dengyu Chen et al. [58] investigated the effect of heating rate (10, 30, and 50 °C/min) on the pyrolysis process. The outcomes showed that in the BET surface area of biochar, the higher heating value of non-condensable gas and bio-oil reached the maximum values of 411 m^2/g, 14 MJ/m^3, and 14 MJ/kg, under the condition of 600 °C and 30 °C/min, 600 °C and 50 °C/min, and 550 °C and 50 °C/min, respectively. Higher pyrolysis temperature and heating rate contributed to achieving both higher mass yield and energy yield of the non-condensable gas.

The residence time of the pyrolysis process determines the end-product distribution. A prolonged residence time promotes polymerization of the pyrolysis constituents and provides sufficient time to react. Low residence time and moderate temperature endorse the formation of char. If the residence time is kept very small, then polymerization is not completed. A shorter residence time promotes the formation of condensable gases and bio-oil [59]. The biochar yield is increased by conducting biomass pyrolysis at pressures higher than ambient pressure. This is because elevated pressure lengthens the residence time of the constituents and supports secondary carbon formation. The pyrolysis vapors are also decomposed on the carbonaceous material and form a char [60]. Bin Zhao et al. [61] investigated the effect of residence time, heating rate, and temperature on the pyrolysis of rapeseed. The outcomes have explained the connection between rapeseed stem biochar and its pyrolysis conditions. The surface area and morphology were considerably affected by residence time, which is often ignored in the scientific literature.

The catalytic biomass pyrolysis process is classified as a primary and secondary catalytic pyrolysis process. The primary catalytic biomass pyrolysis conversion process involves the mixing of catalyst material with the biomass feedstock before feeding it into the reactor. Mixing can either be performed mechanically (dry mixing) or by wet impregnation. Secondary catalytic biomass pyrolysis conversion deals with the treatment/upgrading of the pyrolysis products in a downstream reactor. Catalytic biomass conversion provides an improved product distribution [62]. Biomass pyrolysis reactors are classified as fixed and fluidized beds. The reactor type influences the pyrolysis end-product distribution. The bed height is an important parameter in both types of pyrolysis reactors. Ahmed et al. [63] reported that biochar yield was decreased after increasing the bed height to a certain level. Nitrogen is the most widely used purge gas carrier because of its inert nature. During the pyrolysis of biomass, a large quantity of vapors is formed, which, if not purged, can become involved in the secondary reactions. This changes the composition and nature of the end-products [64]. Expected yields of products from different types of biomass thermal conversion are shown in Figure 2.

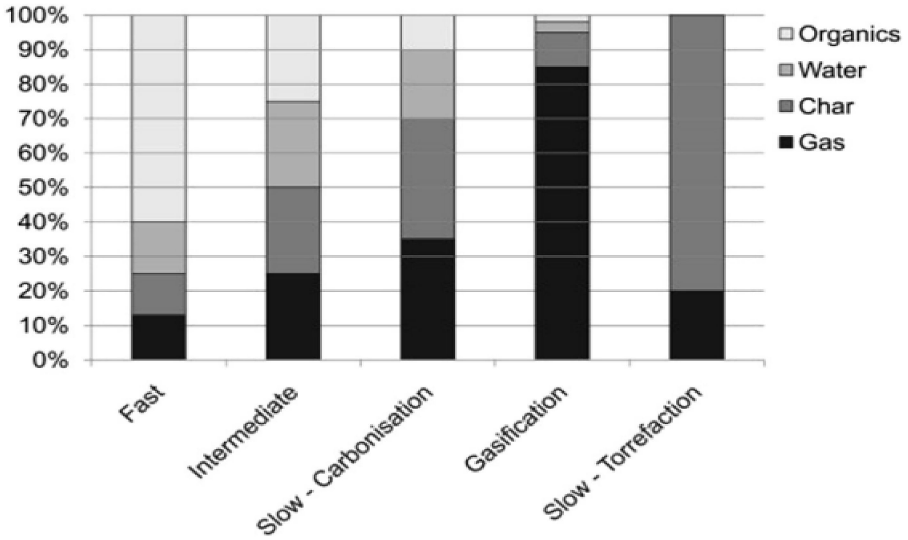

Figure 2. Estimated scales of products from different modes of thermal conversion of biomass [65].

3. Biomass Feedstock Availability and Economic Analysis

With an annual production capacity of 220 billion tons per year, biomass is the world's largest source available for energy generation. In the future, biomass could be deemed the sole source of energy generation, supplying multiple types of gaseous, liquid, and solid products. Biomass contains cellulose, hemicellulose, and lignin as its main constituents [66].

The heating value of any biomass material depends on its inherent composition constituents. For example, for a typical lignocellulosic biomass, its composition ranges as cellulose (30–50%), hemicellulose (15–35%), and lignin (10–20%) [67]. Biomass materials are appropriate feedstock for pyrolysis processes to transform them into a wide range of fuels. These biomass feedstocks for the pyrolysis process can be grouped into seven varieties [68].

Forest residue is the leading quantity, with an annual global production capacity of approximately 31 billion tons. Forest waste materials are the most abundant lignocellulosic waste materials rich in lignin (25–35 wt.%). Forest waste materials include leaves, stems, wood, and bark. These offer a great opportunity to produce multiple products using all thermochemical conversion processes [69]. Another main concern for forest waste utilization is that it is a potential fire hazard. Forest waste materials are high carbon (44–53%) lignocellulosic materials with very little ash content (0.3–8 wt.%). The average lower heating value of forest waste materials varies between 15.4–20.5 MJ/kg, with pyrolysis producing an average bio-oil yield of 35.1 wt.% and energy recovery of 37.2% [70]. Owing to the higher water content in bio-oil (20–30 wt.%), the bio-oil yield and energy recovery values are slightly lower than other protein-rich and high lignin lignocellulosic materials [71].

Food waste materials are produced in every country from domestic households and restaurants. These materials provide the second most sustainable source of biomass, with an annual production capacity of 1.3 billion tons per annum. These biomass materials also contain a heterogeneous range of compounds (proteins, lipids, and digestible sugars) suitable for energy-intensive bio-oil production [55]. The products from the pyrolysis of food waste materials vary greatly according to the types, collection method, season, and origin. An average lower heating value varies between 26–34 MJ/kg, and energy recovery is moderate (30%) compared to other biomass materials. The pyrolysis of some food waste results in a bio-oil yield between 18–22 wt.% [72].

The agriculture sector offers a third sustained source of biomass waste of nearly 1.0 billion tons of annual biomass waste annually. These waste materials are rich in protein and lignin, which are suitable feedstock for the pyrolysis process. Agricultural waste (corn stalk and rice husk) contains cellulose (35 wt.%), hemicellulose (24 wt.%), and lignin (22 wt.%) [73]. In the category of agricultural waste material, herbaceous plants offer higher cellulose content (>38 wt.%) and lower lignin (<20 wt.%). Dedicated plants grown especially for energy production (also referred to as energy crops) have higher biomass production and better glucans, lignin, and xylans content and generate less ash. Therefore, these dedicated plants produce a higher bio-oil yield and offer more energy recovery [74]. Agricultural waste material and dedicated plants have a higher volatile matter (73–88 wt.%) and good energy content (16–30 MJ/Kg) than all other categories of biomass materials suitable for bio-oil production. The average bio-oil yield and energy recovery values from agricultural waste and dedicated plants are approximately 45 wt.% and 65 wt.%, respectively [75].

De-oiled seedcake is a major by-product of the biodiesel industry that is usually obtained after the oil extraction from the Jatropha curcas, canola, and pennycress. The residual oil in seedcakes gives them a higher energy content than lignocellulosic materials [76]. Typical de-oiled seedcake contains lipids (2–20%), a good protein amount (10–40%), very high volatile matter (70–90%), and lower ash content (0.5–10%). Bio-oil yield from the pyrolysis of de-oiled yield has an average value of 40 wt.% and energy recovery of approximately 55% [77]. Crude glycerol is also obtainable as an inexpensive waste by-product from the biodiesel industry and has tremendous potential as a feedstock/co-feedstock in the pyrolysis process. A typical crude glycerol from biodiesel industry contains 35–40% C, 8–10% H_2, 0.30–0.70% S, and 45–55% O_2. The highest gas yield with up to 60 v/v% H_2 can be obtained by the pyrolysis of crude glycerol [78].

Spent grains from the beer brewing industry are also generated in quantities of millions of tons every year as the brewing industry is expanding. These spent grains, which have a lower moisture content, are likely to decompose rapidly, making them highly suitable for biofuel production [79]. Compared to other lignocellulosic biomass materials, they contain fewer polysaccharides, a lower activation energy for decomposition, and a high level of proteins (20–30 wt.%). They usually have a lower ash content (2–7 wt.%) and a heating value of 20–25 MJ/kg. The average bio-oil yield and energy recovery were recorded to be 46 wt.% and 65 wt.%, respectively [80].

Municipal solid waste includes waste materials from pulp and paper, leather industry, yard waste, food waste from restaurants, household waste materials, plastics, and textile waste materials. Sewage sludge is a waste material from wastewater treatment plants and is an ash-rich solid waste material [81]. In the USA (2015), out of 260 million tons of municipal solid waste produced, only half was landfilled, and less than a quarter was recycled [82]. Both municipal solid waste and sewage sludge have tremendous potential to be converted to useful energy fuels/thermal heat by incineration and anaerobic digestion processes (methane production), but it also can be used as a feedstock in thermochemical conversion processes [83]. On average, the bio-oil yield from municipal solid waste is approximately 30 wt.%, which is lower than other biomass materials because it has many inorganic materials (20–45 wt.%) and lower volatile contents (45–65 wt.%). Energy recovery from both municipal solid waste and sewage sludge is approximately 60 wt.% [84].

Anaerobic digestion (AD) is a biological conversion process of biomass conversion (mainly animal manure). The process produces biogas, which is a blend of CO_2 (30–60%) and CH_4 (40–70%). Anaerobic sludge is a solid residue obtained from anaerobic digestion, which is 40–50% of the original organic material [85]. Anaerobic sludge can be a feedstock and, more frequently, a co-feedstock in the pyrolysis process to produce bio-oil because it is biologically stable and contains abundant organic molecules. The digestate has physical and chemical properties similar to municipal solid waste and sewage sludge. The lower heating value of the digest matches that of raw sewage sludge (SS) [86]. The average bio-oil yield and energy recovery from the pyrolysis of sludge is 30.5 wt.% and 56 wt.%, respectively. The bio-oil yield and energy recovery values are slightly lower than municipal solid waste and sewage sludge because much of the energy is used in the anaerobic digestion process [87].

Algae are not included in these seven categories because it contains very low lignin and crystalline cellulose contents. Hence, it is a barrier to its thermochemical energy conversion potential. Nevertheless, other pathways are available to convert algae into biodiesel and value-added products [88].

Feedstock type has a significant effect on the product distribution of the pyrolysis process, physiochemical properties of pyrolysis products, and reaction rate. The characteristics of biomass feedstock that affect the pyrolysis products are as follows [89]:

- Feedstock particle shape and size;
- Bulk density;
- Elemental and chemical composition;
- Energy content (MJ/Kg);
- Protein, lipid, extractives, and ash content.

Therefore, the pyrolysis of the same biomass feedstock from various origins will not give the same product distribution because it will vary in its composition [90]. Each feedstock has unique physiochemical properties; hence, a specific pyrolysis process for different feedstock gives different product distributions [91]. Table 1 lists the chemical composition analysis of different biomass materials. The biomass feedstock properties can be improved using various techniques. Moreover, lignocellulosic materials with different percentages of cellulose, hemicellulose, and lignin are capable of producing pyrolysis products.

Table 1. Physiochemical properties of some biomass feedstocks.

Feedstock	Ultimate Analysis					HHV (MJ/Kg)	VM	Ash	Ref.
	C	H	N	O *	S				
Rice straw	26	4	1	17	0.28	12.50	50	49.50	[92]
Milkweed	37	6	2.50	43	–	16.67	80	11.20	[93]
Linseed	65	9	2.45	30	–	28	83	6	[89]
Wood chip	51.50	6.18	0.30	41.67	0.1	20.70	86	0.30	[94]
Sewage sludge	25.50	4.46	4.84	25.87	2.07	11.10	54.20	37.20	[95]
Potato skin	71.32	6.13	2.57	9.38	–	35	78.55	10.60	[96]
Forestry residue	51.40	6	0.50	40	0.04	20.80	76.70	2.10	[70]

VM: Volatile matter. * calculated by difference.

Table 2 presents an overview of chemical composition of different lignocellulosic biomass materials capable of producing pyrolysis products.

Table 2. Chemical composition analysis of different biomass materials.

Lignocellulosic Biomass	Cellulose	Hemicellulose	Lignin	Ref.
Cotton stalks	41.7	27.3	18.7	[97]
Chili stalks	37.5	28.3	17.3	
Pepper stalks	35.7	26.2	18.3	
Okra stalks	36.3	28.7	17.9	
Bean stalks	31.1	26.0	16.7	
Corncobs	45.0	35.0	15.0	[98]
Wheat straw	30.0	50.0	15.0	
Empty fruit bunch	41.0	24.0	21.2	
Wastepaper	60–70	10–20	5–10	
Date palm leaves	59.11	16.71	16.43	[99]
Date palm leaf base	51.5	24.41	18.5	
Date palm rachis	32.0	19.0	11.0	[100]

The economy of the pyrolysis process mainly links with the abundance of biomass resources. The commercialization aspect of the pyrolysis technology to produce various chemicals and fuels depend on the production parameters and their comparison with fossil-fuel products. Briefly, the economy of the process does not depend on a single factor. Hence, there is a difference in the life cycle production costs of products from pyrolysis [101].

Table 3 lists the economic analysis of some biomass feedstocks, such as the cost of the pyrolysis products depending upon the feedstock, pyrolysis plant capacity, product yield, selection of pyrolysis technology, and discount or subsidy rates.

The economics also vary with local taxes, raw material transportation, utilities, labor wages, maintenance, and waste disposal. The pyrolysis process economy is also influenced by how the feedstock is produced, how it might be sourced, the collection method, and the processing technique [107]. Zhang and Kung [108] reported that the collecting cost for rice straw (agricultural waste) is lower than the harvesting costs of dedicated energy crops. Popp et al. [109] reported that transportation cost has a significant effect on the economy of pyrolysis products. One way to increase the profitability of the pyrolysis process is to expand the size of production [110]. From a detailed discussion and analysis of the biomass pyrolysis feedstock, pyrolysis types, and pyrolysis operating parameters, the following systematic synthesis process can be constructed in Table 4.

Table 3. Pyrolysis cost dependent few parameters.

Feedstock	Technology	Reactor Type	Ton/Day	Yield	Cost $/Liter	Ref.
Corn stover	Fast pyrolysis-Aspen model	Fluidized-bed reactor	2000	Bio-oil	0.68 (2010)	[102]
Wood	Fast pyrolysis-ChemCAD	Circulating fluidized bed	2000	Gasoline and diesel	0.8 (2014)	[103]
Hybrid popular	Fast pyrolysis-non-linear programing	Circulating fluidized bed	250–3600	Gasoline and diesel	0.60–0.90 (2013)	[104]
Hybrid popular	Fast pyrolysis-ChemCAD-ICARUS	Circulating fluidized bed	2000	Gasoline and diesel	0.46–0.54 (2009)	[105]
Corn stover	Fast pyrolysis-Aspen Plus	Fluidized bed-Fischer Tropsch	2000	Gasoline and diesel	1.48 (2015)	[106]

Table 4. Biomass pyrolysis synthesis scheme.

Biomass Feedstock: Lignocellulosic and Protein-Rich **Agricultural Waste Residue, Seedcake, Distiller Grains, Sludge, MSW and SS, Food Waste, Forestry Waste**	
Biomass Pretreatment: *Physical Treatment:* **Drying, Grinding, Palatalization** *Composition Tuning:* **Harvesting Method and Timing, Storage Method, Chemical Treatment, Thermochemical Treatment, Co-Feeding**	
Required product distribution: **>> Biochar with << bio-oil & condensable gases** ***Type: Product (biochar)*** **1. Slow pyrolysis (>50%)** **2. Intermediate pyrolysis (35–50%)**	*Required product distribution:* >> Bio-oil & condensable gases with << biochar *Type: (bio-oil)* 1. Fast pyrolysis (65–75%) 2. Flash pyrolysis (>75%) 3. Vacuum pyrolysis (65–80%) 4. Intermediate pyrolysis (35–50%) 5. Hydropyrolysis (50–75%)
Operating parameters: ***(operating temperature, heating rate, residence time, pressure, particle size)*** **1. Slow pyrolysis (550–950 °C, 0.1–1 °C/s, 300–550 s, 0.1 MPa, 5–50 mm)** **2. Intermediate pyrolysis (500–650 °C, 1–10 °C/s, 0.5–20 s, 0.1 MPa, 1–5 mm)**	*Operating parameters:* *(operating temperature, heating rate, residence time, pressure, particle size)* 1. Fast pyrolysis (850–1250 °C, 10–200 °C/s, 0.5–10 s, 0.1 MPa, <1 mm) 2. Flash pyrolysis (900–1200 °C, >1000 °C/s, <1 s, 0.1 MPa, <0.5 mm) 3. Vacuum pyrolysis (300–600 °C, 1–10 °C/s, 0.001–1 s, 0.01–0.02 MPa) 4. Hydropyrolysis (350–600 °C, 10–300 °C/s, >15 s, 5–20 MPa)
Reactors **1. Fixed Bed Reactor** **2. Augers Reactor** **3. Rotary Kiln Reactor** **4. Catalytic Slow Pyrolysis of Biomass**	*Reactors* 1. Bubbling Fluidized-Bed Reactor 2. Circulating Fluidized-bed Reactor 3. Fixed Bed Reactor 4. Ablative Reactor 5. Entrained Flow Reactor 6. Catalytic Fast Pyrolysis of Biomass
Advanced Pyrolysis Techniques	
Vacuum pyrolysis of biomass	Microwave pyrolysis of biomass
Flash pyrolysis of biomass	Biomass pyrolysis via Solar Energy
Biomass pyrolysis via Plasma technology	

4. Recent Progress in the Biomass Pyrolysis Process

4.1. Fast Pyrolysis Process

In this pyrolysis technology, the decomposition process for the lignocellulosic material in the absence of air is very fast. The main products from the biomass material treated with a fast pyrolysis process are mostly vapors, aerosols, and smaller amounts of charcoal and gas. The dark brown mobile liquid is obtained after cooling and condensing the vapor streams. The calorific value of that liquid is approximately half of the calorific value of fossil fuel. The following are a few important characteristics of the fast pyrolysis process [111].

1. The phenomenon takes place with high heat and heat transfer rates. Therefore, biomass materials need to be very small.
2. The controlled temperature range is 450–550 °C in the vapor phase.
3. The vapor residence times are as short as two seconds.
4. The vapors are converted to bio-oil by instantaneous cooling.

Bio-oil is obtained after the cooling and condensation of pyrolysis vapors. The main product of fast pyrolysis is a blend of polar organics and water. These two components are miscible with each other and have a proportion of 75–80 wt.% and 20–25 wt.%, respectively [112].

Several technologies can be used to accomplish a fast pyrolysis process:

- ➢ Fast Pyrolysis of Biomass via a Bubbling Fluidized-Bed Reactor,
- ➢ Fast Pyrolysis of Biomass via a Circulating Fluidized-bed Reactor,
- ➢ Fast Pyrolysis of Biomass via a Fixed Bed Reactor,
- ➢ Fast Pyrolysis of Biomass via an Ablative Reactor,
- ➢ Pyrolysis of Biomass via an Entrained Flow Reactor, and
- ➢ Catalytic Fast Pyrolysis of Biomass

4.1.1. Fast Pyrolysis of Biomass via Bubbling Fluidized-Bed Reactor

Fluidization is a phenomenon in which the fine solids are transformed into a fluid-like state through contact with a gas or liquid. The upward fluid drag on the solid particles by gas is responsible for the fluidization. The particles in the fluidized bed are present in a semi-suspended state. If the gas flow rate through the fixed bed is increased, the pressure drops due to the fluid drag continue to rise. This phenomenon continues until gas velocity maintains a critical value known as the minimum fluidization velocity. At this stage, the fixed bed transforms to a fluidized bed when the fluid drag is equal to the particle weight [113]. Figure 3 shows a typical bubbling fluidized-bed reactor. Bubbles are made at the openings everywhere that the fluidizing gas enters the bed. They are formed because the velocity at the interface of the bed just above the hole represents the gas input rate in surplus of what can pass through the interstices with a frictional resistance less than the bed weight. Hence, the layers of solids above the holes are pushed aside until they make a void through whose porous surface the gas can enter at the incipient fluidization velocity [114].

The advantages of bubbling fluidized-bed reactors include uniform mixing, uniform temperature distribution, and operation in the continuous state [116]. The use of bubbling fluidized-bed reactors for accomplishing the fast pyrolysis of biomass has been reported by numerous researchers [117].

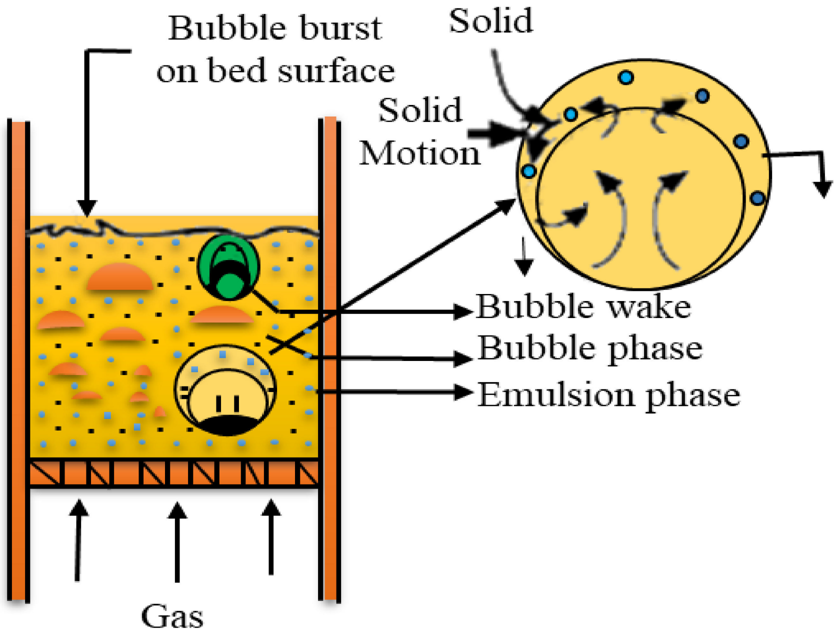

Figure 3. A bubbling fluidized-bed reactor showing gas circulation around bubbles, adapted from P. Basu 2001 (combustion and gasification in fluidized beds) with due permissions [115].

Zhang et al. [118] reported the outcome of crucial operation factors in the fast pyrolysis of biomass (corncob). The pyrolysis was performed in a bubbling fluidized-bed reactor with and without the addition of catalysts. The effective operation parameters were the reaction temperature, gas flow rate, pyrolysis bed height, and the size of biomass feedstock. The catalyst used to alter the results for the investigation on the final products was the HZSM-5 zeolite catalyst. The results suggested that the maximum liquid yield was 56.8 wt.%. The optimal operating parameters identified were a pyrolysis operating temperature of 550 °C, gas flow rate of 3.4 L/min, 0.1 m static bed height, and a particle size of 0.1 to 0.2 cm. The result also shows that the amounts of incondensable gas, coke, and water increase with the addition of a catalyst to fast pyrolysis technology carried out in a bubbling fluidized bed reactor, while the amounts of liquid and char decrease. Dong et al. [119] analyzed the fast pyrolysis of biomass numerically in a fluidized bed reactor. The process was a three-fluid model. In this process, multi-step kinetics was used for biomass thermal decomposition. The hydrodynamics of the fluidized beds with various superficial velocities of fluidizing gases were examined. The results predicted that the superficial velocities should be aimed at carefully. The accuracy of this depends on balancing the char removal efficiency and biomass-heating rate. The presented model system also showed that the heat-penetration model is effective in describing the intra-particle heat transfer. This is validated by the consistency between the simulated and experimental results.

4.1.2. Fast Pyrolysis of Biomass via Circulating Fluidized-Bed Reactor

The circulating fluidized bed reactor has many distinctive properties that make it different from several gas–solid reactors. Hence, it is promising for a wide range of reactions. In an actual circulating fluidized bed, the reactor does not contain any bed and does not have any separate upper surface. On the other hand, it is intermediate in density between the dense fluidization phase and light pneumatic conveying [120]. Circulating fluidized-bed reactors have selection superiority over many other technologies, such as fixed-bed reactors, entrained flow reactors, dense phase fluidized beds, and rotary kilns used in the chemical process industry [121]. The most important features of circulating fluidized-bed reactors that distinguish them from other reactor configurations include internal recycling of huge bulk particles reaching the top of the vessel back to its bottom, a good void range, and no distinct upper bed surface in the column [122]. Figure 4 presents a typical circulating fluidized-bed reactor.

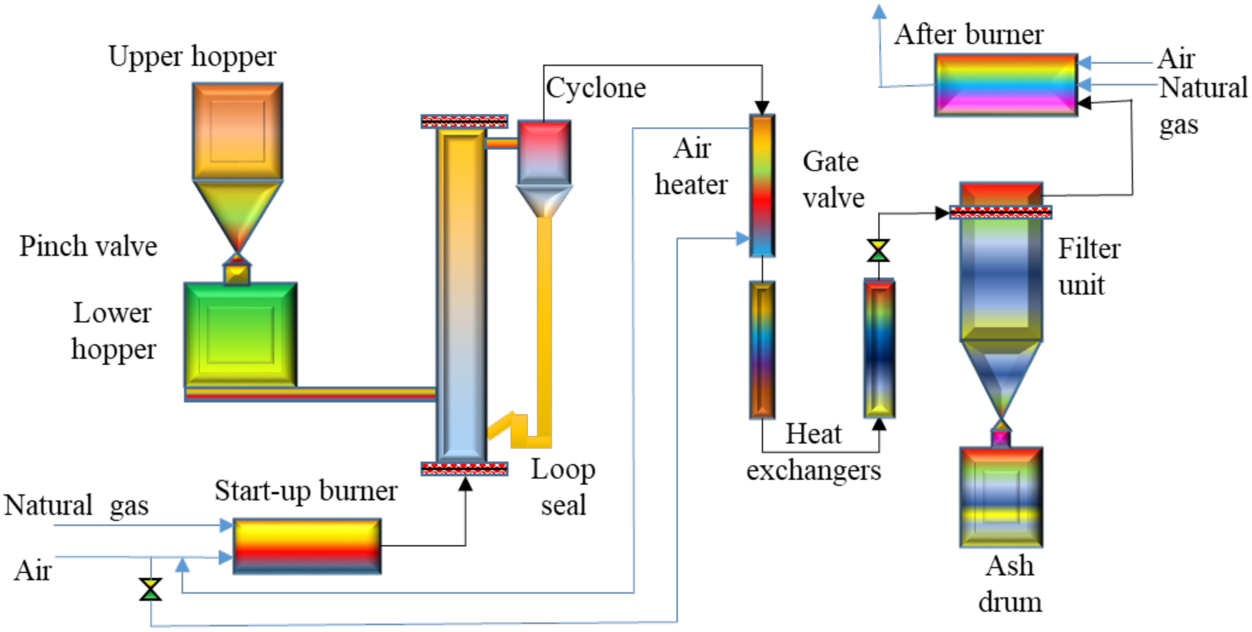

Figure 4. A typical circulating fluidized bed reactor, adapted from Le et al. 2004 with the due permissions [123].

Cao et al. [94] reported bio-oil production in a fast pyrolysis process in an internally circulating fluidized bed. The biomass materials used in this study were sewage sludge, pig dung, and wood chips. The pyrolysis was performed at an optimal temperature of 500 °C. The reported bio-oil yields from sewage sludge, pig dung, and wood chips were 45.2%, 44.4%, and 39.7%, respectively. The elemental characterization of the product shows that the bio-oil from sewage sludge contains more aliphatic species. In contrast, the bio-oil produced from pig dung has a high carbon content, and hence a high heating value. The bio-oil produced from the wood chips is not preferable to use as a fuel because it has high oxygen content, low hydrogen to carbon ratio, and less heating value. Xianwen et al. [124] developed an integrated method for the fast pyrolysis of a biomass material with a circulating fluidized bed reactor. The circulating bed reactor can be modeled and distinguished as two separate zones. These zones represent the pyrolysis (primary reaction zone) and the second reaction zone. Various process parameters, such as the bed temperate, particle size of biomass, and position of the feeder were analyzed. Wood powder was used as the biomass material for pyrolysis. The different compositions and proportions of pyrolysis gas and bio-oil can be seen in the context of the process parameters. The results suggest that the high temperature and prolonged residence time give less bio-oil and leads to secondary reactions. The lower heating rates contribute to more carbonization and minimize liquid production.

4.1.3. Fast Pyrolysis of Biomass via Fixed-Bed Reactors

Fixed-bed reactors are the most common type of reactors used in the process industry. They come mostly in circular cylindrical shapes, even though they are available in all sizes and various other dimensions. Fixed-bed reactors are most commonly filled with solid catalysts [125]. The feed enters from one side, and the product is obtained from the other. The catalyst pellets are fixed at a selected section and do not move against a reference section. Principally, the main chemical reactions occur inside the catalyst [126]. Catalyst recovery and recycling are some of the major criteria for the economy of the fixed-bed reactor and have a major influence on its selection. These reactors are the most important reactors for the large-scale production of chemicals and intermediates. In recent years, they have been used intensively to treat toxic and harmful substances [127].

Amir et al. [128] examined the fast pyrolysis of biomass using the fixed-bed drop-type pyrolyzer. Under the inert conditions, rubberwood sawdust (RWS) and meranti wood sawdust (MWS) were analyzed at various pyrolysis-operating temperatures. The product yield was analyzed for 450 to 650 °C with 50 °C increments in temperature. The same maximum amount of bio-oil was produced from both biomass materials (RWS and MWS) but at different temperatures. Temperatures of 550 and 600 °C were the most suitable for the maximum yield (33 wt.%) from RWS and MWS, respectively. The second part of the research involved the analysis of pyrolysis products obtained from the maximum pyrolysis temperature. The results revealed a high percentage of oxygen and hydrogen in the bio-oil, indicating a high water content.

The presence of a high moisture content in the bio-oil reduced its heating value. The major constituents of non-condensable gases in this research were CO and CO_2. Ly et al. [129] examined the pyrolysis of saccharina japonica algae to produce various products, mainly bio-oil in a fixed-bed reactor. Saccharina japonica is a type of macroalgae that has been cultivated in the Republic of Korea in large quantities for renewable energy production. In this experimental study, various sweeping-gas flow rates (100 mL/min, 300 mL/min, and 500 mL/min) and different pyrolysis temperatures (350 to 550 °C) were investigated to obtain bio-oil, gas, and char. As the pyrolysis temperature was increased, the amount of bio-oil decreased, and the gas yield increased for saccharina japonica. The maximum amount of bio-oil (approximately 41 wt.%) was achieved at a pyrolysis temperature of 350 °C and a sweeping flow rate of 300 mL/min. The gas product included CO. CO_2, H_2, and other hydrocarbons. The biochar contained a high carbonaceous content. Therefore, it is used as a pollution-free solid fuel with a high heating value that can be used to produce activated carbon and other chemicals.

4.1.4. Fast Pyrolysis of Biomass via Ablative Reactor

Ablative reactors are designed to carry out ablative pyrolysis, which is a type of fast pyrolysis. The fundamental principle is the mechanism of heat received by the reacting biomass particles. It is categorized by the dominant mode of heat transfer, which is conduction to the biomass particles. The conditions for ablative pyrolysis are as follows: (a) high relative motion and (b) high contact pressure between the biomass material and heat transfer contact surface. These two combined effects of high contact pressure and relative velocity are responsible for the high ablation rates in the fast pyrolysis of biomass via ablative reactors [130]. Fast pyrolysis through an ablative reactor offers many advantages over conventional fast pyrolysis. The most common of these benefits include (i) a considerably smaller reactor volume, (ii) lower capital costs due to the minimized use of inert gas, (iii) no requirement for recycling gas, (iv) large biomass feedstock can be used directly (up to 50 mm), (v) reduced feed preparation costs, (vi) it can be easily modified for production of renewable products, (vii) high specific throughputs, and (viii) lower operating costs [131].

Luo et al. [132] reported the of whole wood chips and rods in a novel ablative reactor. The biomass material used in the research work was dry wood. The study also included the pyrolysis liquid collection system, which could indicate the influence of key process parameters. The designed system explained the relationships between the parameters and product quality. The model was developed to account for the ablative pyrolysis process. The conversion of whole wood and wood rods directly to pyrolysis products saves considerable amounts of money spent on grinding, chipping, and shredding wood to smaller sizes. These unit operations account for approximately 7–9% of the total process cost. The research presented the development and testing of a laboratory-scale ablative pyrolysis reactor converting wood chips and wood rods into a high yield of bio-oil (60 wt.%). Moreover, the amount and composition of bio-oil from the ablative reactor resembled a similar product from a fluidized bed reactor imparting wood chips smaller than 1 mm. On the other hand, these have a slightly lower heating value (LHV) and higher water content than the same biomass material (<1 mm in size) in a fluidized bed reactor. The study can help develop small-scale mobile and portable ablative pyrolysis reactors for the efficient disposal and conversion of forest residues. Peacocke and Brodgwater [133] presented a novel design for the ablative fast pyrolysis reactor. Figure 5 presents a typical ablative pyrolysis reactor.

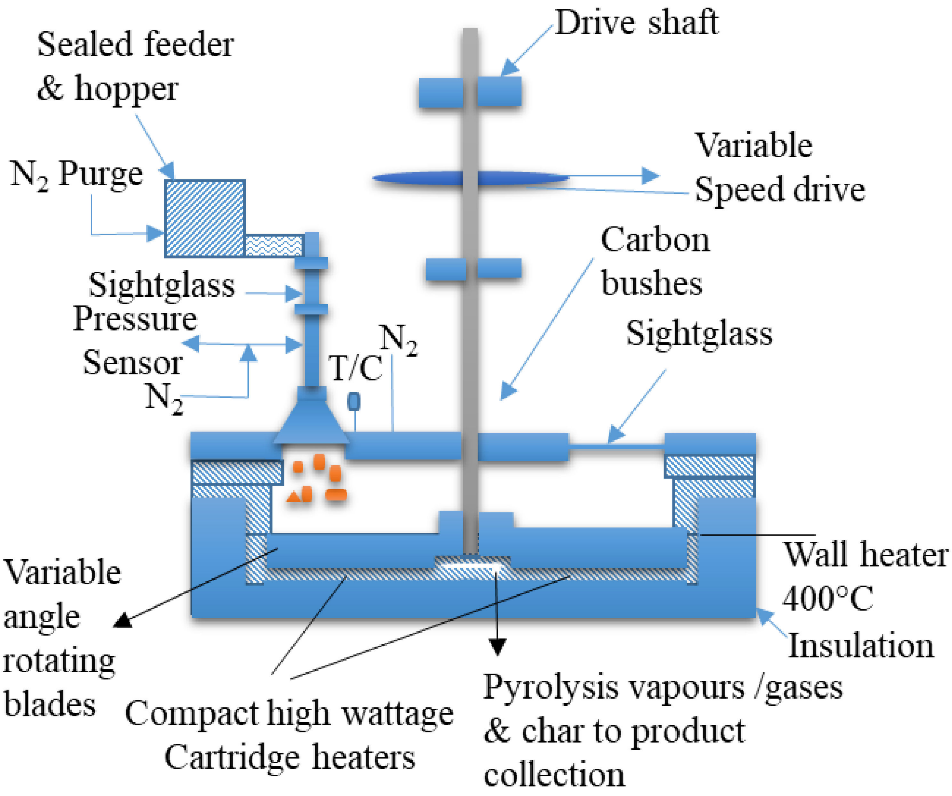

Figure 5. Ablative pyrolysis reactor, adapted from Peacke et al. 1994 with due permissions [134].

4.1.5. Fast Pyrolysis of Biomass via Entrained Flow Reactor

Entrained flow reactors, commonly known as drop tube furnaces, have been used for decades to convert coal and biomass materials into energy fuels. Principally, it consists of an externally heated vertical tube inside which hot laminar gas flow is passed to decompose the coal/biomass material thermally [135]. These reactors are usually operated isothermally, and the gas flow is heated to the reactor wall temperature. The entrained flow reactor allows the coal/biomass to encounter the same heating rate, temperature, and residence time inside the reactor tube. The entrained flow reactor has the following three characteristics for the maximum conversion efficiency: (a) short residence time of biomass in the reactor (few seconds), (b) very small feedstock size (100 µm), and (c) very high temperature (>1000 °C) [136]. The reactor can be divided into two main types: slagging and non-slagging entrained flow reactors. In the slagging entrained flow reactor, the ash leaves the bottom of the reactor as a liquid slag by melting with the reactor walls. In the latter, non-slagging entrained flow reactor, there is no problem with slag, and it is suitable for biomass with a smaller ash content. The entrained flow reactor can be used for a wide range of biomass at high pressures and temperatures [137]. Figure 6 presents the simplified type of an entrained flow reactor.

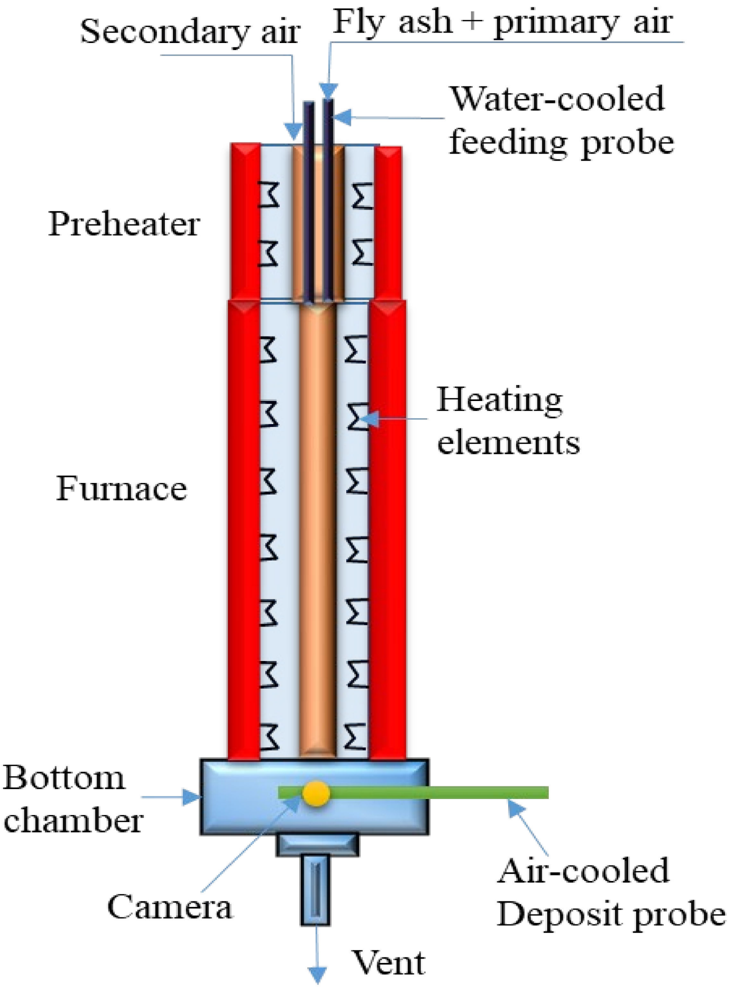

Figure 6. Entrained flow reactor, adapted from Laxminarayan et al. 2019 with due permissions [138].

Dupont et al. [139] performed the experiments in an entrained flow reactor. The study was performed to understand the kinetic processes involved in biomass pyrolysis at instantaneous heating rates (>500 K/s) and high temperatures. The temperature ranged from 1073 to 1273 K. The effects of various parameters, such as the particle size, operating temperature, presence of steam in a gas atmosphere, and residence time, were studied for conversion and selectivity. The biomass particle size was the most important factor among all these influential parameters. Pyrolysis took more than 0.5 s for a particle size of 1.1 mm and less than 0.5 s for 0.4 mm particles. The gas produced from the biomass pyrolysis through the entrained flow reactor was 70 wt.%. The amount of initial carbon was 40% as CO and 5% as CO_2. An equal distribution of hydrogen in H_2, H_2O, CH_4, C_2H_2, and C_2H_4, was observed. Bitowft et al. [140] performed the fast pyrolysis of sawdust in an entrained flow reactor. The examinations of the pyrolysis products were made over a temperature range of 1000 to 1400 °C. The particle residence time was maintained from 0.56 to 1.0 s, and the particle size fractions ranged from 250 to 630 μm. An intermediate calorific value gas was produced during the investigation. The results show that more than 87% of the biomass fed into the system was accounted for in the product streams. The reported cold gas efficiency for all the experiments exceeded 70% with an average value of 79%. Higher temperatures resulted in no tar formation for this experimental setup.

4.1.6. Catalytic Fast Pyrolysis of Biomass

The conversion of lignocellulosic materials into liquid fuels is in high demand because of the increased prices of fossil fuels, national security considerations, and potential climate disasters. Table 5 lists the comparative studies of fast pyrolysis using different types of reactors and approaches.

Table 5. Research studies for fast pyrolysis using different feedstock.

Feed Stock	Pyrolyzer Reactor	Parametric Study	Remarks	References
Stem wood	Fluidized-bed pyrolyzer	Aerosol concentrations and size distributions	Aerosols < 1 µm were formed and aerosols < 1 µm deposited during the cooling of pyrolysis vapors.	[141]
Sawdust, empty fruit bunch, and giant Miscanthus	Circulating fluidized-bed reactor	Heating value, moisture content, and ash content	Giant Miscanthus has the highest heating value amongst three biomass feedstocks.	[142]
Napier grass	Circulating fluidized-bed reactor	Reactor temperature, superficial velocity, and feed rate of feedstock	The new design of the pyrolysis system was developed to reduce the bio-oil production cost.	[143]
Wheat straw	Screw reactor	Moisture content	Moisture content as design and operational parameter for the fast pyrolysis process	[144]
Geodae-Uksae	Bubbling fluidized-bed reactor	Reaction temperature, superficial gas velocity, and sand particle inventory	Key influencing factors were identified, and optimum conditions were proposed.	[145]
Oil palm empty fruit bunch	Bubbling fluidized-bed reactor	Effect of pretreatment by acid washing	The effect of pretreatment using the dilute nitric acid solution in biomass confirmed.	[146]
Waste tire particles	Fixed-bed reactor	Different external heating temperatures	An innovative fixed-bed reactor with internals was employed to pyrolyze waste tire particles.	[147]
Prosopis Juliflora	Fixed-bed tubular reactor	Particle size, operating temperature, and heating rates	The developed kinetic model was able to predict the performance of a fixed-bed tubular reactor in terms of pyrolysis product properties.	[148]
Beetle-killed lodgepole pine	Ablative reactor	Operating temperature and catalyst/biomass ratio	The novel ablative reactor could be converted into a portable unit without the need for biomass pretreatment.	[149]
Rice straw	Free-fall reactor	Particle heating rate and particle's free-fall velocity	The designed free-fall reactor could be used for producing useful bio-products and contribute to solving problematic agriculture waste.	[150]
Wheat straw	Entrained flow reactor	Pyrolysis operating temperature	$PM_{2.5}$ yields during biomass pyrolysis are in the range of 7–34 g/kg and proportional to a pyrolysis temperature.	[151]

Various technologies are under consideration, among which fast pyrolysis is used frequently for bio-oil production [152]. Bio-oil comprises nearly 70% of the energy of the biomass feedstock. On the other hand, certain flaws in the bio-oil properties restrict its commercialization compared to crude oil-based liquid fuels. These properties include (i) lower calorific value, (ii) reduced volatility, (iii) undesired acidity, (iv) instability, and (v) incompatibility with other petroleum fuels [153]. These undesirable properties of bio-oil from lignocellulosic biomass materials are caused by the presence of oxygenated organic compounds, which are dominant in its chemical composition. The removal of oxygen is necessary to broaden the acceptance of bio-oil and to enhance its economic acceptance. Therefore, catalytic pyrolysis using various commercially available catalysts, such as zeolites, to produce aromatic range fuels is the process used to accomplish this goal in pyrolysis technology [154]. Chen et al. [155] examined the fast catalytic pyrolysis of biomass material using the ZSM5 catalyst. They reported that carbon monoxide, carbon dioxide, coke, and hydrocarbons were the main products obtained from pyrolysis. The main goal was to increase the hydrogen content in the hydrocarbons and eliminate the excess oxygen from the biomass. Therefore, the researchers reported the effective hydrogen to oxygen ratio as an outcome of this study. The mathematical form of this hydrogen to oxygen ratio was H/C = H-2O-3N-2S/C. The relation helps us understand the chemistry involved in converting oxygenates during the catalytic conversion of biomass. On the other hand, the H/C ratio for the biomass-derived oxygenates was less than the H/C ratio of petroleum-derived feedstock.

Jia et al. [156] performed the catalytic fast pyrolysis of oak in a micro fluidized-bed reactor. The two zeolites, i.e., microporous and hierarchical, were used at 500 °C and different biomass/catalyst ratios. SPI-MS was used to monitor the formation of the pyrolysis products during the stepwise injection of wood particles within the micro fluidized-bed reactor. The selectivity in the targeted mono-aromatic compounds was doubled after the desilication of zeolite. TEM-EDX was used for the characterization of coked zeolites. Three different types of coke were verified: (a) the coke trapped inside the catalyst pores, (b) the coke formed on the outer surface of the crystals, and (c) the coke originators left in the mesoporous. The evacuation of the catalytic products was promoted by the mesopores, which increased the selectivity in mono-aromatic hydrocarbons. The results also showed that the desilicated zeolite imparts more selectivity to mono-aromatics and stability upon the coke deposit than the functioning of microporous zeolite. Wang et al. [157] performed the reactive fast catalytic pyrolysis of biomass material to produce high-quality bio-crude. Reactive catalytic fast pyrolysis was performed under atmospheric pressure hydrogen. The studies were made in a laboratory-scale fluidized-bed reactor while modifying the multiple process parameters. The key parameters were the operating temperature, hydrogen concentration, and catalyst. The results showed that the quality and yield of bio-crude were enhanced in hydrogen in reactive catalytic fast pyrolysis. A molybdenum-type catalyst was reported to be the most effective in the hydrodeoxygenation phenomenon. Hydrodeoxygenation converts the biomass pyrolysis vapors to produce a hydrocarbon-rich bio-crude with a minimum oxygen content (< 10 wt.%). The moderate pyrolysis temperature of 450 °C and higher hydrogen concentration supports the increased bio-crude yields and quality.

4.2. Slow Pyrolysis Process

Biochar, also known as charcoal, is the main product of the slow pyrolysis process. Slower heating rates are used in the slow pyrolysis of biomass materials, which is approximately between 0.1–0.8 °C/s [158]. Compared to the fast pyrolysis process, the residence time in the slow pyrolysis process is kept longer. The approximate residence time in most pyrolysis reactors is 5–30 min or sometimes 25–35 h [159]. The temperature was between 300 °C to 550 °C [160]. The biomass feedstock, operating temperature, heating rate, and pyrolysis environment influence the biochar and bio-oil yield [161]. The pyrolysis environment accounts for whether pyrolysis occurs in the presence of N_2 or CO_2 and even in altered-bed materials [162]. The woody biomass contains fewer minerals than the herbaceous biomass and produces extra products. The increase in the pyrolysis temperature decreases the biochar yield. This is because, at elevated temperatures, organic materials are combusted along with the destruction of cellulose and hemicellulose materials [163]. Several technologies are used to accomplish a fast pyrolysis process:

- ➢ Slow Pyrolysis of Biomass via Fixed-Bed Reactor,
- ➢ Slow Pyrolysis of Biomass via Augers Reactor,
- ➢ Slow Pyrolysis of Biomass via Rotary-Kiln Reactor, and
- ➢ Catalytic Slow Pyrolysis of Biomass

4.2.1. Slow Pyrolysis of Biomass via Fixed-Bed Reactor

As discussed in Section 4.1.3, fixed-bed reactors are used widely in many process applications. These reactors have much importance in biomass pyrolysis because they offer many unique properties. Therefore, they are used frequently by researchers and industries for the slow pyrolysis of biomass, in which the aim is to obtain a solid product char. The fixed beds are made from a solid catalyst to increase the product yield and modify or alter the process conditions. Therefore, their application in the slow pyrolysis of biomass has great importance. Many researchers have used fixed-bed reactors for the slow pyrolysis of biomass.

Kabir et al. [164] examined the slow pyrolysis of oil palm mesocarp fiber (OPFM) and palm frond (PF) and compared the obtained results. A fixed-bed reactor was used because of its simple design. The pyrolysis process was conducted at different N_2 flow rates and temperatures to obtain the preferred products, which are bio-oil and bio-char. The products obtained from the slow pyrolysis process (heating rate of 10 °C/min) at a flow rate of 200 mL/min and temperatures ranging from 500 °C to 600 °C showed reduced gas production and a maximum yield of OPMF oil and PF oil. The proximate analysis of pyrolysis provided low ash, high HHV, and a high amount of fixed carbon, which is desirable compared to other biomass feedstocks. Ultimate analysis resulted in low oxygen to carbon ratios and low nitrogen and sulfur contents (negligible NOx and SOx emissions), highlighting these bio-oils as an excellent renewable source biofuel. Using gas chromatography-mass spectrometry (GC-MC), these bio-oils contained mixtures of oxygenated compounds and aromatic compounds, which are important for better fuel properties.

Wang et al. [165] examined the slow pyrolysis of pinewood using a fixed-bed reactor by gas sweeping to minimize the secondary reactions. The yield and characteristics for different biomasses differ. The characteristics of pinewood were clarified by determining the yields of gas, tar, and char. The experiment was performed at temperatures from 200 to 700 °C. The four major incondensable gases formed were H_2, CO, CH_4, and a smaller amount of CO_2. Thirty-eight liquid compounds were obtained from the pyrolysis process, including saccharide, carboxylic acid, furan, ketone, and aldehyde, resulting from dehydration and decarboxylation. While cellulose maintained its actual structure, it decomposed at 300 to 450 °C, providing large amounts of liquids and gaseous products. The residues of this process decomposed at temperatures from 450 to 700 °C to form several types of gases.

4.2.2. Slow Pyrolysis of Biomass Using the Augers Reactor

Small- and medium-sized industries have become increasingly interested in the use of auger reactors for the pyrolysis of lignocellulosic biomass materials. The simplicity in its construction and operation makes it popular among the other technologies [166]. The operating mechanism of the auger reactor involves the continuous feeding of the biomass material into the inlet of a screw feeder, which supplies the material to the heating zone of the pyrolysis chamber along the axis of its rotation. The system could have a single or twin-screw feeder depending on several factors, such as the feeding rate and required feedstock particle size for the heating zone. Biochar is received at the bottom of the reactor after the decomposition of biomass materials. Pyrolysis gases and other volatilities also leave the reactor. The system has the following advantages: (i) simple operation, (ii) no requirement of carrier gas, and iii) low energy consumption. One major advantage is the controlled residence time of biomass in the heating zone by adjusting the rotational speed of the screw feeder. A typical yield of bio-oil from the auger reactor is in the range of 40–60% of the feedstock. The yield depends mainly on the operating conditions and is generally less than that obtained in fluidized-bed reactors. Figure 7 shows a simplified auger reactor used for biomass pyrolysis [167].

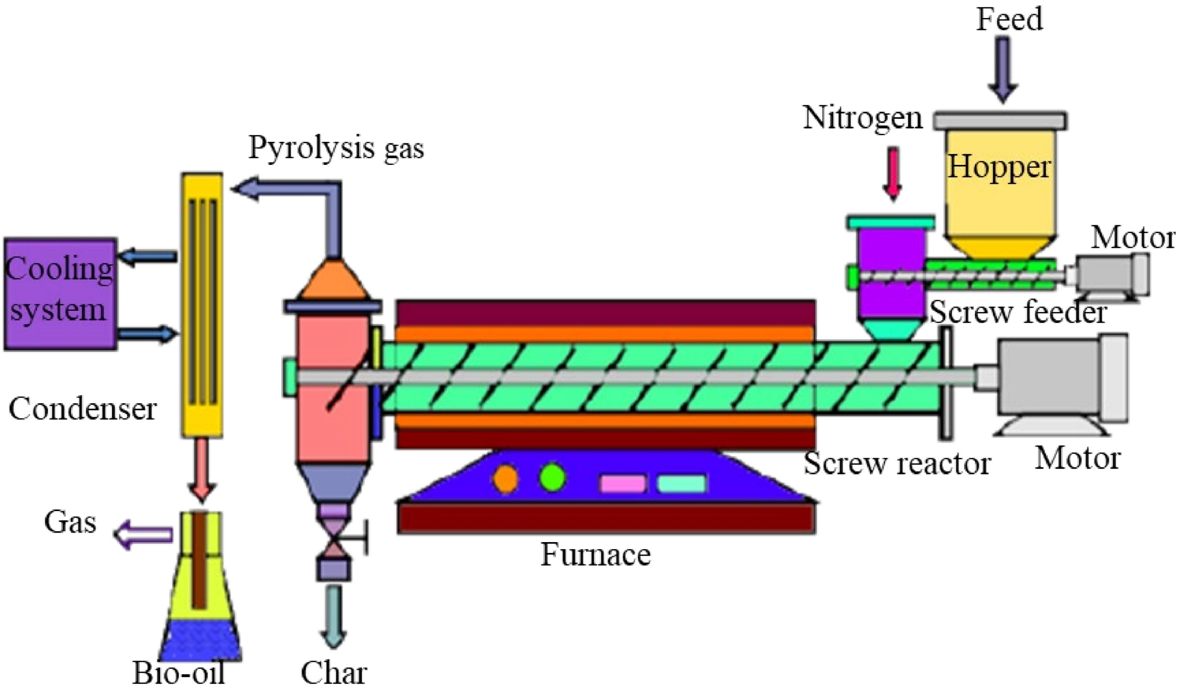

Figure 7. Augers pyrolysis reactor, adapted from Pichestapong et al. 2013 with due permissions [168].

Manuel et al. [169] reported the production and characterization of fuel properties for biomass-based bio-oil and bio-diesel blends using slow pyrolysis auger reactors. The synthesis of pyrolysis-based bio-oil has been of particular interest using the simple system. The biomass material used for this experimental study was pine chips and pine pallets. The preparation of bio-oil and the fuel properties of the bio-oil/biodiesel blends are reported. The liquids condensed from pyrolysis consist of two phases: (a) an aqueous phase and (b) a dense, oily phase (bottom phase). Another additional phase called the polar phase is formed after removing water from the aqueous phase. The oily bottom phase has an affinity with biodiesel, making it soluble. The factors that account for the poor fuel properties are the presence of water and low-molecular compounds. These factors are also responsible for the lower solubility of bio-oil with biodiesel. Important fuel properties on which bio-oil/bio-diesel blends can be assessed are pH, viscosity, density, heating value, and water content.

Shi-Shen Liaw et al. [170] examined the operating temperature effects on the yield of pyrolysis liquid products. The biomass material used in their study was Douglas firewood, and they applied slow pyrolysis using the augers reactor technology. The operating temperature was 200 to 600 °C for the experimental tests. The bio-oil yields gained (59 wt.%) from the pyrolysis through the auger reactor were similar to those of fluidized bed reactors. The maximum bio-oil yield was achieved at a reaction temperature of 500 °C. The mass percentage of the water yield from the auger reactor was compared with the other biomass materials processed in fluidized bed reactors. They confirmed that the pyrolysis of biomass in an auger reactor could produce a good yield of bio-oil and bio-char. Slower heating rates and secondary reactions, however, affect the composition of the pyrolysis products.

4.2.3. Slow Pyrolysis of Biomass via Rotary Kiln Reactor

The pyrolysis of biomass in a rotary kiln finds use as an intermediary stage in multi-stage gasification and as a process to produce biochar. Rotary kilns are the favored reactor structure for the thermal treatment of particulate solids. Substantial research has been conducted to determine their performance for the utilization of lignocellulosic biomass materials [171]. Rotary kiln pyrolyzers are preferable over many other reactors because of their many various unique advantages. The distinctive properties of products from biomass materials can be obtained by the slow rotation of the inclined rotary kiln pyrolyzers. The residence time of the feedstock in the kiln chamber can be controlled, and appropriate adjustments for optimal operation can be made. These kilns also allow the use of biomass with a wide range of sizes, shapes, and calorific values, which can be fed continuously or in batches [172]. These reactors are also less sensitive to the fuel nature. Hence, they can accommodate an enormous diversity of biomass materials without any pre-treatment [173]. Figure 8 presents the experimental setup of a laboratory-scale rotary kiln used in biomass pyrolysis.

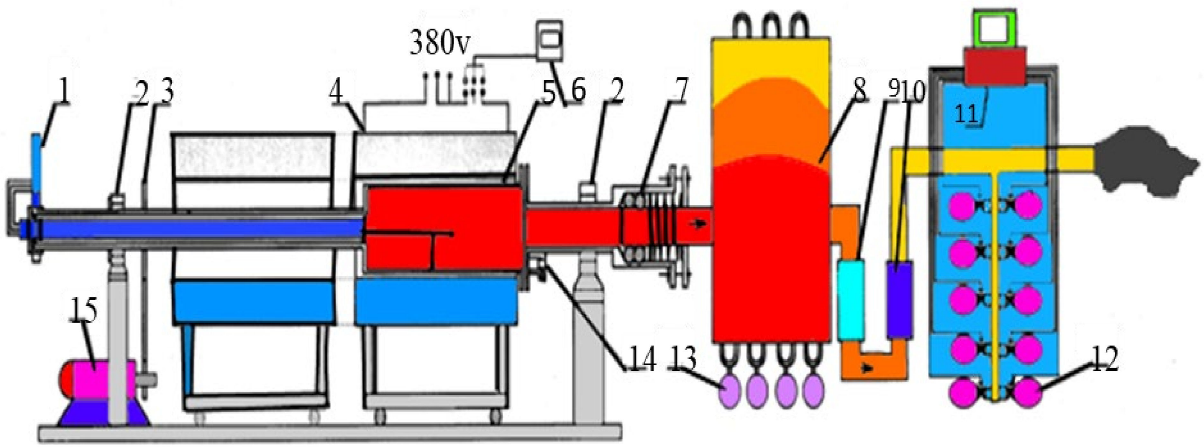

Figure 8. Laboratory-scale rotary kiln pyrolyzer configuration. (1) Thermometer; (2) bearing; (3) gear transmission; (4) electrical furnace; (5) rotary kiln; (6) temperature controller; (7) seal; (8) tube type condenser; (9) filer; (10) total flow meter; (11) computer; (12) gas sampling device; (13) tar reservoir; (14) feed and discharge opening; and (15) feed and discharge, adapted from Li at al. 199 with due copyright and reprint permissions [174].

Fantozzi et al. [175] examined the production of syngas and char from biomass and waste by using a slow pyrolysis process in a rotary kiln. They used a laboratory-scale designed electrical rotary kiln. The gas cleaning system consisted of a wet scrubber that removes the tar and the dust particles. There is also a monitored combustion chamber for an analysis of the LHV of the producer gas. They reported the effects of the pyrolysis temperature and residence time on syngas production, char yields, and amount of tar. The study primarily developed the relationship between theoretical and experimental calculations. The association developed in their research is helpful for determining and designing the working envelope of a rotary kiln as a function of the feedstock bulk density and moisture content.

Colin et al. [176] assessed the rotary kiln pyrolysis of biomass material. The biomass material in this study was wood chips. The modeling and simulation of the system were performed to forecast the effects of various operating parameters on the product yields. The target of the study was to analyze the flow pattern of the biomass material during the pyrolysis process, which is also an important parameter for rotary kilns and influences the product formation. Two other important factors are the mean residence time and the bed depth profile. Both parameters were calculated using the standard Saeman model. The mean residence time for the biomass materials was determined using residence time distribution (RTD) experiments. For these experiments, biomass materials (raw and torrefied wood chips) were used in a powdered form inside the rotary pyrolysis kiln. The mean residence time of the rotary pyrolysis system correlated with many process parameters, such as the inclined slope of the kiln, rotational speed for pyrolysis, biomass inlet feeding rate, and flow rate. The installation of a small plug flow was emphasized if some segregation phenomena were observed. The Saeman model was adjusted to forecast precisely the load profile and the mean residence time of particles with parallelepiped form.

The inconsistency amid the experimental and calculated results was minimized from 25% to 5% for the mean residence time and mean solid hold-up.

4.2.4. Catalytic Slow Pyrolysis of Biomass

The presence of a catalyst in the fast biomass pyrolysis aims to increase the bio-oil yield and alter its composition by decreasing the oxygenated content in its chemical composition. The catalytic slow pyrolysis of biomass was performed to increase the biochar yield, which is the primary product of slow pyrolysis. Therefore, the use of catalysts in slow pyrolysis is important for controlling the bio-char quality and composition. Catalysts are employed for several reasons during the process, including (i) lower pyrolysis temperature, (ii) higher chemical and physical stability, and (iii) higher yield of target components. The technology of catalytic slow pyrolysis of biomass is under consideration for further research by the scientific community and has been implemented in industries for biochar production. Catalysts are known to be effective bio-oil upgraders because they exhibit high resistance to deactivation due to their uniform pore structure and suitable acidity. Several studies have been reported that catalysts play vital roles in the manufacture of good quality recovery of products [177]. Catalytic pyrolysis of plastic is a promising technology and requires specific reactor configurations and operating conditions. Rashid Miandad et al. [178] performed the catalytic pyrolysis of different types of plastics wastes (PS, PE, PP, and PET) as single or mixed in different ratios, in the presence of modified natural zeolite (NZ) catalysts, in a small pilot scale pyrolysis reactor. The experiments were carried out in a small pilot-scale pyrolysis reactor at 450 °C, using a heating rate of 10 °C/min and reaction time of 75 min. The catalytic pyrolysis of PS produced the highest liquid oil (70 and 60%) compared to PP (40 and 54%) and PE (40 and 42%).

Du et al. [179] performed the slow catalytic pyrolysis of biomass and identified the multiple routes and mechanisms of char and coke production. These two products cannot be considered identical because they inhabit different sites on the surface of the catalyst and respond separately to the deactivation phenomenon of the catalysts. The catalyst used for this research was ZSM-5, which was examined to determine the char and tar yields from biomass and the level of catalyst deactivation from pine sawdust, glucose, and cellulose as biomass feedstock in these experiments. The composition, oxidation reactivity, catalyst surface area, pore size distribution changes, and bonding groups were analyzed for the char and tar produced by the slow thermal and catalytic pyrolysis of biomass material. According to their study, the catalyst surface was covered with char in the macropores. The coke accumulates inside the zeolite micropores, which were facilitated by hydrogen transfer and pyrolysis addition reactions. The influence of the catalyst on glucose and pine slow catalytic pyrolysis is related to that on cellulose slow catalytic pyrolysis due to macropore blocking by char formation. Russell et al. [180] utilized the slow catalytic biomass pyrolysis process to increase the charcoal yield and the synthesis of low-molecular oils. Significant research work to reduce CO_2 production and enhance the product yield and quality from biomass pyrolysis is in progress. There is the probable use of the catalytic slow pyrolysis process to produce charcoal, which can be used for cooking and soil remediation. Aluminosilicate catalysts had high potential to make this process more efficient and increase the yield. They concluded that this catalytic process could be useful for slow pyrolysis using low-cost aluminosilicate minerals, particularly bentonite clay. The study also reported the increase in charcoal yield with the addition of bentonite clay (60 wt.%). At 700 °C with a 60% clay filling, the charcoal yield improved 16 wt.% (dry ash-free basis), but at the same time, 19% of additional gas was generated at the expense of 35% of the oil from raw pine pyrolysis. Table 6 lists the comparative studies of slow pyrolysis using different reactors and approaches.

Table 6. Research studies for slow pyrolysis using different feedstock.

Feed Stock	Pyrolyzer Reactor	Parametric Study	Remarks	References
Orange bagasse	Semi-batch reactor	Operating temperature, heating rate, and N_2 gas flow rate	Biochar has an HHV of 27.76 MJ/kg because of lower O_2 content than its parental biomass.	[181]
Lignin-rich digested stillage	Fixed-bed reactor	Operating temperature, heating rate, and holding time	It is considerably better than straw-based biochar with identical H/C and O/C ratios.	[182]
By-product lignin samples from wood-based bioethanol production	Laboratory-scale batch reactor (fixed bed reactor)	Pyrolysis operating temperature and heating rate	A detailed analysis of fuel characteristics, moisture uptake, and the flow properties of lignin chars derived from slow pyrolysis was presented.	[183]
Wood chips	Rotary kiln reactor	Bed height, bed velocity, and heat flow, flow rate nitrogen, operating temperature	A modular numerical model for the pyrolysis of biomass in a rotary kiln is presented.	[184]
Maize	Rotary kiln reactor	Operational temperature, solids residence time, and solid space-time	The result suggests a strong effect and pyrolysis temperature and a noticeable effect of space velocity.	[185]
Oil sludge pyrolysis	Rotary kiln reactor	Particle motion in rolling mode and temperature distribution	A dynamic model of oil sludge pyrolysis in a rotary kiln with a solid heat carrier was developed.	[186]
Furfural residue	Auger pyrolysis reactor	Effects of temperature and additives	Microwave-assisted pyrolysis of furfural residue was performed in auger reactor to optimize process parameters for maximum biochar production.	[187]
Douglas for wood	Auger pyrolysis reactor	Effect of thermal pretreatment temperatures	Treatment below 300 °C does not have a major effect on product yields.	[188]
Pinewood	Auger pyrolysis reactor	Effect of catalytic properties (acidity, pore size, and pore structure)	An integrated reactor system is reported for catalytic pyrolysis of pine wood.	[189]
Corn straw	Fixed-bed reactor	Effect of different moisture content, and different ash content	This work provides an overall understanding of corn combustion for a large boiler system.	[190]

5. Advanced Pyrolysis Processes

In addition to the two main classes of biomass pyrolysis technologies (slow pyrolysis and fast pyrolysis), there is another category of pyrolysis that is referred to as advanced pyrolysis. These processes lie in between the operating domains of both fast and slow pyrolysis and have benefits that are sometimes not possible with a single category of pyrolysis technology. Hence, a wide range of categories is available for these advanced biomass pyrolysis processes. The most developed technologies among these biomass pyrolysis processes are as follows:

1. Vacuum pyrolysis of biomass,
2. Microwave pyrolysis of biomass,
3. Flash pyrolysis of biomass,
4. Biomass pyrolysis via plasma technology, and
5. Biomass pyrolysis via solar energy.

5.1. *Vacuum Pyrolysis of Biomass*

Vacuum moving-bed reactors are used for the vacuum pyrolysis of biomass materials. It is not a type of fast pyrolysis, but the aim is the enhance the bio-oil yield. The working principle suggests that the introduction of vacuum conditions reduces the residence time of the pyrolysis vapors. This hinders the occurrence of secondary vapor-phase reactions. Compared to other pyrolysis techniques, vacuum pyrolysis can handle large biomass particles because of less heat transfer demand. The inert carrier gas medium is also not needed in this pyrolysis technology [191]. The concept is to employ the conditions of slow and fast pyrolysis simultaneously. Therefore, the coarse biomass particles are heated slowly but at temperatures higher than in slow pyrolysis. The pyrolysis gases are removed very quickly from the heating zone with the application of reduced pressure. Vacuum pyrolysis of biomass requires high investment and maintenance costs because a special control system is needed to feed the biomass and discharge gases while maintaining the vacuum conditions [192]. Despite this flaw, it has the following advantages: (i) good product quality, (ii) liquid product condensation, (iii) particle size, (iv) ease in component extraction, and (v) very little or no char formation [65]. Figure 9 shows a laboratory-scale vacuum pyrolysis reactor.

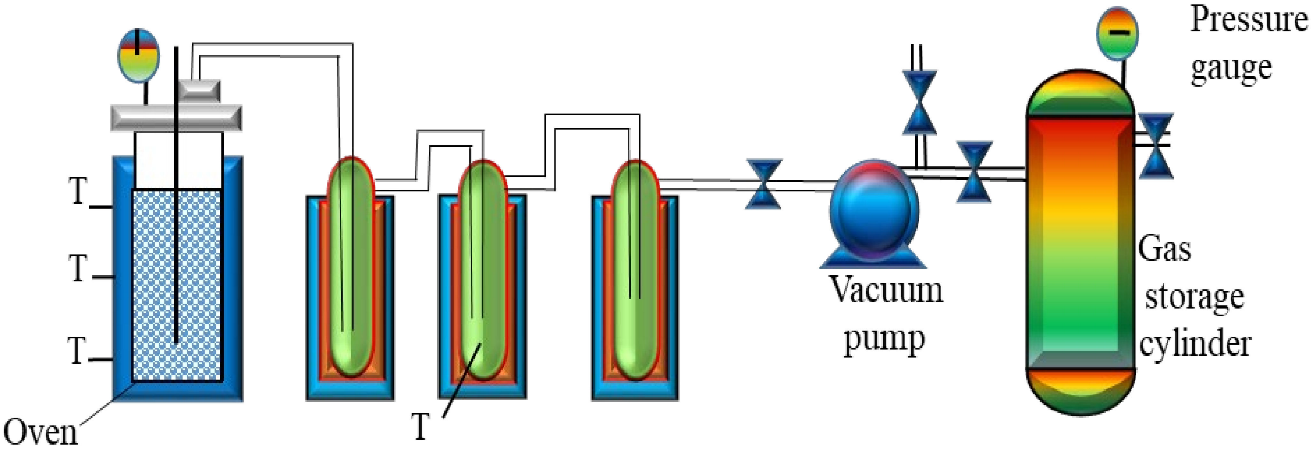

Figure 9. Laboratory-scale vacuum pyrolysis reactor, adapted from Perez et al. 2002 with due permissions [193].

Garcia et al. [194] investigated the yield and properties of pyrolysis products. The technology used for the study was the vacuum pyrolysis of biomass materials. The focus was on analyzing the properties of bio-oil. Softwood bark (SWBR) and hardwood rich in fiber (HWRF) were used as the biomass feedstock in vacuum pyrolysis. The thermogravimetric technique was used to analyze the lignin, cellulose, and hemicellulose content. The results showed that the SWBR biomass holds 14.8 wt.% of extractives and an accumulative lignin content of 44.8 wt.%, while the second studied biomass HWRF contains 40.1 wt.% of cellulose and 27.8 wt.% of hemicellulose material. Vacuum pyrolysis produces the immiscible phases for bio-oil produced, which is later separated by decantation. The upper oil layer is comprised of 16 wt.% SWBR and incorporates higher than 50 wt.% of the extractive-routed compound mixture. HWRF presents a portion of 1.3 wt.% of the entire initial oil, which was a waxy phase consisting of paraffin, sterols, and fatty acid methyl esters. On the other hand, the bottommost layer from both the biomasses was identical to the bio-oils gained from bark-free wood. Xu et al. [195] performed the vacuum pyrolysis of the biomass using the catalyst. The Mo-Ni/Al_2O_3 catalyst was used to upgrade the bio-oil. The biomass material used was pine sawdust, and the bio-oil was produced under the optimal operating parameters. A various set of nickel-based catalysts were made, and their catalytic activities were monitored. The assessment was carried out by upgrading the glacial acetic acid (model compound). The modified Mo-10 Ni/Al_2O_3 catalyst was used to upgrade the pyrolysis crude bio-oil. The pH of the crude oil increased from 2.16 to 2.84, and the water content increased from 46.2 wt.% to 58.99 wt.% after upgrading. The hydrogen content increased from 6.61 wt.% to 6.93 wt.% and the dynamic viscosity decreased slightly. The GC-MS spectrometry outcomes revealed a three-fold increase in the ester compounds after the upgradation process. Recently, Ying et al. [196] used the microwave vacuum pyrolysis technique to convert cassava stem into biochar. The morphology of the biochar has abundant pores, indicating it to be a good catalyst and a surface for the adsorbance of heavy metals in wastewater treatment. For conventional use as an energy fuel, it had a calorific value between 19 and 21 MJ/kg. That study confirmed that low-grade cassava stem could be converted to energy fuel and be used as a catalyst source using microwaves.

5.2. Microwave Pyrolysis of Biomass

The microwave pyrolysis of biomass has been under consideration in the scientific community for a few decades, and progressive research is being carried out. Microwave pyrolysis technology differs in the principle of operation compared to other well-established biomass pyrolysis techniques because the heating of biomass material is intrinsic, not extrinsic [197]. A very high heat source is not required to decompose the biomass material. The biomass material with a high dielectric constant or loss factor is preferable for microwave pyrolysis. Water is a good example of a component feasible to be subjected to microwave pyrolysis. When a biomass material with a high moisture content is pyrolyzed by microwave heating, the water is first driven off rapidly. The remaining biomass retains heat and starts forming char [198]. Microwave pyrolysis is electrically conductive, and eddy currents are formed that establish prompt heating. Hence, controlling the microwave operating conditions for the required results is the main task. The microwaves can penetrate only 1–2 cm. Therefore, a microwave reactor offers interesting scale-up challenges. An environment is formed in microwave pyrolysis due to the uniform heating of the biomass material, leading to learning and exploring the fundamentals of the pyrolysis mechanism. This also helps us to understand the effects of the thermal gradient in a pyrolysis particle and the secondary reactions that occur during biomass pyrolysis. Figure 10 presents the process flow diagram for the microwave pyrolysis of biomass material [65].

Bu et al. [199] reported the microwave pyrolysis of biomass using a catalyst and consuming activated carbon (AC). The effects of the catalytic microwave pyrolysis on the production of phenol and phenolics were investigated. Various pyrolysis-operating parameters were also analyzed to report their consequences on the yield of products. Pyrolysis bio-oil with a high concentration of phenol (39%) and phenolics (70%) was produced. The better results were linked with the rapid dissociation of lignin due to the AC. Therefore, these results were better than those performed in the absence of AC. Zinc powder was used as a catalyst medium, and formic acid or ethanol was utilized as the reaction medium. A high concentration of esters (43%) was obtained in the upgraded bio-oil because of the catalyst. The characterization performed by GC-MS showed that the maximum esters developed were long-chain fatty acid esters. The study results suggest that after removing the oxygenates, the high content of esters and phenols produced can be used instead of traditional fossil fuels. Refining can lead to their use in chemical and process industries for organic synthesis.

Robinson et al. [201] examined the microwave pyrolysis of biomass. The biomass material used for this study was wood pellets. The technology involved a single-mode microwave cavity. The dielectric properties of the wood pellets were calculated up to 700 °C. The water acted alone as the microwave absorbing phase in the wood pallets as biomass in microwave pyrolysis below 600 °C. The research presents a new aspect of using the microwave pyrolysis of biomass without using carbon-rich dopants. Water formed below 600 °C alone is sufficient to encourage the pyrolysis of wood pallets. Their research also highlighted many mechanisms that connect the power density inside the pyrolyzed material. The pyrolysis products, i.e., bio-oil and pyrolysis gas, were dependent on the heating rates, operating temperature, and power density. The wood pellets used in the research work had a minimum threshold value of 5.0×10^8 W/m^2. Microwave pyrolysis will not proceed if the value is less than this standard value. This research has great worth in understanding the basic mechanisms of the microwave pyrolysis of biomass. In a recent study, Ren et al. [202] converted horse manure to biochar by microwave pyrolysis. The quality of biochar was affected by temperature, catalyst loading, and carrier gas flow rate. The biochar had a calorific value of 35 MJ/kg and a high surface to volume ratio. Biochar with a high surface area is a good candidate for a bio-adsorbent and an additive for soil improvement. A microwave pyrolysis temperature of 350–450 °C and catalyst/manure ratio of 1:1 were optimum for this investigation. Synthesis gas at 73.1 vol% with heating value 14.85 MJ/m^3 was also obtained.

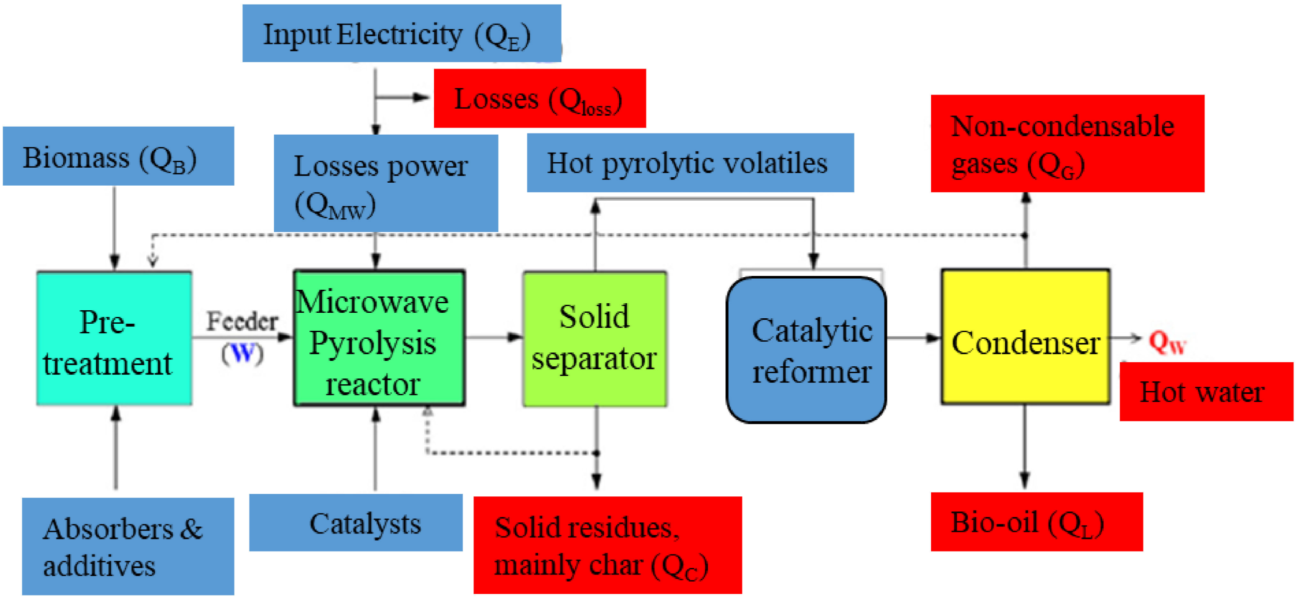

Figure 10. Process flow diagram for microwave biomass pyrolysis, adapted from Yin et al. 2012 with due permissions [200].

5.3. Flash Pyrolysis of Biomass

There are certain physical conditions of biomass pyrolysis that have a high impact on the product quality, product composition, and product yield. These parameters are (i) operating temperature, (ii) heating rate, and (iii) residence time. In biomass pyrolysis, more liquid products with less char and gas formation occur if the operating conditions are in the following constraints (a) higher heating rate, i.e., 10^4 K/s, (b) temperature <650 °C, and (c) rapid quenching. The biomass pyrolysis operated under these conditions is referred to as flash pyrolysis. Higher heating rates with temperatures >650 °C favor the formation of gaseous products, and slow heating rates with the lowest maximum temperature favor the formation of char [203]. The residence time of only a very few seconds or even sometimes less with high temperatures demands a pyrolysis reactor configuration capable of very high heating rates. Most flash pyrolysis studies were carried out in an entrained flow reactor or fluidized-bed reactor [204]. Biomass flash pyrolysis technology is versatile, simpler, and requires a little capital investment. The technology produces bio-oil with a yield of 60–75 wt.% and consists mainly of a complex mixture of oxygenated compounds whose composition depends on the biomass material used and the pyrolysis operating conditions [205]. Figure 11 represents a simplified pictorial of biomass flash pyrolysis. Pokorana et al. [206] reported that municipal wastewater treatment sleds are difficult to manage and expensive problems to solve. Landfill is a common disposal process. Many European countries rely solely on landfill and the dumping of waste materials. Landfill requires considerable space to fulfill the requirements continually. The soil also must be protected against the toxic and hazardous compounds of municipal sludge. Instead of landfill for these wastes, thermal treatment is the most feasible alternative to deal with the issue. The carbon and sulfur emissions caused by combustion need to be controlled to protect the environment. Pyrolysis from a thermochemical route has the potential to solve the severity of this issue. The process of degrading the biomass occurs in an inert atmosphere. Various types of products are achieved, i.e., bio-oil, biochar, and pyrolysis gases. Flash pyrolysis is a technology to enhance the liquid product from the pyrolysis process. The heating rate in flash pyrolysis is very fast, and a dark brown liquid consisting of a composite blend of oxygenated hydrocarbons is formed. Liquid bio-oil production can be stored until its application.

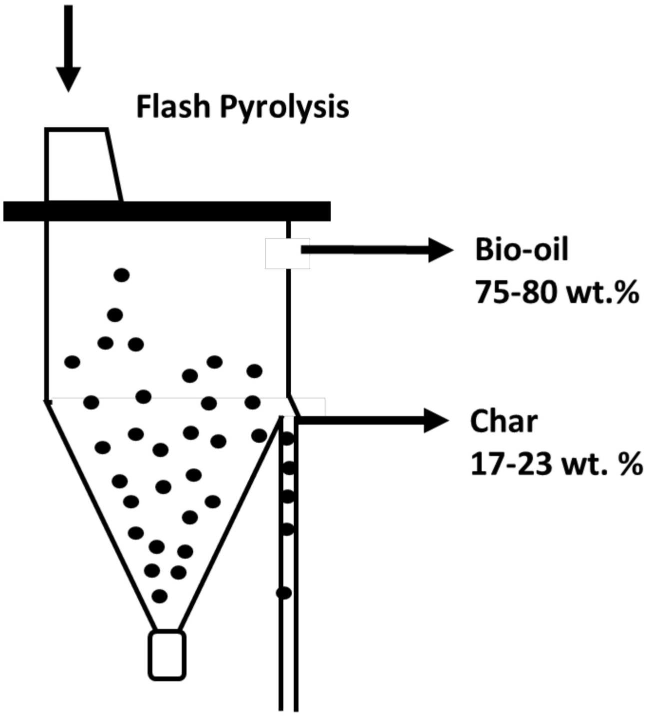

Figure 11. Biomass flash pyrolysis, adapted from Amutio et al. 2013 with due permissions [207].

Goyal et al. [20] published an article on biomass pyrolysis to produce excess bio-oil. The flash pyrolysis technology was adopted to enhance the yield of liquid fuel. Fast pyrolysis was performed, allowing the pyrolysis reaction to take place in a few seconds or even less. This research scheme implies the application of flash pyrolysis through the entrained flow reactor and fluidized bed reactor. The pyrolysis in both reactors was carried out at very high heating rates. The size of the cellulose materials ranged from 105–250 µm. Flash hydro-pyrolysis technology was carried out in a hydrogen atmosphere at pressures up to 20 MPa. Another technology is solar flash pyrolysis, in which concentrated solar energy is used to perform flash pyrolysis. Solar energy is collected through solar collectors, solar towers, and dish connectors.

In the latest study published by Matamba et al. [208], flash pyrolysis of a palm kernel shell was performed. The operating temperature and pressures were 600–900 °C and 0.1–4.0 MPa, respectively. They examined the effects of pressure in flash pyrolysis for the increased production of the desired product. Increased pressures and temperatures particularly stimulated the formation of polycyclic aromatic hydrocarbons and H_2 gas. At lower temperatures and pressures, the bio-oil samples produced were composed primarily of phenolics. Higher temperatures and pressures improved hydrogen transfer to a light gaseous phase. The production of hydrogen peaked at 40.82 g of H_2/kg of PKS at 900 °C and 2.0 MPa. They showed that the pyrolysis of biomass at high pressures could be a preferable technique for the polygeneration of hydrogen gas and aromatic hydrocarbons as chemical feedstocks.

5.4. Pyrolysis of Biomass via Plasma Technology

Compared to conventional biomass pyrolysis techniques, plasma pyrolysis technology offers many unique properties. These advantages are possible at low temperatures and slow heating rates [209]. The problems that are associated with conventional biomass pyrolysis, such as low gas yield and high tar amounts, can be eliminated by plasma pyrolysis technology. This is possible because of the fast reaction times, high energy density, and temperature offered by plasma pyrolysis technology [210]. Many plasma pyrolysis applications lie in the destruction of noxious materials because of the high-power energy required for its operation. Therefore, thermal plasma technology for biomass pyrolysis has been less explored due to economic constraints. The temperature obtained in thermal biomass plasma pyrolysis is very high (3000–10,000 K), and much of the energy is radiated and conducted to the surroundings [211]. Many energy species, such as electrons, ions, atoms, free radicals, and activated molecules, are present in the thermally activated plasma. The temperature exceeds 3000 K when thermally activated by an electric arc discharge. When carbonaceous materials, such as biomass or coal, are treated with plasma, they decompose with sudden heating, and volatile components are released. These components are mostly CH_4, CO, H_2, C_2H_2, and various light hydrocarbons [212].

Huang et al. [213] examined the plasma pyrolysis process for the production of various products. Two products that were the focus of this research were the pyrolysis syngas (CO + H_2) and carbon absorbent. The type of technology implemented in this research work was a radio-frequency plasma reactor. The scope of the study was broadened to different temperatures and pressures (3000–8000 Pa). The power supplied to the plasma reactor ranged from 1600 to 2000 W. The process parameter conditions affected the pyrolysis products. The char amount produced, combustible gas amount, syngas composition, and the quality of char obtained were measured. The maximum syngas yield (66 wt.%) was obtained because of the power supply of 1800 W and pyrolysis operation pressure of 500 Pa. The syngas composition (CO and H_2) consists of 76 vol% on a N_2-free basis. The solid produced has a large surface area with a high pore volume. This also has many micropores with potential use as activated carbon. Tang et al. [214] published the results of the experiments on the plasma technology pyrolysis reactor. The advanced pyrolysis technology utilized for the research work was the argon/hydrogen plasma pyrolysis reactor. The experimentation was performed on a laboratory-scale reactor. Hydrogen, carbon monoxide, and methane were the combustible pyrolysis gases from this pyrolysis arrangement. The results showed that this technology has a high benefit of carbon conversion into combustible gases. The conversion was 79% for carbon and 72% for oxygen in the gaseous products. The producer gas has high potential applications as syngas. The use of biomass material as an energy resource has many ecological benefits. Therefore, biomass has been given priority over fossil fuels for utilization in plasma pyrolysis reactors.

5.5. Pyrolysis of Biomass via Solar Energy

Solar energy-assisted biomass pyrolysis is an endothermic process of converting the biomass material into an inert atmosphere, which is suitable for its decomposition. The necessary thermal energy is supplied by concentrating solar energy. An optical system assists in redirecting and focusing the solar energy on the biomass pyrolysis reactor. Hence, the required biomass pyrolysis temperatures are achieved by the concentrated solar energy. Three possible mechanisms are developed to transfer solar energy to biomass materials. These methods include (i) passage through the reactor walls, (ii) direct application of solar irradiation of the biomass materials, and (iii) through intermediate heat carrier fluid. The secondary pyrolysis reactions in the gas phase can be minimized or eliminated by irradiating the biomass material directly from solar energy because, in this method, the biomass becomes the hottest part, and the reactor walls remain at a lower temperature [215]. The plasma pyrolysis reactor configuration is shown in Figure 12 [216].

Biomass solar pyrolysis can also be accomplished using thermo-solar systems. This system provides the heating source by redirecting the solar radiation from a large surface to a smaller area. This system has three core components: (a) solar concentrator, (b) solar collector, and (c) supporting structure [217].

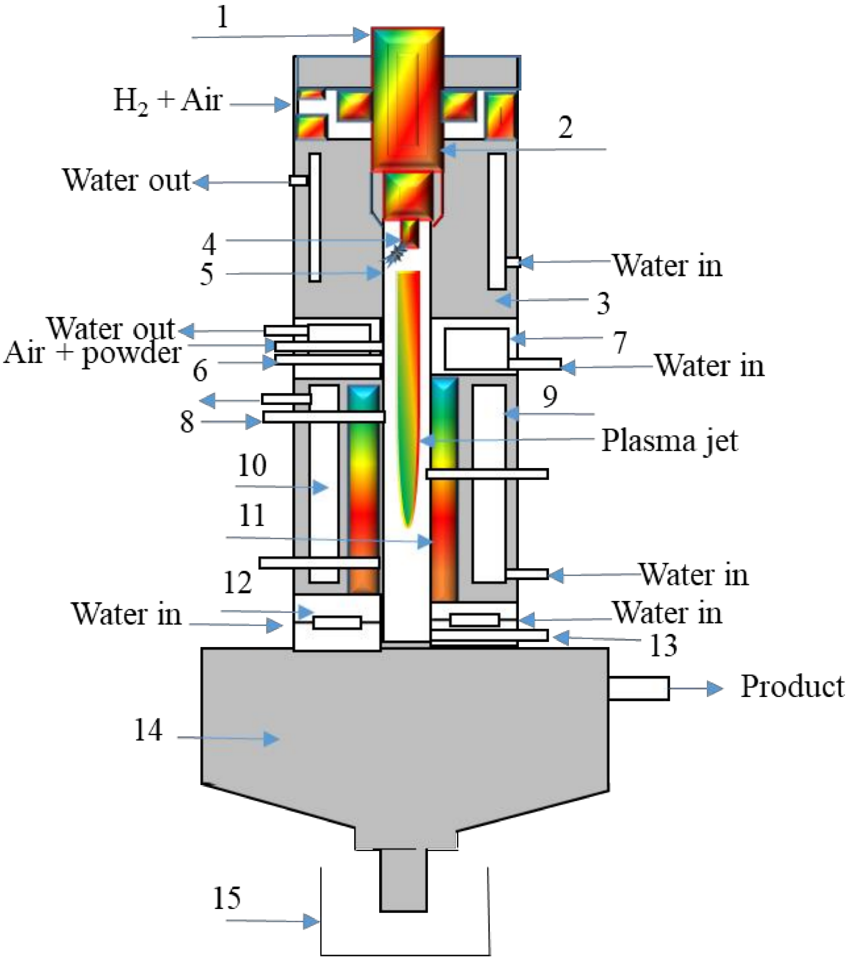

Figure 12. Plasma pyrolysis reactor configuration. (1) Cathode; (2) insulation; (3) anode; (4) arc; (5, 11) graphite linings; (6, 8, 13) sampling holes; (7) injector; (9) reactor; (10) cooling water; (12) water spray; (14) separator; (15) water filter, adapted from Zhao et al. 2001 with due permissions [216].

Adinberg et al. [218] presented an innovative solar pyrolysis process and experimental apparatus for the thermochemical conversion of biomass into valuable products. The core thematic scheme lies in the distribution of biomass materials into the molten inorganic salt medium. The energy is supplied for pyrolysis through solar energy. The reactions took place in a high-temperature liquid phase by absorption, concentrating, keeping, and relocating the solar energy to the desired operation and application. A tailor-made solar pyrolysis reactor (laboratory-scale) was designed to have the potassium and sodium carbonate salts. The complete kinetics of the solar-assisted fast pyrolysis and the characteristics of the heat transfer mechanisms for the biomass particles were studied in molten salt media. The reaction temperature and heating rate influence the pyrolysis products and yields. The preferable optimal temperature and heating rates were 1073–1188 K and 100 K/s, respectively. The study concluded that the pyrolysis of biomass materials in molten salt phases and the use of solar energy for its operation is a feasible, economical, and continuous way of producing valuable solid and liquid pyrolysis fuels. These results were validated through the commercial-scale solar pyrolysis biomass reactor. Zeng et al. [219] exploited the laboratory-scale pyrolysis solar reactor to examine the effects of operating temperature and the rate of heating for beech wood as the biomass material. These effects were studied with special focus on the char yield and its properties. The solar pyrolysis reactor was designed to operate over a temperature range of 600 to 2000 °C and continuous heating ranges of 5 to 450 °C/s. The char yield, composition, and structure changed with the operating pyrolysis temperature and heating rates. The products were examined by scanning electron microscopy (SEM), X-ray diffraction, and CHNS (total carbon, hydrogen, nitrogen, and sulfur analysis). The acknowledged char structure was affected by slow heating rates and high temperatures. Pyrolysis temperatures up to a maximum of 1200 °C resulted in a considerable increase in the surface area and pore volume of the produced char. On the other hand, these properties showed opposite results beyond this temperature limit. TGA of char reactivity was measured to determine the progress of the char surface area and pore volume with temperature and heating rate. Chen et al. [220] recently performed upgrading of bio-oil via solar pyrolysis of the biomass pretreated with aqueous phase bio-oil washing, solar drying, and solar torrefaction. The pretreated biomass was dried at 100 °C and for 30 min and torrefaction at 250 °C and 30 min using a parabolic trough solar collector system. The outcomes showed that solar energy can guarantee the temperature essential for biomass drying torrefaction and may substitute for electric or fossil fuel-based heating. Table 7 shows the kind of parametric studies carried out by different researchers for advanced pyrolysis process.

Table 7. Research studies for advanced pyrolysis technologies using different feedstock.

Feed Stock	Pyrolyzer Reactor	Parametric Study	Remarks	References
Kraalbos, Schotzbos, and Asbos	Vacuum pyrolysis	Pyrolysis temperature, pyrolysis time, pressure, and initial moisture content	The study of vacuum pyrolysis of intruder plant species showed that it is possible to produce economically viable, high-energy charcoal and oil products.	[221]
Birchbark and birch sapwood	Vacuum pyrolysis	Distribution of phenols, charcoal, and water as a function of temperature	Under vacuum, stepwise thermal decomposition of biomass under low-temperature conditions is less destructive, which simplifies the analysis of pyrolysis oil.	[222]
Sycamore wood	Microwave pyrolysis	Effect of energy input on the pyrolysis process	A novel application of microwave pyrolysis within a liquid medium is proposed.	[223]
Rice straw, rice husk, corn stover, sugarcane bagasse, and bamboo leaves	Microwave pyrolysis	Empirical equations were determined to predict product yields and gaseous concentrations.	The energy return on investment of microwave pyrolysis can be approximately 3.56, so the technique should be energetically and economically feasible.	[224]
Hardwood waste material and wheat straw	Flash pyrolysis	Bed temperature and heating rate	A continuous atmospheric pressure flash pyrolysis process to produce liquids from biomass has been demonstrated on a scale of 2–3 kg/hr.	[225]
Wood	Flash pyrolysis	Operating temperature and heating rate	The proposed kinetic model can predict the organic liquid yield as a function of the operating parameters of the process.	[226]
Waste wood sawdust	Plasma technology pyrolysis	Comparison of catalysis, plasma, and plasma-catalysis for hydrogen-rich gas production and hydrocarbon tar reduction	Two-stage pyrolysis plasma/catalysis has been developed for enhanced H_2 production.	[227]
Crushed wood	Plasma technology pyrolysis/gasification	The reaction temperature and heating rate	The project aims to demonstrate the economic viability, environmental performance, and safety of biofuels.	[228]
Agave	Solar pyrolysis	Operating temperature and heating rate	The main findings include: (i) solar pyrolysis temperature and heating rate scarcely impact char composition (ii) structure, surface area, and electrochemical performance are highly affected by both.	[229]
Corn stover	Solar energy-assisted pyrolysis	Kinetic, thermodynamics and physical characterization was conducted	The results indicate that the corn stover can be a great bioresource for chemical production with solar pyrolysis.	[230]

6. Future Perspective and Commercialization of Pyrolysis Technology

The pyrolysis economics and environmental constraints will be optimized further to produce more valuable products and enhanced pyrolysis process efficiencies. Pyrolysis production technology towards more demanding products and increasing process efficiencies have been linked mainly to the reactor configuration and feedstock logistics [231]. Another way to fulfill this goal is to use different catalysts to maximize the conversions and improve the yield quality [232]. Another emerging solution to add more value to the pyrolysis technology products is converting bio-oil into crude oil. Crude oil is in much more demand and can be integrated easily into the present commercial fuel market. Similarly, bio-oil to transportation fuel is another research area that can help expand the scope of pyrolysis products [233]. Some models have been presented and tested to overcome the issues related to feedstock logistics. For example, mobile pyrolysis units near the feedstock location eliminate feedstock handling and transportation charges. With this arrangement, multiple feedstocks can be processed [234]. On the other hand, the fruitful results depend mainly on the suitable selection and configuration of the pyrolysis reactor. Not all feedstock materials can be processed with the same pyrolysis technology. The desired product and yield can determine the correct choice of pyrolysis technique that needs to be adopted. The following research areas need to be considered to improve the pyrolysis reactor configuration further [235,236]:

1. Pyrolysis reactors should be efficient and effective in heat transfer,
2. Should speed up the reactivity of pyrolysis,
3. Produce bio-oil with a lower molecular weight,
4. Pyrolysis products should have zero toxicity,
5. Thermally stable pyrolysis reactors,
6. Less ash agglomeration in reactor beds, and
7. Should have good control over temperature and heating rates.

The magnitude of greenhouse gases (GHG) released from the pyrolysis processes is very small compared to conventional fuels. Nevertheless, there is a research scope to expand the environmental benefits further because pyrolysis is an emerging technology with the benefits of using multiple feedstocks [237]. Above all, the most valuable benefit is the production of a wide range of fuels. Hence, a comprehensive assessment of the pyrolysis process is required to highlight the gaps and direct the research in potential progress areas. Table 8 presents an overview of the life cycle global warming potential (GWP) for various feedstock. GWP is the best approach for analyzing the effects of pyrolysis on the environment and its contribution to global warming. The positive and negative values of GWP represent the increase and decrease in emissions, respectively. Biochar used for soil remediation has better global warming potential than using pyrolysis products for energy applications. Table 9 lists some commercially installed pyrolysis reactors.

Table 8. Life cycle global warming potential (GWP) of some pyrolysis products.

Feedstock	Reactor	Plant Capacity Ton/Year	Product Yield L/DT	Application	GWP	Ref.
Corn stover	Rotary kiln	84,000	-	Soil amendment	−865	[238]
Barley straw	Rotary kiln	100,000	-	Soil amendment	−900	[239]
Sewage sludge	-	2000	-	Energy generation	−750	[240]
Poplar wood	Fluidized bed	-	300	Gasoline and diesel	0.74	[241]
Forest residue	Hydroprocessing	-	350	Gasoline	1.21	[242]
Forest residue	Fluidized bed	-	114	Chemicals	−0.53	[243]
Wood residue	Fluidized bed	-	320	Bio-oil	0.11	[244]

Table 9. Some commercially installed pyrolysis reactors.

Technology	Location	No. of Units	Max. Size Kg/h
[a] **Fixed-bed and moving-bed**	Anhui Yineng Bioenergy Ltd., China	3	600
[a] **Vacuum pyrolysis**	Pyrovac, Canada	1	3500
[a] **Ablative reactor**	PyTec, Germany	2	250
[a] **Rotating cone**	BTG, Netherlands	4	2000
[a] **Circulating fluidized bed**	Metso/UPM, Finland	1	400
[a] **Fluidized-bed**	RTI, Canada	5	20
[b] **Transported fluidized-bed**	Ensyn, Canada	8	4000
[b] **Bubbling fluidized-bed**	Dynamotive, Canada	1	3800
[b] **Indirect heating rotary kiln**	Mitsubishi Heavy Industries	1	4000
[b] **Rotary cone**	BTG, Malaysia	1	2000
[b] **Heated kiln pyrolysis followed by gasification**	Choren, Germany	1	6800
[c] **Fluidized bed**	Phrae, Thailand	1	10–20

[a] = [65], [b] = [27], [c] = [245].

7. Conclusions

Pyrolysis is a promising technology for altering biomass into more valuable renewable energy. The process can deliver sustainable and green energy to meet domestic, industrial, and commercial needs. This review conveys a summary of current efforts and developments as well as the environmental and economic features of this energy conversion technology. In pyrolysis, less-valued biomass material is transformed into high-value biochar, bio-oil, and combustible gases. The perspective to decrease the growth of greenhouse gases (GHG) from pyrolysis depends on several factors, such as the type of biomass feedstock used, type of pyrolysis conversion technology, the scope of the pyrolysis unit, and the way co-products are recycled. Slow pyrolysis can deliver superior ecological outcomes as it yields additional biochar that can be applied to soil to sequester carbon. Fast pyrolysis has financial benefits through the production of bio-oil, which is a higher-value product. Advanced pyrolysis processes can also provide high welfare for specific applications. The success of pyrolysis can be determined by the biomass feedstock prices, product yields, aptitude to produce advanced value products, and production balance. Table 10 summarizes the detailed advantages and disadvantages of different pyrolysis reactors. Furthermore, the current review paper also highlights important research gaps in the pyrolysis process using different types of pyrolyzers. The implementation of artificial intelligence will be a breakthrough in the field of the pyrolysis process. Hybrid energy systems using biomass pyrolysis processes with other renewable energy sources are needed to explore cost-effective and energy-efficient processes. The integration of pyrolysis reactors with other biomass conversion technologies can help enhance the product yields.

Table 10. Advantages, disadvantages, and bio-oil yield range of various pyrolysis reactors.

Reactor Type	Advantages	Disadvantages	Oil Yield
Fixed-bed	Simple and reliable design Biomass size dependent	Long residence time Difficult to remove char	35–50%
Bubbling fluidized-bed	Simple design and easy operation Suitable for large scale	Small particle sizes are needed	70–75%
Circulating fluidized-bed	Good temp. control Large particle size could be used	Suitable for small scale Complex hydrodynamics	70–75%
Rotating cone	No carrier gas required Less wear	Complex process Small particle	65%
Vacuum	Produce clean oil Can process large particle (3–5 cm) No carrier gas required	Slow process Solid residence time is too high	65%
Ablative	Inert gas is not required Large particle sizes can be processed	Reactor is costly Low reaction rate	70%
PyRos	Compact and low cost High heat transfer Short gas residence time	Complex design High impurities in the oil High temp. required	70–75%
Microwave	High heating rates Large size biomass can be processed High temperature	High electrical power consumption High operating costs	60–70%

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