



Review Recent Advances in Biomass Pyrolysis Processes for Bioenergy Production: Optimization of Operating Conditions

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Abstract: Bioenergy has emerged to be among the primary choices for the short- and medium-term replacement of fossil fuels and the reduction in greenhouse gas (GHG) emissions. The most practical method for transforming biomass into biofuel is thermochemical conversion, which may be broken down into combustion, torrefaction, pyrolysis, hydrothermal liquefaction, and gasification. In this study, producing biofuels using a biomass pyrolysis process was investigated. This study explored the pyrolysis process and operating conditions to optimize the process parameters to maximize the desired product yields and quality. The pyrolysis process produces three main products, which are bio-oil, bio-char, and gas. There are three classifications for the pyrolysis method, with each of them producing a majority of a certain product. First, slow pyrolysis is conducted in the temperature range of 300–950 °C and residence time of 330–550 s. It produces around a 30% oil yield and 35% char yield, and thus, the majority yield of slow pyrolysis is char. Second, fast pyrolysis produces around 50% oil, 20% char, and 30% gas yields with a temperature range of 850–1250 °C and a residence time of 0.5–10 s. The average yield of flash pyrolysis was found to be 75% bio-oil, 12% bio-char, and 15% gas, which is conducted within less than 1 s. It was reported that the pyrolysis of biomass was simulated using ASPEN Plus, where the effects of several parameters, such as the temperature, heating rate, and residence time, on the product yield and composition were investigated. Pyrolysis was performed under different conditions ranging from 400 to 600 °C. The effects of different catalysts on the pyrolysis process were studied. It was found that the addition of a catalyst could increase the yield of bio-oil and improve the quality of the product. The optimal operating condition for the pyrolysis process was determined to be a temperature of 500 °C, which resulted in a higher bio-oil yield. It was found that the biofuel yield was enhanced by selecting appropriate raw materials, such as rice husk, along with the pyrolysis temperature (e.g., 450 °C) and particle size (350-800 µm), and using a low residence time and pressure.

Keywords: integrated system; pyrolysis methods; parameters; simulation

1. Introduction

In contrast with past decades, which was a world where the affordable and limitless supply of fossil fuels could be relied upon, the present energy crisis has greatly increased uncertainty [1]. Hence, the worldwide scientific community has focused a lot of attention



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and efforts on developing a highly sustainable resource that might replace conventional energy sources [2].

The only renewable resource that can be utilized to make solid, liquid, and gas fuels is biomass [3]. Also, biomass provides 14% of the energy used by the world [4]. Biofuels that are liquid offer greater benefits than those that are solid or gaseous with respect to storage, transportation, and high energy density [5]. They can also be incorporated into boilers, motors, or turbines [6]. The biomass composition, along with the reaction mechanism related to the size of the feed particles, temperature, reaction duration, and heating rate, have an impact on the production of various fuels [7].

There are two kinds of biofuels: primary and secondary; both are produced using biomass [8]. Also, they are divided into three generations. In the first generation of biofuels, starches or sugars from food crops, such as maize, sugarcane, and rapeseed, were fermented to make bioethanol or biobutanol, and oil crops were trans-esterified to produce biodiesel [9]. An analysis of the first generation's life cycle showed that there was no net gain in energy. There was a debate going on among people that it is better to donate food to poor people rather than use it to produce fuel, and thus, researchers shifted to the second generation [10]. Agricultural waste (non-edible food) like lignocellulosic biomass was used to make second-generation biofuels. After shifting to the second generation, this generation's life cycle assessment (LCA) showed that the net energy gain has increased. Researchers then shifted to the third generation, which is a new technology to produce fuels from algae. Due to their significant lipid composition, ability to fix CO_2 , and quick growth rate, microalgae are a favorable feedstock for the generation of biofuel. Bioethanol, biodiesel, and biohydrogen are the exemplification of third-generation biofuels that are made from microalgae, seaweeds, and other microorganisms. The limits and shortcomings of first- and second-generation biofuels were resolved by third-generation biofuels. Largescale neutral lipid buildup, high yield, CO₂ capture, and wastewater bioremediation are further benefits [11].

Biomass can come from a diversity of sources: plant materials, microorganisms, and municipal solid waste. Forest timber feedstocks and agricultural waste are examples of plant resources [12]. Hard wood and soft wood are the two basic divisions of woody feedstocks. Sugar, starch, and oil seed crops are first-generation feedstocks. Sugarcane, sugar beets, corn, sorghum, cassava, and wheat are examples of crops used to make sugar and starch. Sunflower, oil palm, soy, coconut, jatropha, and rapeseed are examples of oil crops. Algae and lignocellulosic biomass from plants are utilized as plant resources for second-generation biofuels. The biomass known as lignocellulosic comprises grasses, trees, and crop wastes [4]. In recent years, the pyrolysis of biomass has attracted substantial interest as a potential source of bio-oil, gas, and bio-char [13]. There are a great number of articles that were published on this topic throughout the last decade, as shown in Figure 1.

Several methods have been applied to convert biomass into biofuels, as shown in Figure 2. The most practical method for transforming biomass into biofuel is thermochemical conversion, which may be broken down into combustion, torrefaction, pyrolysis, hydrothermal liquefaction, and gasification [14]. By adjusting the process variables, the main goal of thermochemical conversion is to remove undesired by-products. Pyrolysis is a viable method for transforming biomass into biofuel at temperatures between 250 and 600 °C when it is inert. In fact, one new strategy is to use the pyrolysis method to manufacture bio-based chemicals and fuels from biomass [15]. The products of pyrolyzing biomass can be broken down into three categories: bio-oil, bio-char, and syngas. These three byproducts have the ability to be used as sources of energy or in other applications, and they have several advantageous properties, including being friendly to the environment, having low costs, and degrading naturally [16].



Figure 1. Number of publications per year on biomass pyrolysis.

Biofuels can be found in liquid form, gaseous form, or solid form. A variety of liquid biofuels are available. There is a possible carbon-neutral biofuel option in the form of bioethanol made from lignocellulosic biomass. Bioethanol's benefits as a biofuel include having a high octane number, low boiling point, increased heat of vaporization, and equivalent energy contents [17]. Vehicles may utilize fuel blends containing 85% (v/v) bioethanol without requiring any mechanical adjustments [18]. Both greenhouse gas (GHG) emissions and oil consumption may be substantially reduced by blending. There are three main processes that make up this system: pretreatment, enzymatic saccharification, and fermentation. Since 2008, a variety of work has been done to reduce costs by, for example, employing enzyme mixtures for improved saccharification, utilizing microbes for enhanced product yield, and manufacturing certain lofty value-added products to enhance the process economics. Biobutanol provides improved safety, lower hygroscopicity, lower igniting difficulty, more inter-solubility, higher viscosity, and better lubricity than its petroleumbased counterpart [19,20]. Features of bio-methanol, such as its great performance and lack of emissions, make it a safe fuel source [4]. The fact that methanol breaks down entirely into CO₂ and water in a steam environment makes it a useful component in fuel-cell-driven cars. 7-[3-(methylaminomethyl) phenoxy]methyl]quinoline-2-amine (M85) is composed of 85% methanol and 15% gasoline and may be utilized in most cars and trucks with just minor mechanical adjustments [4]. Ultrasonic processing of algal biomass can be used for biodiesel manufacturing [21]. To produce biodiesel, 51 percent of the lipids in the algal biomass are isolated and trans-esterified with CH₃OH (methanol) as a catalyst [22]. One of the available methods is fast pyrolysis, which is used to convert biomass into bio-oil [4]. Bio-oil is a liquid that has a distinct smokey aroma and its color is dark brown. Acids, alcohols, esters, ketones, phenols, aldehydes, and oligomers are all part of the complex combination that makes up these substances [23]. High water content, viscosity, ash content, oxygen concentration, and corrosiveness are all drawbacks of bio-oil as a fuel [4]. The high costs of manufacturing and low fuel quality of bio-oil are the main obstacles impeding its commercialization [24]. A method was devised to enhance the qualities of the bio-oil made from rice husk [25]. The enhanced oil's density was found to decrease from 1.24 to 0.95 g/cm^3 , and its heating value rose from 16.0 to 27.2 MJ/kg. Additionally, the oil's pH decreased from 4.4 to 2.3 after the refinement process [4].

Regarding gaseous fuels, there are two kinds of gaseous biofuels, which are gas and biohydrogen. Last, but not least, there are solid biofuels, where the most significant type is bio-char. Bio-char is a carbon-dense byproduct of biomass breakdown at temperatures between 350 and 700 °C. Bio-char is useful both as a fertilizer and a soil conditioner. Reducing atmospheric CO₂ concentrations, increasing soil carbon stocks, and increasing

soil carbon capture are all ways in which it contributes to climate change mitigation [26]. There are nutrients in bio-char that help plants thrive. Soils conditioned with bio-char made from Miscanthus by heating it to 400 °C for 10 min suppressed the growth of maize seedlings. Soil conditioning using bio-char made from Miscanthus and collected after heating at 600 °C for 60 min yielded contrasting results [4]. This suggests that improved yields from seedlings of different varieties and species need bio-char produced in different ways [4,27].

While significant progress has been made in the area of biomass pyrolysis, there are still several research gaps that need to be addressed to optimize the operating conditions for bioenergy production, including the following: (i) There is a lack of selecting the standardized operating conditions for biomass pyrolysis. Different studies have used varying temperatures, residence times, heating rates, and catalysts, making it difficult to compare and generalize the results. The optimization of these operating conditions is crucial to maximizing the yield of desired bioenergy products and minimizing the formation of undesired by-products. (ii) Regarding the simulation of biomass pyrolysis, including the decomposition conditions, further research is needed to investigate the biomass pyrolysis simulation and identify the optimal conditions for maximizing the desired product yields. (iii) The techno-economic analysis and life cycle assessment: The economic viability and environmental sustainability of biomass pyrolysis processes are essential for their successful implementation. However, there is a lack of comprehensive techno-economic analyses that consider the optimization of the operating conditions. Further research is needed to evaluate the economic feasibility.

This study aimed to investigate the pyrolysis parameters to produce bio-oil, bio-char, and gases. The recent development methods were studied to provide a wide variety of sustainable bioenergy outputs with added value. There were several issues found with the current oil/tar spraying techniques in anaerobic digestion (AD), including microbial toxicity and low production.



Figure 2. Treatment technologies for biomass [28].

2. Thermal Conversion

The three most common forms of thermal conversion are pyrolysis, gasification, and incineration. They are distinct from one another because of the ways in which they are used and, by extension, the results of their processes [29]. Charcoal, liquid, and gaseous byproducts can be produced from the pyrolysis of biomass in the absence of oxygen, as shown in Figure 3 [30].



Figure 3. Schematic diagram for the pyrolysis method.

3. Pyrolysis Classifications

There are three distinct pyrolysis methods, namely, slow pyrolysis, fast pyrolysis, and flash pyrolysis [31,32]. Table 1 compares and contrasts these processes, highlighting the variations between them in terms of temperature, solid residence time, heating rate, biomass particle size, and product yield. The type of procedure and the process operating parameters determine the product distribution [33]. Figure 4 shows the majority percentages of each product, which are bio-oil, bio-char, and gas.

| Parameters | Slow Pyrolysis | Fast Pyrolysis | Flash Pyrolysis | Reference |
|--------------------------------|----------------|----------------|-----------------|-----------|
| Temperature (°C) | 550-950 | 850-1250 | 900-1200 | |
| Heating rate ($^{\circ}C/s$) | 0.1-1.0 | 10-200 | >1000 | [22] |
| Residence time (s) | 300-550 | 0.5-10 | <1 | [33] |
| Particle size (mm) | 5-50 | <1 | < 0.5 | |

3.1. Slow Pyrolysis

Since ancient times, slow pyrolysis has been utilized to increase char generation at low temperatures and low heating rates [31]. The generation of solid char and other liquids occurs in this procedure because the vapor residence time is excessively long (5 to 30 min) and elements in the vapor phase are inclined to react with one another. Slow pyrolysis, however, has several technological drawbacks that make it unsuitable for producing high-standard bio-oil [31]. Due to the prolonged residence time, the main product cracks, which may have a detrimental effect on the production and quality of the bio-oil. Additionally, considerable energy input is required because of the lengthy residence times and limited heat transmission [32].

3.2. Fast Pyrolysis

Fast pyrolysis entails rapidly heating biomass to temperatures between 850 and 1250 °C, with heating rates between 10 to 200 °C/s per second, over a period between 1 and 10 s [33]. Because the oil product yield in rapid pyrolysis is so much higher than the bio-char and syngas product yield, it is employed for bio-oil production [33]. Fast pyrolysis typically yields 60–75% liquid product, 15–25% charcoal product, and 10–20% non-condensable gaseous products [34]. Its goal is to heat the biomass to an appropriate

temperature for thermal cracking to occur while minimizing the amount of time the liquid biomass is exposed to heat, which promotes the formation of char [35]. High temperatures used in quick pyrolysis turn biomass into a liquid before it can react to generate char [33]. These days, the fast pyrolysis process is used for more than only producing energy; it is also used in the food industries and for certain chemicals. Liquid fuels and a variety of specialty and chemical reactions may be produced using fast pyrolysis technology, which has recently gained significant attention [36]. To separate the processing of solid biomass from its consumption, this liquid yield may be transported and stored conveniently and cheaply [36]. Further, it possesses the ability to supply a variety of useful compounds, each of which has far greater value-added than fuels. In comparison with other processes, fast pyrolysis technology, particularly when used on a tiny scale, can offer cheap investment costs and great energy efficiency [37]. There are several possible benefits to producing bio-oil via rapid pyrolysis, such as the storing and transporting of liquid fuels, its low cost, the neutral CO_2 balance, and the utilization of second-generation materials, which has led to increased interest in this method in recent years [38]. Bio-oil raw materials and waste materials (forest residue, municipal and industrial waste, etc.) have a large energy density compared with ambient gases [39].



Figure 4. Yield of pyrolysis process at different conditions.

3.3. Flash Pyrolysis

A bio-oil output of up to 75% may be attained using the flash pyrolysis of biomass [40], making it a potential technique to produce solid, liquid, and gaseous fuel from biomass. In this process, the particles are heated quickly, the reaction temperature is high (between 450 and 1000 $^{\circ}$ C), and the gas is released within less than one second [41]. However, there are some technological constraints to be considered, such as (i) the low thermal stability and corrosive properties of produced bio-oil; (ii) the presence of solids in the oil; (iii) further polymerization and condensation reactions can lead to an increase in the viscosity of the bio-oil over time, making it more challenging to handle, pump, and process; (iv) biomass

used in flash pyrolysis often contains alkali metals, such as potassium and sodium, where these alkali metals can be released and dissolved in the bio-oil during pyrolysis; and (v) during flash pyrolysis, small amounts of water can be generated as a byproduct, where this pyrolytic water can mix with the bio-oil and affect its stability, quality, and compatibility with downstream processes [42].

4. Parameters That Affect the Pyrolysis Process

Temperature, feed particle size, residence time, biomass type, catalyst, heating rate, and pressure are all important parameters that affect the pyrolysis process. Both the primary and secondary processes involved in the degradation of biomass during pyrolysis need heat and mass transport. Primary degradation occurs at low temperatures (about 200–300 °C) and involves the breakdown of the complex biomass structure. This process produces intermediate products, such as volatiles, char, and bio-oil. The principal products differ based on the biomass mix and the pyrolysis conditions. Volatiles are gases and vapors that are produced during pyrolysis. Char is the solid residue that is left over after the volatiles have been discharged. It is a carbon-rich, high-surface-area substance that can be utilized as a solid fuel or as a precursor for the synthesis of activated carbon. Bio-oil, commonly known as pyrolysis oil or biomass oil, is a black, viscous liquid produced via volatile condensation. To obtain higher-value products, bio-oil can be improved further using techniques such as hydrotreating or fractional distillation. Secondary degradation occurs at higher temperatures (usually above 500 °C) and is characterized by the thermal cracking of the primary products formed during primary degradation. This process produces more gases, such as light hydrocarbons (e.g., ethylene and propylene), and boosts the overall production of gases and liquids. Secondary decomposition reactions are often faster and more exothermic than primary decomposition events. Syngas, also known as synthesis gas, is a carbon monoxide (CO) and hydrogen (H_2) mixture that can be created during the secondary breakdown of biomass. Secondary biomass breakdown can generate several additional gases and vapors, including higher hydrocarbons, tars, and light oxygenates. These products can be developed and treated further for specialized uses. Several parameters influence both the primary and secondary degradation processes in pyrolysis, including the temperature, heating rate, residence duration, and composition of the biomass feedstock. It is feasible to modify the pyrolysis process to produce desired product yields and qualities for a variety of applications, including bioenergy, biofuels, and bio-based compounds, by optimizing these parameters. The breakdown of lignin, cellulose, and hemicellulose into simpler compounds is an example of a primary reaction. The decomposition of intermediates is a key feature of secondary reactions. First, the major products must be broken down into smaller molecules so that cellulose may be converted into sugars; second, the transformation of the main products into huge molecules and char takes place [43].

4.1. Temperature

The pyrolysis process relies on several factors, one of which is temperature. A variety of temperature values are required for the breakdown and devolatilization of biomass constituents. Heavily tarred substances result from the breakdown of hemicellulose and non-condensable gases at temperatures below 300 °C. When biomass is heated to temperatures above 550 °C, it breaks down into its parts and releases several different chemical substances [43]. Acetic acid, levoglucosan, hydroxy-acetaldehyde, and 5-hydromerthylfurfural are all cellulose-derived chemicals, whereas phenolics were derived from lignin [35]. The literature contains several studies that addressed the importance of temperature in the pyrolysis process and bio-oil yield, including the ones listed in Table 2.

| Biomass | Temperature (°C) | Oil Yield (wt. %) | References |
|------------------|------------------|-------------------|------------|
| Wheat straw | 600 | 34 | |
| Rice husk | 450 | 70 | |
| Coal | 500 | 42 | |
| Sunflower cake | 550 | 41 | [44-47] |
| Hardwood samples | 532 | 66.89 | |
| Soybean cake | 530 | 41 | |
| Bagasse | 500 | 66.1 | |

Table 2. Effect of temperature on bio-oil yield products.

The ideal temperature for producing bio-oils in high yields during fast pyrolysis was reported to be between 400 and 500 °C. The char yield decreased as the pyrolysis temperature increased. Additionally, it was found that additional devolatilization of the primary char balances the generation of secondary char at higher temperatures. At temperatures between 300 and 400 °C, around 80 to 90% of the entire bulk conversion was achieved [48]. The final pyrolysis temperature has a considerable impact on the content and oil of the liquid effluent. Another study showed that a higher temperature resulted in higher biomass conversion efficiencies because more energy was needed to break down the cellulose bonds at higher temperatures. The rate of the solid cake's decomposition varied with temperature. When the temperature of the soybean cake was raised from 400 $^{\circ}$ C to 700 °C, an additional 11.82 wt.% of the material was decomposed [49]. Sunflower cake's yield at 450–700 °C was 10.7 wt.% [50]. The highest liquid yield was achieved during the pyrolysis process between 500 and 550 °C. Secondary reactions, such as the rate of production of gasses increased when the temperature increased to 600 °C. However, the oil yield increased at around 570 °C, whereas the gas yield increased when the temperature values increased from 430 to 730 °C [51]. Stabler species were generated during secondary breaking when the ultimate pyrolysis temperature was raised, where the functional-groupcontaining compounds were found. Polycyclic aromatic hydrocarbons, such as pyrene, phenanthrene, and others, were formed and accumulated at higher temperatures. Since dehydration and decarboxylation take place at high temperatures, the bio-oil contents increased while the oxygenated concentration decreased [43].

4.2. Size of Feed Particles

Oil production and quality are both affected by the size of the feed particles used in the process. A common trend in biomass pyrolysis is the preference for smaller particle sizes due to the ease and uniformity with which they heat up. For rotating cone pyrolysis, it was recommended that particles be no more than 20 mm in diameter; for fluid bed systems, this number should be no more than 2 mm; and for a circulating fluid bed, it should be less than 6 mm. Some of the materials and their respective optimal particle size are summarized in Table 3 [52–54].

| Substrate | Optimal Particle Size | Reference |
|-----------------------------|------------------------------|-----------|
| Wood particles | 350–800 μm | [52] |
| Hazelnut | 0.225 < dp < 0.425 | [52] |
| Municipal solid waste (MSW) | Uncrushed, 1–2 cm | [53] |
| Rapeseed | <0.4 mm->1.8 mm | [54] |

Table 3. Particle sizes used in the pyrolysis process with different sources of biomass.

Particles of wood with a diameter of 350 μ m were fully pyrolyzed, whereas particles with a diameter of 800 μ m were converted at a height of 0.9 m [52]. The maximum yield was achieved at 0.45–0.6 mm for hazelnuts and municipal solid waste (MSW) [53]. At a size of 0.6 to 0.85 mm, rapeseed produced the highest yield [54]. In the pyrolysis examination of orange trash, researchers found three distinct particle size ranges (300–180, 180–150 μ m,

and <150 μ m) [55]. For particles less than 150 μ m in size, it was found that the thermal behaviors of the beginning and end of the pyrolysis process were varied. Because of variations in surface area, this variation was the result of heat and mass transport processes. However, the liquid output dropped because the larger biomass particles demand more heat and have a low heat transfer coefficient. Limitations in heat transport resulted in higher activation energy for large particles [56]. A high liquid yield was attained from large particles if these particles differ from one another in terms of characteristics like bulk density and oxygen content of the oil. Liquid products were generated when there was less obstruction. There were fewer reactive species and less energy in the liquid because of the increased oxygen level. If the particle size were to be reduced, it would cost more to complete the pyrolysis process since grinding equipment would be required. The technique is more expensive since it uses energy to reduce the size of a particle from its original, larger form. It was noted that different types of biomasses and pyrolizers produced different particle sizes. Optimizing the liquid product yield required careful consideration of both the pyrolizer and biomass sources selection [43].

4.3. Residence Time

One of the most crucial factors in the production of liquid fuels is the residence time. In pyrolysis, a fraction of a minute or less of residence time is optimal for maximizing liquid production. Low residence times are often favored for producing high-quality bio-oil. In pyrolysis, the yield of the liquid products is increased as time goes on due to a secondary reaction. More time in the reactor could be necessary for complete conversion; however, the best potential yield from the liquid is obtained after a short time. The yields of the liquid products increase due to the short residence period at a lower pressure. By varying the residence period from 15 to 40 min with fir sawdust, the effect of residence time was observed [57]. At 30 min, the product liquid yield was the highest (21.22%). It was noticed that bio-oil production increased with the biomass heating rate, even at durations above 40 s. The quantity of oxygen present during pyrolysis was also a factor in the final quality of the oil produced. Two-step pyrolysis, consisting of pyrolysis and oil generation, was used to reduce the oxygen levels.

To produce liquid products with good quality and yield, the residence time must be optimized [43]. When pyrolyzing raw sorghum bagasse at 525 °C, raising the vapor residence time from 0.2 s to 0.9 s lowered the bio-oil yields from 75% to 57% while simultaneously boosting char and gas yields [58]. Similar to this study, the oil yield from pyrolysis of sweet gum hardwood at 700 °C dropped from 22 wt.% to 15 wt.% when the vapor residence time was increased from 0.7 s to 1.7 s [59]. Product distributions as a function of vapor residence time were studied; however, the relationship between the vapor residence time and pyrolysis temperature, and its effect on yields and quality, needs further investigation [60].

4.4. Types of Biomass

Biomass can be classified into two main groups, namely, vegetable-derived and animalderived, as shown in Figure 5. Lignocellulosic material is made up of three different components: cellulose, hemicellulose, and lignin, all of which can be found in different proportions. Hemicellulose degrades between 470 and 530 °C, cellulose between 510 and 770 °C, and lignin between 550 and 770 °C. Toward the end, ash is produced from the biomass, which contains trace quantities of inorganic substances, like potassium, sodium, phosphorus, calcium, and magnesium. The final product's elements are extremely sensitive to their constituents. More cellulose and hemicellulose are present at the outset, leading to greater oil output. All three components have distinct temperatures at which they degrade. Cellulose is crystalline and breaks down faster, whereas lignin is complicated and has a greater degree of polymerization [43]. Stronger structural integrity makes decomposing the lignin more challenging, but it results in a bigger char yield [61]. However, the deterioration of this material may be aided by the application of a high heating rate and temperatures, leading to a greater liquid output. Because of the high volatility and reactivity caused by the presence of such a huge quantity of volatile material, bio-oil production is stimulated [62]. In their study of bio-oil production from rice straw and bamboo sawdust, the biomass with a higher volatile material concentration produced a higher yield [63].



Figure 5. Schematic diagram of biomass types.

The percentages of cellulose, hemicellulose, and lignin in hazelnut shells were 30 wt.%, 23% wt.%, and 38% wt.%, respectively. The percentages of cellulose, hemicellulose, and lignin in farm waste were 17 wt.%, 7 wt.% and 18 wt.%, respectively. Therefore, when lignin levels increased, the bio-oil yields declined but the bio-char yields increased. Agricultural byproducts showed a higher bio-oil output than hazelnut shells.

4.5. Catalyst

Biomass pyrolysis can be conducted with or without catalysts [64]. Catalysts have been utilized to enhance several characteristics of bio-oils, including their ability to be repolymerized, their total acid number, their corrosivity, and their compatibility with petroleum products. Certain pyrolysis processes require specific catalysts [65]. Fluidized and fixed-bed reactors are commonly used in catalytic pyrolysis. These catalysts can be either provided in a solid or vapor phase. The results of the two procedures were distinct because of the differences in contact time and response mechanism. In situ and ex situ pyrolysis improvements of beetle-killed trees were performed in the presence of an HZSM-5 catalyst [66]. More benzene and toluene were produced in the ex situ upgrade, but the specificity for xylenes and aromatics containing carbon 9 was higher in the in situ upgrade. In the presence of a ZrO_2 -FeOx catalyst, woodchips made from Japanese cedar have a catalytic effect [67]. The ratio of catalyst loading to the feed rate of pyroligneous acid production determined the amount of feed that was converted to ketone. Rapeseed cake was converted gradually between 150 °C and 550 °C, depending on the kind of catalyst utilized. Noncatalytic test (34.06 wt.%) > Na_2CO_3 (27.10 wt.%) > HZSM-5 (26.43 wt.%) > Al_2CO_3 (21.64 wt.%) [68] in terms of total organic compounds. Using rapid pyrolysis, desilicated ZSM-5 zeolite was employed as a catalyst for lignocellulosic biomass [69]. The conversion rate and the amount of unwanted coke may both be optimized by carefully regulating the amount of desilicated ZSM-5 utilized in the process. To acquire a large liquid yield, the catalyst choice is crucial. As the catalytic utilization increases, coke generation is reduced, leading to a greater yield of aromatics [43]. By facilitating

the dissociation of complex biomass molecules and promoting the production of desired products, catalysts improved the pyrolysis reactions. Catalysts can lower the activation energy required for the pyrolysis reactions, thereby reducing the operating temperature and enhancing the reaction rate. This led to faster and more efficient conversion of biomass into desired products. Catalysts help with increasing the yield of bio-oil, which is a valuable product obtained from biomass pyrolysis. They can promote the cracking of larger molecules, resulting in higher production of lighter hydrocarbons that make up bio-oil. Using certain catalysts can influence the distribution of pyrolysis products, favoring the formation of specific compounds. For example, certain catalysts can promote the production of valuable chemicals, such as furans or phenolic compounds, which have various applications in the chemical industry. Biomass pyrolysis can sometimes lead to the formation of coke, which is a solid carbonaceous residue. Catalysts can suppress coke formation by catalyzing secondary reactions that consume coke precursors or by promoting the gasification of carbonaceous species. Another undesired product that can form during biomass pyrolysis is tar. Tar is a complex mixture of high-molecular-weight compounds that can be problematic in bio-oil production and utilization. Catalysts can help with reducing tar formation during pyrolysis by catalyzing tar-cracking reactions or by promoting secondary reactions that convert tar into more desirable products. Some catalysts can be regenerated and reused, allowing for multiple cycles of biomass pyrolysis. This can contribute to the economic feasibility of the process by reducing catalyst costs and improving the overall process sustainability. Catalysts can enhance the pyrolysis reactions by facilitating the breakdown of complex biomass molecules and promoting desirable product formation. Cracking compounds with greater molecular weights into lighter hydrocarbon products is a common method utilized with catalysts to improve the kinetics of pyrolysis reactions [70]. However, the distributions of products produced by various catalysts vary depending on the parameters in which they were used. Pyrolysis catalysts were divided into three categories according to their intended use. The first class was combined with biomass just before it was introduced to the reactor [71]. The second group was introduced into the reactor, allowing for direct interaction with the vapors, solids, and tars [72]. The third set was transferred to a secondary reactor that followed the pyrolysis reactor.

4.6. Heating Rate

The degradation of biomass into products relies heavily on the heating rate. The rapid breakdown of biomass into its parts in fast pyrolysis calls for a very high heating rate. Also, the highest yields of liquid products are achieved with the shortest residence time and highest heating rate. Thus, fewer undesirable chemicals are generated as a result of the shorter contact duration of the secondary reaction. It was proposed that a heating rate of up to 1000 °C/s might be used. Increases in the production of aliphatic and carbonyl chemicals were observed during rapid pyrolysis of coconut biomass [73]. The optimal temperature for maximizing oil production was observed to be influenced by the heating rate. Different heating rates (50 °C/s, 150 °C/s, and 250 °C/s) were applied to the esparto biomass, and the results showed that at 500 °C, the liquid yield was 45 wt.% for the 50 °C/s and 150 °C min⁻¹ conditions, and 57 wt.% for the 250 °C min⁻¹ condition. The ideal temperature increased from 500 °C to 550 °C at a heating rate of 250 °C/s [43]. The formation of volatiles was increased by increasing the heating rate. If the heating rate is high enough, the temperature will rise to its maximum, but if the heating rate is low enough, the temperature will remain at its minimum [74]. High heating rates are associated with high-quality final products because they reduce the amount of water present, stop secondary reactions from occurring, and create less oxygen [43].

4.7. Pressure

In most cases, atmospheric pressure is used for pyrolysis [43]. Researchers concluded that when completing pyrolysis, the pressure is greater than that of the atmosphere, which

results in a greater bio-char yield [33]. Char is formed when the pressure is raised, causing the vapors to remain exposed to the carbon-based substance for a longer duration and for secondary carbon to be produced via decomposition [75]. The amount of carbon in bio-char can be affected by the high pressure within the reactor. Increases in the energy density of bio-char result from high-pressure pyrolysis of biomass, which increases the bio-char's carbon content [76]. Gases, including nitrogen and argon, as well as water vapor, are employed in the pyrolysis process. Nitrogen gas (N₂) is a common inert gas. It was found that the yield of liquid oil was unaffected by the existence of inert gas. By doubling the flow rate from 50 cm³ min⁻¹ to 100 cm³ min⁻¹ [77], the liquid yield was increased by 3 wt.%. Nonetheless, a high liquid product yield may be achieved with a minimal gas flow. The higher the gas flow rate, the more gases are produced, as more volatile substances are evaporated. Also, steam can be utilized as a sweep gas. It was noted that the liquid yield improved when steam was used as the sweep gas [78]. If the oxygen content of the gas is processed, it is reduced by decreasing the gas flow rate, and the bulk density of the gas is increased, and thus, more liquid product is produced.

5. Pretreatment of Biomass

Microwave pretreatment is a promising technology for the conversion of lignocellulosic biomass into sustainable biofuels due to its ability to enhance the efficiency of the conversion process. On rare occasions, microwave pretreatment was investigated. Based on a few studies, here are some recent advances in microwave pretreatment [79]. Improvement of enzymatic hydrolysis: Microwave pretreatment improves the efficiency of enzymatic hydrolysis of lignocellulosic biomass. A study showed that microwave pretreatment of corn stover at 180 °C for 10 min resulted in a 70% increase in glucose yield during enzymatic hydrolysis compared with untreated corn stover. Reduction in energy consumption: Microwave pretreatment can reduce the energy consumption required for the conversion of lignocellulosic biomass into biofuels [80]. A study showed that microwave pretreatment of corn stover at 160 °C for 10 min reduced the energy consumption of the subsequent hydrolysis and fermentation processes by 25%. Enhancement of biofuel production: Microwave pretreatment can also enhance the production of biofuels from lignocellulosic biomass [81]. A study showed that microwave pretreatment of corn straw at 200 °C for 10 min resulted in a 26.7% increase in ethanol yield during fermentation compared with untreated corn straw. Optimization of process parameters: The efficiency of microwave pretreatment can be further improved through the optimization of process parameters, such as temperature, time, and power [82]. Another study showed that optimization of the microwave pretreatment parameters for corn stover, such as a temperature of 180 $^\circ$ C, a time of 10 min, and a power of 800 W, resulted in a 72.3 wt.% increase in glucose yield during enzymatic hydrolysis [83].

6. Pyrolysis Product Properties

The pyrolysis of biomass yields three main byproducts: char, gases, and oil, which when cooled to room temperature, condenses into a dark brown viscous liquid. It is between 350 °C and 500 °C where the most liquid is produced [84]. Due to differences in pyrolysis operations, various reactions take place at varying temperatures. At increased temperatures, molecules in the liquid and residual solid were broken down into tiny ones, enriching the gaseous component [85]. The production of charcoal is obtained at a low temperature with a low heating rate approach. The production of liquid products requires a low temperature, high heating rate, and short gas residence time procedure. The production of fuel gas is achieved at a high temperature with a low heating rate and long gas residence time [31].

6.1. Bio-Oil

The condensed vapor of a pyrolysis process is known as bio-oil, which is a liquid. An alternative fuel oil use is possible. Compared with the heat content of hydrocarbon fuels, bio-oils are only about 40% as effective [31]. Since it is a liquid, it can be readily transported and stored, and its energy density is higher than that of biomass gasification fuel [82]. Pyrolysis oil, known as "bio-oil" or "bio-crude", has a wide variety of oxygenated molecules. Carbonyls, carboxyls, and phenolics are just a few of the chemical functional groups found in bio-oil that present opportunities for its use [86]. In spite of this, the thermophysical characteristics of pyrolysis bio-oil are affected by a wide variety of elements that are now poorly understood [87]. An overview of some of the physical oil's features and characteristics is given in Table 4.

| Properties | Oil Characteristics | Interpretation | Ref. |
|-------------|---|---|------|
| Form | Free-flowing, organic liquid with a dark reddish-brown color | Oil's chemical composition and the presence of micro-carbon | [31] |
| Odor | Unique scent: a sharp, smokey odor. | Acids and aldehydes with smaller molecular weights | [31] |
| Density | Extremely high in comparison to fossil fuel Bio-oil from pyrolysis: 1.2 kg/L 0.85 kg/L for fossil fuels | High levels of moisture and significant molecular contamination | [31] |
| Viscosity | 40–100 cP | Various feedstock types, water content, and the gathering of several non-heavy ends | [88] |
| Heat value | 26.7 MJ/kg | High oxygen content | [89] |
| Aging | With time, there is an increase in viscosity, a reduction in volatility, phase separation, and gum deposition | A high pH value and complex structure | [31] |
| Miscibility | Petroleum fuel is completely immiscible in non-polar solvents, yet miscible with polar solvents | Polar in nature | [31] |

Table 4. Physical properties and characteristics of bio-oil.

Approximately 300 to 400 different chemicals make up pyrolysis oil [88]. The pyrolysis oil changes physically and chemically during storage, as several reactions happen and volatiles are released as a result of aging [89]. According to several studies, aging effects and reactions are sped up at higher temperatures, but if pyrolysis oil is preserved in a cold environment, the impacts can be mitigated [90]. Scientists found that the thermal efficiency of pyrolysis oils in combustion engine operations is comparable to that of diesel fuel; however, they showed severe ignition delay [91]. In order to reliably ignite pyrolysis oil, a modest amount of preheated combustion air is required. Heating rate, pyrolysis temperature, and residence time are only a few of the process factors that might affect pyrolysis oil yields, quality, and stability [92,93]. The ash amount and composition of the pyrolysis oil can be changed based on the reactor type (ablative/fixed), particle size, and char formation, all of which influence the rate, efficiency, and mechanism of biomass pyrolysis. Early interest in bio-oil was motivated by worries about crude oil shortages, yet recently, the environmentally friendly benefits of biomass fuels have grown to become an even more compelling and significant element. Due to the issues encountered when using bio-oils as fuel in conventional machinery designed for use with petroleum-derived fuels, such as boilers, engines, and gas turbines, the industry has yet to adopt them as a commercial standard. The major causes of this include bio-oil's viscosity, coking, and corrosion [31].

To produce energy, heat, and chemicals, bio-oil will be substituted for fossil fuels. Some applications for bio-oil are illustrated in Figure 6.



Figure 6. Applications of bio-oil.

6.2. Bio-Char

Significant mass loss in the form of volatiles occurs during the thermal breakdown of lignin and hemicellulose to produce a hard amorphous carbon matrix known as bio-char. The main solid yield is bio-char (also known as charcoal), which consists of unconverted organic solids and carbonaceous wastes created from the partial or total breakdown of biomass components, in addition to a mineral fraction [58]. The type of feedstock and the pyrolysis conditions determine the char's physical and chemical characteristics [58]. Biomass and pyrolysis conditions determine the percentage of bio-char generated (10–35%). Figure 7 displays the variations in bio-char yields across three temperature ranges during pyrolysis [31,94]. The quantity of bio-char is significant in the low-temperature (450–500 °C) zone due to weaker devolatilization rates and low carbon conversions. The generation of bio-char is drastically cut back in the second zone of average temperature (550–650 °C). It was found that between 18–17 wt.% bio-char was the greatest production percentage in this temperature range. Extremely poor bio-char output was observed in the region with temperatures greater than 650 °C [95]. The impact of varying temperatures on bio-char production is shown in Figure 7.



Figure 7. Different temperatures with different bio-char yields [31].

The physical features of bio-char may be considerably altered by adjusting some variables [96], including the reactor type and form, biomass type and drying treatment, platform molecules, particle size, chemical activity, heating rate, residence time, pressure, and inert gas flow rate [97]. Higher heating rates (up to 105–500 °C/s), shorter residence times, and finer platform molecules all contribute to the production of finer bio-char, while slower pyrolysis operating conditions and larger particle size of the feedstock provide coarser bio-char [98]. Further, bio-char made from wood-based biomass is often more coarsely granular [99]. In contrast, pyrolysis procedures produce finer and more brittle organized bio-char from agricultural wastes [100].

6.3. Gaseous (Syngas)

Potential byproducts of biomass pyrolysis include carbon dioxide, carbon monoxide, hydrogen, and hydrocarbons with reduced carbon numbers like methane and ethane. Certain gases like propane, ammonia, nitrogen oxide, sulfur oxide, and alcohols with minimal carbon numbers are obtained [58]. In slow pyrolysis operations, bio-gas is also generated, ranging from roughly 10 wt.% to 35 wt.%. Nevertheless, flash pyrolysis at high temperatures can produce more syngas. For instance, using calcined dolomite as a catalyst, it was reported that syngas was generated from the pyrolysis of municipal solid waste in a bench-scale downstream fixed-bed reactor at temperatures between 750 °C and 900 °C [101]. A temperature of 900 °C resulted in a gas output of 78.87 wt.% [102]. Secondary processes, including decarboxylation, decarbonylating, dehydrogenation, deoxygenation, and cracking, are subsequently performed on the volatile molecules and tar to produce the various components of syngas [103]. Tar decomposition and thermal cracking favor higher temperatures, leading to a greater proportion of syngas but lower oil and char production [104]. Moisture content affects heat transmission during pyrolysis, which is bad for producing syngas. Gaseous products are drastically reduced due to the high moisture content, which aids in the separation of water-soluble components from the gaseous phase [105]. When compared with wet biomass, the early stages of pyrolysis create the most gas for a specific temperature when using dry biomass. This happens because higher relative humidity lengthens the time required for a surface to dry [106]. Pyrolysis gas can be used for a variety of purposes, including the generation of heat or electricity through gas burning and compression ignition engines [107], whether alone or in combination with coal; the generation of specific gas elements, including (CH_4, H_2) or other volatiles; and the synthesizing of liquid biofuels. The heated pyrolytic gas can be recycled back into the pyrolysis reactor as a carrier gas, or it can be utilized to warm the inert sweep gas [58].

7. Simulation

Software simulation is required to determine the impact of pyrolysis temperature on the production of bio-char, as it is a time- and energy-efficient approach. The simulation process of biomass using Aspen Plus is shown in Figure 8 [107].

Using Aspen Plus, users can create detailed models of the pyrolysis process, including the complex chemical reactions and heat transfer mechanisms involved [108]. It allows users to define the reaction kinetics of the pyrolysis process based on experimental data or theoretical models. This includes specifying the rate of primary and secondary reactions during the decomposition of the feedstock. The software provides a vast database of thermodynamic properties for various substances, which can be used to accurately model the behavior of different species during pyrolysis [109]. Also, the tool is efficient in maximizing the pyrolysis process's operational parameters, including the heating rate, temperature, solid residence time, and feedstock size. Numerous experimental pyrolysis studies on fruit wastes, including the hulls of the Karanja (*Pongamia pinnata*) fruit [110], fruit bunches of the oil palm (*Elaeis guineensis*) [111], empty fruit bunches of the sweet lime (*Citrus limetta*) [112], peels of lemon [113], pomegranate (*Punica granatum* L.) [114], watermelon peel (*Citrullus lanatus*) [115], jackfruit (*Artocarpus heterphyllus*) peel [116], pine (*Pinus*) fruit shell [117],

casuarina (Casuarina equisetifolia) fruit waste [118], coconut (Cocos nucifera) shell, and longan (Dimocarpus longan) fruit seed [118], were carried out. There were even a few studies on the pyrolysis of orange peel, banana peel, mango endocarp, apricot kernel shell, and date seed. There have not been many studies that used Aspen Plus in pyrolysis experiments, despite the fact that it is used in practice. Ismail et al. used Aspen Plus to conduct a pyrolysis investigation on used tires [119]. The Aspen Plus model was effectively used to estimate the pyrolysis yield production, as well as to look into how temperature affected the pyrolysis product output. A scientist used Aspen Plus to carry out a microwave pyrolysis investigation on four biomass wastes, including Calophyllum inophyllum seed, Acacia nilotica, Bael shell, and rice husk [120–122]. The goal of the simulation research was to pinpoint the biomass that produced the highest output of bio-oil. According to the Aspen Plus findings, *C. inophyllum* biomass had the greatest bio-oil output (48 weight percent). Another researcher investigated the pyrolysis of municipal green trash using modeling and experiments [121]. The study aimed to validate the experimental results using Aspen Plus. The goal of the research was to maximize the output of bio-oil by optimizing the pyrolysis process operational variables, including the feedstock size, temperature, moisture, and air-to-fuel ratio. The simulation and experimental findings were found to be in good agreement, demonstrating that the Aspen Plus simulator is an efficient tool for predicting pyrolysis products. The simulation findings also showed that Aspen Plus can be utilized to sucwtcessfully optimize pyrolysis operating parameters, and the findings may be used for experimental analysis. Utilizing an Aspen simulation model and typical pyrolysis settings, the pyrolysis products of five different fruit wastes were examined. These wastes were orange peel, banana peel, mango endocarp, apricot kernel shell, and date pits [123,124]. Before using simulation to predict the yields of fruit waste pyrolysis, the model was first used to validate it by utilizing published data. The simulation's findings showed that all of the fruit wastes had high syngas yields of 46–55 wt.%. and high bio-char yields of 39–51 wt.%., but a poor bio-oil yield of 11 wt.%. The high volatile content of 50–78 wt.%. of all the fruit wastes was responsible for their significant syngas output. Date pits had the greatest bio-char output of 50.92 wt.%. and mango endocarp had the greatest syngas production of 54.23 wt.%. among the fruit wastes. Date pits have a high elemental carbon concentration and a medium cellulose composition, which contributed to their strong char output. Mango endocarp's large elemental oxygen and hydrogen concentrations and extremely high holocellulose concentration were likely responsible for the fruit's high syngas output. According to the research, all of the selected fruit wastes were utilized as pyrolysis feedstocks to produce syngas. The research further predicted the bio-char from date pits pyrolysis.

Aspen Plus software has been widely utilized in other domains, including the manufacture of biodiesel and ethanol [125], coal or biomass gasification [126], and flue gas pollution control [127]. There is less research on utilizing it to model the process of biomass pyrolysis to create bio-char. Several studies demonstrated that Aspen Plus software can accurately and realistically model chemical manufacturing processes. An appropriate model was selected to investigate the impact of temperature variations on bio-char generation based on various pyrolysis settings and reactions. In addition, software simulation was used to determine the heat duty of the reactor at various pyrolysis temperatures, allowing for the analysis of the reaction process from the viewpoint of heat balance. Second, the biomass was pyrolyzed in a nitrogen stream using a tube furnace, and the yield of bio-char was determined by dividing the mass of the resulting product by the mass of the raw materials. The effect of temperature on the synthesis of bio-char was examined using various pyrolysis temperature values.



Figure 8. Effect of pyrolysis temperature on the yield of bio-char, as examined using a software simulation [107].

8. Product Treatment

8.1. Bio-Oil

The acidity, viscosity, chemical instability, and poor heating value [128] of bio-oil prevent it from being utilized as a "drop-in" transportation fuel [129]. The chemical discrepancies between bio-oil and fuel-grade hydrocarbons suggest that oxygen extraction is necessary; nevertheless, this process is costly [88]. There are two ways to get rid of the oxygen: either as H₂O (requiring the addition of hydrogen) or as CO₂ (reducing the fuel output) [130]. The bio-oil can be deoxygenated in one of two major ways: catalytic cracking or catalytic hydrodeoxygenation. Acidic zeolites and high temperatures (773-823 K) are required for catalytic cracking. This reduces biofuel production while increasing bio-char formation (>20 wt.%) [131]. Hydrogen unit activities in chemical engineering can be defined by the term "hydrotreatment" [132]. Hydrodeoxygenation, hydrocracking, and hydrogenation are all terms used to describe the same process when hydrogen is present with the intention of deoxygenating, cracking, or hydrogenating a molecule or complex mixture [133]. Two-stage hydrotreatment of bio-oil is a popular method [134]. At certain temperatures (100 and 300 $^{\circ}$ C), the active carbonyl and carboxyl functional groups must be converted into alcohols in the initial phase, known as stabilization [135]. However, the reactivity of certain acids (such as acetic acid) can be affected by factors such as the reaction temperature, residence time, and catalyst type [136]. A second process, namely, cracking and hydrodeoxygenation (HDO), is conducted around (350 °C and 400 °C) [137].

8.2. Bio-Char

Water quenching or leaching, heat treatments/aeration, aging/weathering, activation, particle size reduction, and palletization/granulation are used for post-treatment bio-char processing. Advantages of treatment methods are listed in Table 5.

| Treatment | Advantages | Reference |
|-----------------------------|---|-----------|
| Water quenching or leaching | Bio-char has easily soluble components that need to be removed. Essential procedure for shutting down pyrolysis in many low-tech setups, such as conical kiln "fame-curtain" pyrolyzers. | [138] |
| Heat treatments/aeration | It was proposed that off-gassing ethylene can be achieved by the very straightforward aeration of bio-char after its manufacture. Toxic naphthalene is removed. | [139] |
| Aging/weathering | It enhances bio-char properties through surface oxidation and increases the porosity. | [140] |
| Activation | Increases the surface area.Increases the pore volume. | [141] |
| Particle size reduction | - Particle fusion occurs during pyrolysis at high pressures, leading to bio-char that is more dense, and hence, smaller in size. | [142] |

Table 5. Types of bio-char treatments.

8.3. Gas Treatments and Applications

An electric furnace can be utilized to heat feedstock before it is fed into a fixed-bed reactor. An inert gas, like nitrogen, is compressed into the reactor (1). Throughout the operation, gases and vapors are released, and bio-char is gathered. Figure 9 shows the possible treatment process of pyrolysis products.



Figure 9. Waste treatment and pyrolysis products. (1—N2 bottle; 2—reactor; 3—heat exchanger; 4—separation unit, 5—water trap; 6—gas flow meter; 7—rotameter) [143].

The gas is released from the reactor (2), then cooled in a heat exchanger (3). Then, the gas mixture is fed into a separation unit (4) to separate gases from the stream. After the

gas is separated, it is further purified by passing it through a water trap (5) to remove the leftover water; after the water is trapped, the stream is passed through a gas flow meter (6) to measure the production yield of gases. Flow rate of nitrogen gas is measured using rotameter (7) [143].

With no free oxygen present, waste is heated to a temperature of about 500 $^{\circ}$ C using an external heat source. To generate electricity, the feedstock is broken down into its volatile components to generate syngas, which is then fed into a boiler to generate steam, with the exhaust gas being treated in an emission control unit [144]. As shown in Figure 10, waste is first pretreated, which involves screening to remove contaminants (metals, glasses, and stones), shredding to reduce the particle size, and drying to remove any water. Then, pretreated waste is moved through a pyrolysis kiln to produce char and gas. The gas produced is then transferred to a combustion chamber. A boiler is used to produce gas and steam. Char produced from the pyrolysis kiln is treated in a char treatment unit to produce syngas, increasing the gas yield to produce electricity. A flue gas stream is passed through a flow gas treatment to make it safer for the environment. Syngas is collected to increase the gas yield. Steam is either used directly in domestic heating or used to produce electricity.



Figure 10. The use of pyrolysis waste for energy recovery and generation.

9. Recent Developments

The unsustainable treatment and disposal of food waste (FW) is a global environmental crisis, along with the recalcitrant organic residues (RORs) produced by FW treatment plant processes. There is an urgent need to fully harness FW and ROR through the introduction of recycling renewable technology. Two potential methods for degrading FW and its leftovers are anaerobic digestion (AD) and pyrolysis, which together provide a wide variety of sustainable bioenergy outputs with added value. There are a few issues with the current oil/tar spraying techniques used in anaerobic digestion (AD), including their microbial toxicity and low production [145].

9.1. Pyrolysis and Anaerobic Digestion Integrated Process

Pyrolysis, which can produce gas, oil, and a solid residue (char) that can all be further recycled, is an alternative approach to increase the energy and economic value of recalcitrant organic residue (ROR) usage [146–148]. Scientists throughout the world are increasingly interested in this method for its potential to valorize a wide range of waste products and yield useful products, as indicated in Table 6 [149–152]. A pyrolysis and AD coupling arrangement may be broken down into three distinct types: AD and pyrolysis, pyrolysis and AD, and AD–pyrolysis–AD.

| Waste | Coupling Technology Process | Remarks | Ref. |
|--|---|---|-----------|
| Lignocellulosic biomass | - AD-pyrolysis - Pyrolysis–AD - AD-pyrolysis–AD | When comparing the AD-pyrolysis process with the standard AD process, the electricity benefit may be increased by around 42%. Few efforts have been made to combine pyrolysis with AD, and there is a pressing need for more research into the hazardous substances produced during pyrolysis. The decomposition of biomass using AD-pyrolysis–AD is feasible, and the resulting sludge and residues may be put to good use. | [149] |
| Paper mill sludge | AD combined with pyrolysis | The integrated method increases energy independence throughout the treatment phase. | [150] |
| Food waste | Combining AD and pyrolysis | This research shed light on the evaluation of AD pyrolysis for FW treatment and its subsequent transformation into gas, oil, and solid yields for energy generation. This integrated method allows for the efficient concentration of nutrient elements optimized for use in soil conditioning and agronomy. | [151] |
| Recalcitrant organic residues (ROR) | Two-stage pyrolysis coupled with AD | During bio-methanation, ROR's high H_2 to CO ratio (60:20 vol.%) in syngas produces almost 100% more CH ₄ than the control. With a high CO content, the breakdown rate of H_2 is slowed down because of the higher concentration of H_2 . Conventional ROR treatments have limitations that can be avoided by combining second-stage pyrolysis with the AD process. By using AD to process FW, a byproduct rich in hydrogen (H ₂) is produced, as well as improved bio-methanation. | [152–155] |

Table 6. Waste products and coupling technology process.

9.2. Challenges and Disposal of Recalcitrant Organic Residues Using the Anaerobic Digestion of Food Waste

Composting and the AD process are widely used in the process of food waste valorization. Anaerobic digestion (AD) involves the biological breakdown of organic materials in the absence of oxygen. Despite the fact that treating FW can help with AD, roughly 30% of the total food waste materials end up as ROR after screening and biological treatment, as shown in Figure 11 [156]. Plastics and high lignin matters are the main types of solid residual matter produced during the AD process, and neither can be completely degraded without biochemical treatment. Plastics, lignin, and biomass all present significant treatment issues; nevertheless, they may be used for other purposes, such as resource recovery and power generation [157–159]. There are many treatment challenges that arise regarding ROR disposal. Landfilling, open burning, and incinerating these waste products are all inefficient ways to dispose of them. More environmental challenges (such as soil deterioration, GHG emissions, and water pollution) are being brought about by the disposal methods now in use. The rapid increase in ROR production rates necessitates immediate action in the form of environmentally responsible waste management strategies [160–163].



Figure 11. Pyrolysis and anaerobic digestion integrated process [156].

10. Bio-Oil Using Microalgae

The fast growth and high lipid content of microalgae make them a great candidate as a source of bio-oil, which can be extracted from microalgae through two common methods: hydrothermal liquefication (HTL) and pyrolysis [164]. Using these methods, microalgae are heated in the absence of oxygen to produce bio-oil. The biomass is rapidly heated to a high temperature, causing the microalgae cells to break down and release volatile organic compounds, which are then condensed into bio-oil [165,166]. The characteristics of the bio-oil produced include a high energy content, high viscosity, and high acidity. The composition of bio-oil depends on the type of microalgae, as well as the pyrolysis conditions, such as temperature, heating rate, and residence time. A study showed that pyrolysis of Nannochloropsis microalgae at 450 °C for 30 min yielded bio-oil with a heat value of 35.7 MJ/kg, a viscosity of 79.9 cP, and an acidity of 4.6 mg KOH/g [167].

Hydrothermal liquification (HTL) is a process in which heat and water are used under high pressure to cause degradation; it involves four stages: heating, pressurization, depressurization, and separation [168]. During the heating stage, the microalgae are heated to a high temperature in the presence of water, causing the biomass to break down and released organic compounds, which are condensed into bio-oil [169]. The characteristics of bio-oil produced showed a high energy content, low viscosity, and low acidity [170]. The composition of bio-oil also depends on the type of microalgae, as well as the operating conditions, such as temperature, pressure, and residence time. It was shown in a study that the HTL of Chlorella vulgaris microalgae at 300 °C and 20 MPa for 30 min resulted in bio-oil with a heat value of 31.5 MJ/kg, a viscosity of 2.87 cP, and an acidity of 0.35 mg KOH/g [171].

11. Production of Bio-Char from Crop Residues and Its Application for Anaerobic Digestion

Bio-char has attracted substantial interest as a potential material to improve soil fertility and boost plant growth. Bio-char has also been utilized as a feedstock in anaerobic digestion, which turns organic matter into gases and provides a renewable energy source.

Several studies were conducted to examine the formation of bio-char from crop leftovers and its use in anaerobic digestion. For example, one study looked into the production of bio-char from corn stover and its use as a co-substrate for anaerobic digestion. The results showed that adding bio-char boosted gas yield and improved anaerobic digestion process stability [172]. A similar study investigated the production of bio-char from wheat straw and its use in anaerobic digestion. The results showed that adding bio-char boosted methane output and improved substrate biodegradability [173]. Another study looked into

methane output and improved substrate biodegradability [173]. Another study looked into the production of bio-char from rice straw and its use in anaerobic digestion. The addition of bio-char enhanced the gas yield while decreasing the ammonia and hydrogen sulfide contents in the gas [174]. These studies showed the potential of bio-char as a feedstock for anaerobic digestion, as well as its capacity to improve gas production and quality. However, more research is needed to optimize the generation of bio-char from crop residues and its use in anaerobic digestion under various conditions.

12. Economic Studies

An economic study of the pyrolysis process involves evaluating the costs and potential revenues associated with implementing and operating a pyrolysis plant. The financial viability and profitability of the process are assessed. Some key factors typically considered in an economic study of pyrolysis are the capital cost, feedstock cost, operating cost, product revenues, energy generation and utilization, by-product handling and disposal, and revenue streams and incentives [175]. The capital cost includes the cost of acquiring or leasing land and preparing the site for construction, purchasing or installing pyrolysis reactors, feedstock handling systems, product collection and storage equipment, auxiliary systems, and other required infrastructure. Second, the feedstock cost includes costs associated with acquiring the biomass feedstock, including harvesting, collection, and transportation to the pyrolysis plant, and a consideration of the potential fluctuations in feedstock prices due to market conditions, seasonality, and availability. Third, operating costs include personnel salaries and training; employee benefits; electricity and fuel required for operating the pyrolysis process, including heating the reactors and powering various equipment; ongoing costs for maintaining and repairing equipment and infrastructure; and expenses associated with laboratory analysis and quality control [176,177]. Then, product revenues include assessing the market demand and price for bio-oil, evaluating potential markets and applications for bio-char, and identifying potential uses for syngas, including on-site energy generation, heat production, or conversion into other value-added chemicals. Energy generation and utilization include assessing the feasibility and potential revenue from generating electricity, heat, or steam from the excess energy produced during the pyrolysis process, and evaluating energy costs and potential savings from utilizing the generated energy internally, reducing reliance on external sources. Then, by-product handling and disposal involves analyzing costs associated with by-product handling, such as transportation, storage, and potential treatment or disposal methods for residues or waste streams, and exploring opportunities for by-product utilization, such as selling bio-char for agricultural applications or exploring synergies with other industries. Revenue streams and incentives include investigating potential revenue streams from renewable energy credits, carbon credits, or government incentives that promote renewable energy and sustainable practices, and identifying tax benefits, grants, or subsidies that are available for biomass-based projects. In Figure 12, a Sankey diagram illustrates the heat pathways [178]. The heat input, including electric energy, is analyzed. Electric energy is transformed into thermal energy and electric energy losses, and energy from biomass and charcoal is changed to product energy and its losses. It was found that heat losses from the bottom to the top of the reactor were about 28–35% [175]. This amount of losses directly affects the product yields [176]. The amount of liquid products is slightly lower than the theoretical and designed values.



Figure 12. Sankey diagram showing the heat energy [178].

13. Conclusions

Thermochemical conversion is the most practical method for transforming biomass into biofuel. The pyrolysis process produces three main products, which are bio-oil, biochar, and gas. The optimal operating temperature for a high yield of bio-oil from biomass was found to be in the range of 450–550 °C. A high bio-char production was found below 500 °C. The addition of a catalyst can increase the yield of bio-oil and improve the quality of the product. Biofuel yield is enhanced by selecting raw materials, such as using rice husk, along with an appropriate pyrolysis temperature (e.g., 450 °C) and particle size (350–800 μ m), and using a low residence time and pressure. The paper concludes that bioenergy has emerged as one of the primary choices for the short- and medium-term replacement of fossil fuels and the reduction in greenhouse gas (GHG) emissions.

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