






Review

# Influence of Catalyst on the Yield and Quality of Bio-Oil for the Catalytic Pyrolysis of Biomass: A Comprehensive Review

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**Abstract:** In the modern world, as the population rises and fossil fuel supplies decline, energy demands continue to rise. Moreover, the use of fossil fuels harms the ecology, contributing to pollution and global warming. In order to overcome these difficulties, several approaches are revealed, such as the utilization of biomass as a renewable source of energy. Studies revealed that biomass can be converted into bioenergy via several thermal conversion processes, like pyrolysis, gasification, and torrefaction. Pyrolysis is the most convenient process to obtain three different types of biofuels (biochar as a solid, bio-oil as a liquid, and syngas as a gas). The biofuels produced in this process are normally lower in quality and cannot be used directly as fuel because they contain many undesirable components. Catalytic pyrolysis is one of the best processes to upgrade the quality of biofuels. Several varieties of catalysts are used in the catalytic pyrolysis process (ex situ and in situ). Due to stable operating conditions, both catalytic and non-catalytic pyrolysis procedures produce biochar that has a consistent output. Meanwhile, the effects of catalysts in the catalytic pyrolysis process considerably enhance the quality and quantity of bio-oils and syngas. By removing the unwanted oxygenated and nitrogenous components, the bio-oils produced through the catalytic pyrolysis method have a higher calorific value, reduced viscosity, and improved stability. Many researchers have looked at ways to increase the rate of pyrolysis, whereas a few have focused on maximizing the effects of the factors in order to improve the efficiency of catalytic pyrolysis. This review addresses the impact of catalysts on the catalytic pyrolysis of biomass to enhance the quality of the bio-oils in great detail. Machine learning and techno-economic analysis were investigated, as well as the future potential of the catalytic pyrolysis method for the generation of bio-oil.

**Keywords:** biomass; catalysts; catalytic pyrolysis; bio-oil; machine learning; techno-economic analysis



**Citation:** Reza, M.S.; Iskakova, Z.B.; Afroze, S.; Kuterbekov, K.; Kabyshev, A.; Bekmyrza, K.Z.; Kubenova, M.M.; Bakar, M.S.A.; Azad, A.K.; Roy, H.; et al. Influence of Catalyst on the Yield and Quality of Bio-Oil for the Catalytic Pyrolysis of Biomass: A Comprehensive Review. *Energies* **2023**, *16*, 5547. <https://doi.org/10.3390/en16145547>

Academic Editors: Venko N. Beschkov and Albert Ratner

Received: 24 May 2023  
Revised: 17 July 2023  
Accepted: 20 July 2023  
Published: 22 July 2023



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## 1. Introduction

One of the most important resources for people is energy, which forges a close connection between nature and life. Energy needs are growing daily since there are no alternatives for them in the social and economic growth of a nation [1–3]. The primary energy source is the combustion of fossil fuels, which increases emissions of greenhouse gases, mostly

carbon dioxide (CO<sub>2</sub>) [4,5]. The implications of worldwide climate change and environmental obligations make renewable energy sources necessary today. Also, the need for energy from sources of renewable energy that should be both ecologically and economically advantageous is being driven by the depletion of fossil fuel supplies [6,7]. These problems can be solved using renewable energy sources, including biomass, wind, solar, geothermal, and tidal, where there is great potential for converting biomass to biofuels [8,9].

Agricultural waste, municipal trash, food waste, grasses, wood waste, and other types of waste are among the primary sources of biomass [10]. Dry plant material, also known as lignocellulosic biomass, is a plentiful and inexpensive source of renewable energy. Biomass can be converted into bioenergy through thermochemical or biochemical conversion processes. In these conversion phases, the thermochemical conversion implicates heat, and the biochemical conversion implicates enzymes [11]. In these methods, thermochemical conversion is the most promising and efficient way to convert biomass into bioenergy when compared to the biochemical process [12].

Among the major thermochemical conversion methods (pyrolysis, gasification, and combustion) [13], pyrolysis is more appropriate because of its benefits for storage, transportation, and solicitation flexibility [14]. Biochar, bio-oil, and syngas are the three primary byproducts of the pyrolysis of biomass [15]. It was also found from the literature that excess vapor cracking occurs at high operating temperatures to boost gas production. Low temperatures increase char yield, but temperatures in the 400–600 °C range produce the highest bio-oil output in various reactors [16]. Biochar is often used to produce activated carbon (AC), improve soil, generate heat, and capture CO<sub>2</sub> [17]. AC is ideal for catalytic applications, including water and air filtration, due to its enormous surface area, considerable porosity, and structural durability [18]. Bio-oils can be purified and utilized as low-grade fuel for heating and diesel engines [19]. Syngas is upgraded and refined, before being utilized to generate energy and power in fuel cells and gas generators [20].

The majority of unwanted components (volatile acids, oxygenated compounds, and water) that are present in bio-oils after pyrolysis lower the heating value of oil. The catalytic pyrolysis procedures used to produce upgraded bio-oils are of great interest to researchers [21]. Catalysts are materials that speed up chemical reactions while remaining unchanged. In catalytic pyrolysis, catalysts can decrease oxygenated and nitrogenous components, enhance calorific value, reduce viscosity, and improve the solidity of the bio-oils [22]. Catalysts for the catalytic pyrolysis process most frequently include zeolites, metal oxides, clay, dolomite, and activated carbon [23].

The kind of catalyst employed, the structure of the biomass, and operational parameters like temperature, catalyst-to-biomass ratio, reactor type, particle size, heating rate, and residence time, affect the yield and quality of the bio-oil generated during catalytic pyrolysis [24,25]. Normally, the yield of bio-oil produced by catalytic pyrolysis is somewhat lower than that of non-catalytic pyrolysis [26]. According to earlier research, different catalysts have distinct potentialities in the catalytic pyrolysis process [27]. The release of oxygen and carbon oxides (CO<sub>x</sub>) during catalytic pyrolysis eventually affects the yield and quality of bio-oils for the deoxygenation reactions (dehydration, decarbonylation, and decarboxylation) [28].

Pyrolysis has great promise, but commercialization is still difficult to achieve. As an outcome, it is becoming increasingly important to fully comprehend its dynamics to enable process build up. However, biomass pyrolysis is a complicated, sluggish, and expensive process. In spite of these difficulties, machine learning (ML) has come to be seen as a potential technique for assisting and advancing pyrolysis research. The handling of vast amounts of data, flexibility in complicated systems, and computing efficiency are some of the benefits of using ML. Due to its enormous potential, ML may be successfully used to simulate pyrolysis processes and produce predictions that are equivalent to those made by conventional models [29]. In addition, a vibrant field of research focuses on the effectiveness of machine learning in process optimization and control, product yield prediction, real-time monitoring, and techno-economic analysis (TEA) during catalytic

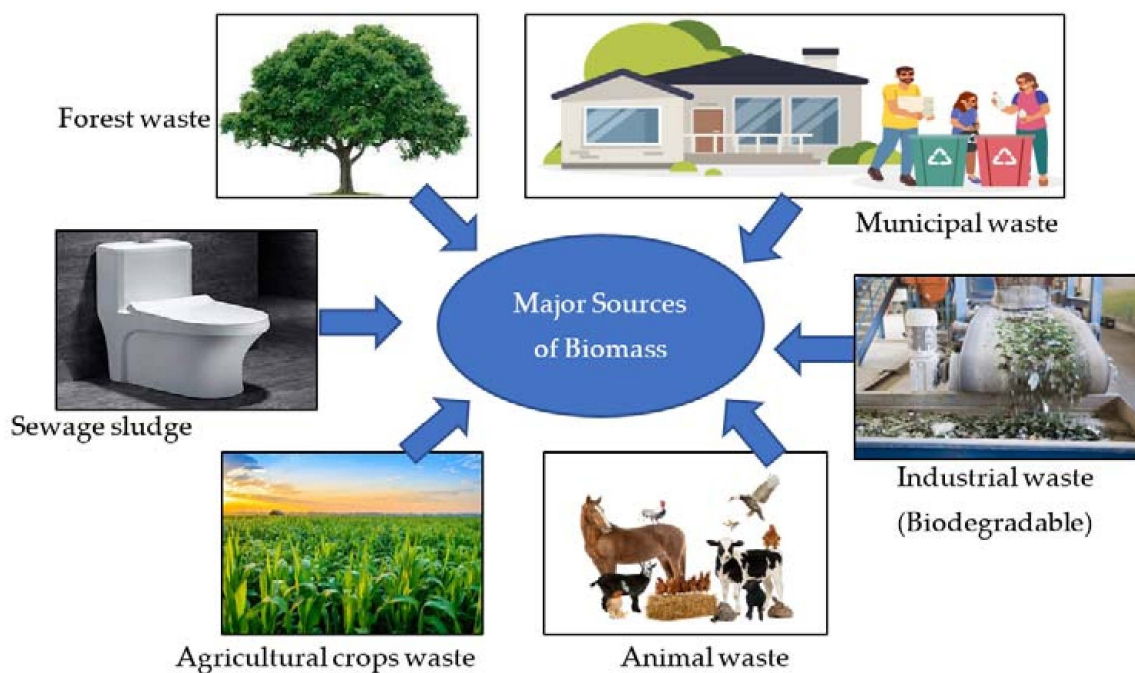
pyrolysis. The incorporation of ML appears to be the most effective strategy for expediting research and development and expanding the scope of the catalytic pyrolysis of biomass.

The primary focus of this study is on state-of-the-art catalytic pyrolysis using lignocellulosic biomass for the generation of bio-oil for environmental sustainability. This review summarizes the impacts of various biomass types, catalyst types, and other parameters that significantly influence the yield and quality of bio-oils. The present study also includes machine learning and techno-economic analyses of the catalytic pyrolysis process. It provides a fundamental understanding of present developments and the direction of future research.

## 2. Biomass and Thermochemical Conversion of Biomass

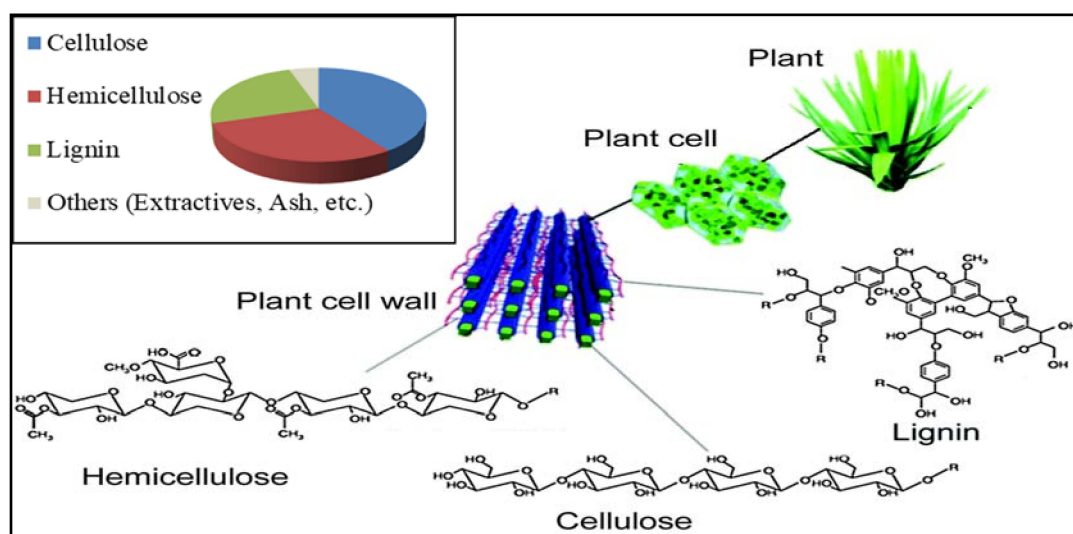
### 2.1. Biomass

Biomass is the waste product of plants or animals that cannot be used as food or feed. Plants, food waste, crops and forestry waste, agro-industrial waste, garbage, municipal solid waste, and biodegradable industrial solid waste are examples of different biomass sources (Figure 1) [30]. Woody biomass is made up of trees, bushes, and shrubs, whereas herbaceous biomass refers to plants with non-woody stems, such as those that yield grains and cereals. As a possible source of renewable energy, biomass—also known as a feedstock or solid biofuel—can reduce greenhouse gas emissions more than fossil fuels. If these biomass materials are not adequately handled, transported, or disposed of, they will pose an environmental threat by producing greenhouse gases [31,32].



**Figure 1.** Major sources of biomass (reproduced from Jawaid et al., 2017) [30].

Hemicellulose, which makes up 20–40% of the biomass, is followed by cellulose, which makes up 40–60% of the biomass, and lignin, which makes up 10–25% of the biomass [33,34]. Comparing cellulose to hemicellulose and lignin, during the catalytic pyrolysis process, cellulose produced the greatest amount of aromatic hydrocarbons [35]. Figure 2 illustrates the structure and major constituents of lignocellulosic biomass.



**Figure 2.** Biomass compositions (Modified from Zhang et al., 2014; Thakur and Thakur 2015; and Mansor et al., 2019) [33,34,36].

### 2.1.1. Cellulose

Cellulose is the crystalline and amorphous form of a glucose molecule with the formula  $(C_6H_{10}O_5)_n$ , which is bonded through hydrogen bonds and Van der Waals forces [37]. It is extremely insoluble in water and has a high resistance to depolymerization. In biomass, this is the most important part of the cell wall. Crystalline cellulose has a high resistance to degradation compared to amorphous cellulose [38]. More volatile matter may be produced by biomass with increased cellulose content to produce significant amounts of bio-oil for the generation of biofuel [39]. The bulk of olefins generated during the pyrolysis process come from biomass with a greater cellulose or hemicellulose content than from feedstock with a higher lignin content [40].

### 2.1.2. Hemicellulose

Hemicellulose is the amorphous and heterogeneous branch of polymers with the overall formula  $(C_5H_8O_4)_n$ . It is a component of the cell wall with a lack of strength and a lower molecular weight than cellulose [37]. It is a pronged glucose or xylose polymer with lactose, xylose, arabinose, fucose, glucose, mannose, and glucuronic acid as supplements [38]. The degree of polymerization makes it amorphous, readily hydrolyzable, and unable to combine with cellulose. Hemicellulose can support the pyrolysis process to produce volatile and gaseous materials due to its lower molecular weight and shorter polymer chains [41]. In the catalytic pyrolysis process, hemicellulose is one of the most effective elements to produce higher amounts of aromatic hydrocarbons [42].

### 2.1.3. Lignin

Lignin is a 3D (three-dimensional), cross-connected polymer made up of phenylpropane units joined together by hydroxyl and methoxy groups. It protects hemicellulose and cellulose from enzymes, spores, and bacteria by being contained in the outer layer of the tissue [43]. Lignin is made up of three simple structural units: guaiacyl type (G-type), hydroxyl phenyl (H-type), and syringyl type (S-type) [44]. Boiling water, salt, or any other alkali solvent does not cause lignin to dissolve [45]. Lignin has a higher carbon content than cellulose and hemicellulose, as well as a lower oxygen concentration [46]. It decomposes at a slower rate in pyrolysis since it is often used to generate biochar [47]. Lignin is the least thermally degradable component during pyrolysis, which produces the phenolic compounds in bio-oils [48].

#### 2.1.4. Organic Extractives

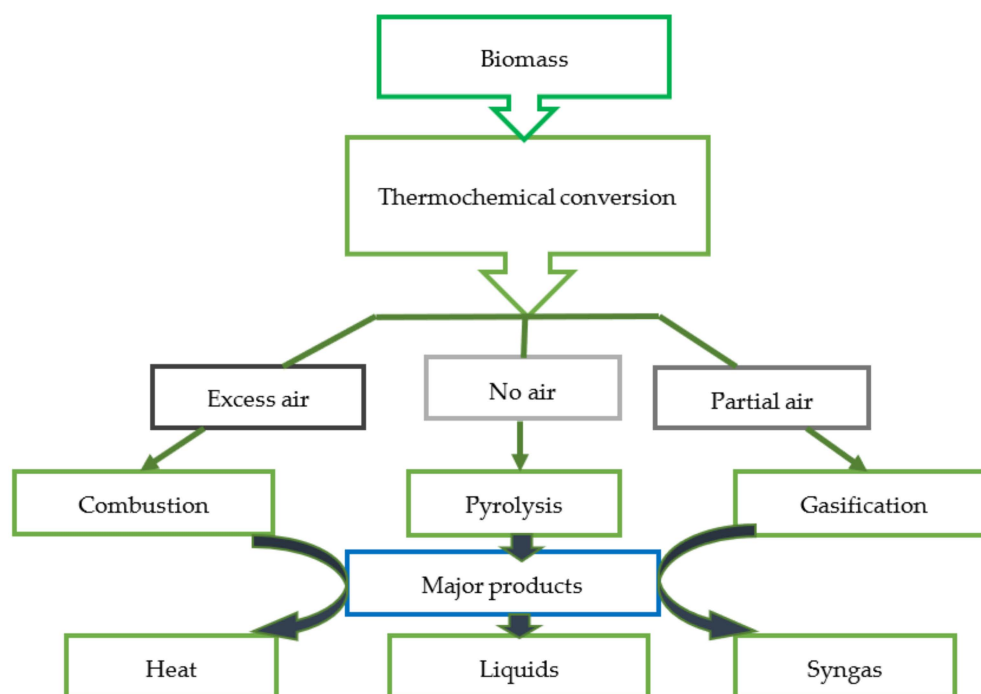
Biomass extractives include alkaloids, mineral oils, glycosides, fats, gums, pectins, resins, starches, phenolics, proteins, waxes, and terpenes [49]. They are made up of both water-soluble (sugars and proteins) and ethanol-soluble (waxes and chlorophyll) constituents [50]. Extractives can be inorganic or organic. The biomass with a higher amount of extractives is in pyrolysis as inorganic extractives produce low-quality bio-oils, and organic extractives cause clogging in the reactor [51].

#### 2.1.5. Inorganic Matter/Ash

Biomass also holds many minerals or inorganic elements that produce ash after complete combustion [52]. The elements of ash in the biomass are mostly potassium (K), silicon (Si), sodium (Na), calcium (Ca), phosphorus (P), iron (Fe), manganese (Mn), aluminum (Al), chromium (Cr), zinc (Zn), and magnesium (Mg) [49]. According to Antal et al. [53], the majority of the ash in char is made up of alkali metals, which have a catalytic influence on the yield, reactivity, and characteristics of pyrolysis products. Inorganics may accumulate on the surface of the catalyst or inside its pores throughout the catalytic pyrolysis process, which might lead to the catalyst losing its effectiveness. Since the inorganics may be isolated before the catalytic reactions for ex situ procedures, the inorganics have a greater impact on in situ catalytic pyrolysis processes than on ex situ processes [54].

#### 2.2. Thermochemical Conversion of Biomass

Thermochemical conversion is the method of transforming biomass into solid, liquid, and gaseous products. There are several types of thermochemical processes, like pyrolysis, gasification, and combustion [55]. Figure 3 demonstrates the thermochemical conversion processes and their major products [56].



**Figure 3.** Thermochemical conversion processes with main products (regenerated from Bridgewater 2006 and Patel et al., 2016) [55,56].

Which form of thermal conversion will take place is virtually entirely controlled by heat and oxygen. The basic premise behind these ideas is that when oxygen is added, the biomass will transition from pyrolysis to gasification, followed by combustion with the further addition of oxygen. Pyrolysis is the most basic form of conversion. It only

needs a small amount of heat and no oxygen to begin breaking down biomass molecules. Gasification is the intermediate stage of conversion. Compared to pyrolysis, it takes higher heat, but more crucially, it also needs a tiny amount of oxygen. Combustion is the ultimate stage of conversion. It combusts to provide the system with all the oxygen it can take and enough heat to set it off. Therefore, pyrolysis produces just a small quantity of heat, followed by gasification, which produces more heat, and combustion, which produces the maximum heat [57].

### 2.2.1. Combustion

Fuel and oxygen are burnt during combustion, which is an exothermic reaction that generates heat, carbon dioxide, and water [58]. The steam turbine uses combustion to turn the blades positioned on the shaft linked to the generator by producing hot steam from the burning of fuel. This process converts heat energy to kinetic energy, mechanical energy, and ultimately electrical energy [59]. However, because it causes global warming by releasing carbon dioxide into the atmosphere, the use of fossil fuels is not entirely environmentally friendly. When burning biomass, additional polluting gases can be produced, including potassium chloride (KCl (g), K<sub>2</sub>Cl<sub>2</sub> (g)), hydrogen chloride, HCl (g), and sodium chloride, NaCl (g) [60,61].

### 2.2.2. Gasification

Gasification is a thermochemical conversion process that converts carbonaceous materials, such as biomass or coal, into fuel gas when the gasifying agent, air, is present. The gas produced, which is composed of H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, CO, and N<sub>2</sub>, is known as “syngas.” Additionally, syngas produces a little amount of char, ashes, and tar [62]. With this approach, waste may be managed efficiently, limiting the impact of landfills and greenhouse gas emissions [63]. Syngas can be an effective fuel for solid oxide fuel cells (SOFCs), enhancing and raising the value of biomass as a renewable energy source. Gas cleaning is important in the gasification process for use in SOFCs. Various forms of catalysts are also used in gasifiers to upgrade the products [64,65].

### 2.2.3. Pyrolysis

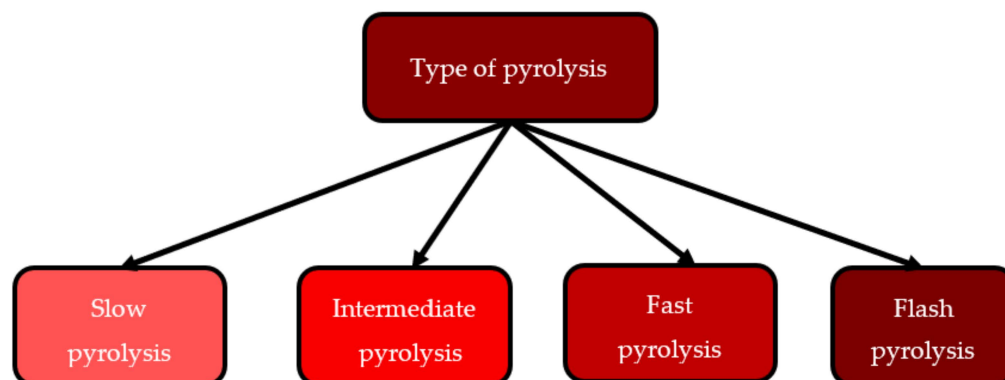
Pyrolysis is the process of thermally breaking down biomass into smaller molecules at higher temperatures and in an inert atmosphere [56]. The primary outcomes of pyrolysis are biochar, bio-oil, and syngas. Slow pyrolysis is concerned with biochar processing, while fast pyrolysis is mostly used to generate bio-oils and syngas [66]. During the decomposition process, the volatiles are released as vapor, and the non-volatiles are converted into solid biochar. The condensable vapors are referred to as bio-oil, which is also identified as pyrolysis oil, bio-crude oil, and biofuel oil, whereas the non-condensable gases are known as syngas, biogas, and bio-syngas [67]. When biomass is heated, volatile substances are liberated from the particles, forming non-condensable gases [68]. Syngas is produced predominantly by gasification. It is mostly employed in catalysis. Carbon monoxide and hydrogen are the two most crucial syngas ingredients for chemical synthesis. It may be used to produce methanol and ammonia, which lessen the need for natural gas in each case [69]. Meanwhile biogas is the anaerobic digestion or fermentation of biodegradable materials, such as biomass, manure, sewage, municipal trash, green waste, plant material, and energy crops [70]. Typically, carbon dioxide and methane make up their compositions.

## 3. Pyrolysis of Biomass

### 3.1. Types of Pyrolysis

There are four main categories of pyrolysis: slow, intermediate, fast, and flash pyrolysis (Figure 4). The circumstances and parameters for each form of pyrolysis vary, depending on factors including heating temperature, residence duration, heating rate, and sample size [71]. The operating conditions and typical product yields for each kind of pyrolysis

are shown in Table S1, where the production of bio-oil increases from the slow to the fast pyrolysis process [72,73].



**Figure 4.** Types of pyrolysis processes (reproduced from Tripathi et al., 2016) [71].

### 3.1.1. Slow Pyrolysis

In the slow pyrolysis process, the temperature used is between 300 and 500 °C, with a very long solid residence time of several minutes to several hours at a lower heating rate. The main products of this process are mainly biochar and low-value energy products [74].

### 3.1.2. Intermediate Pyrolysis

In intermediate pyrolysis, the reaction temperature ranges from 400 to 600 °C, and the residence period can reach several minutes. The sample can be either coarse, shredded, or finely ground [14]. Intermediate pyrolysis is effective for bio-oil production from grasses, straws, and agricultural residues [75]. In this process, high production of bio-oil can be achieved at a moderate temperature (500 °C) with an increasing reaction time [76].

### 3.1.3. Fast Pyrolysis

Fast pyrolysis has a reaction temperature between 400 °C and 1000 °C, a high heating rate of up to 1000 °C/s, and a brief residence time of less than 2 s [72]. Small particle size, fast heating rate, and moderate pyrolysis temperatures (400 and 650 °C) are the common characteristics of the fast pyrolysis process [73]. In this technique, the production of bio-oil might increase to 80%, while the biochar and syngas yields are very low [77]. The kinetic behavior of fast pyrolysis is perplexing because of the complexity of chemical reactions. The mineral composition of the feedstock for the catalytic activity also has an impact on yields [78]. Catalytic fast pyrolysis is a potential technique that might enable the conversion of biomass into portable fuels. The catalytic fast pyrolysis of biomass has not been used commercially despite its benefits in terms of simplicity and economic efficiency [79].

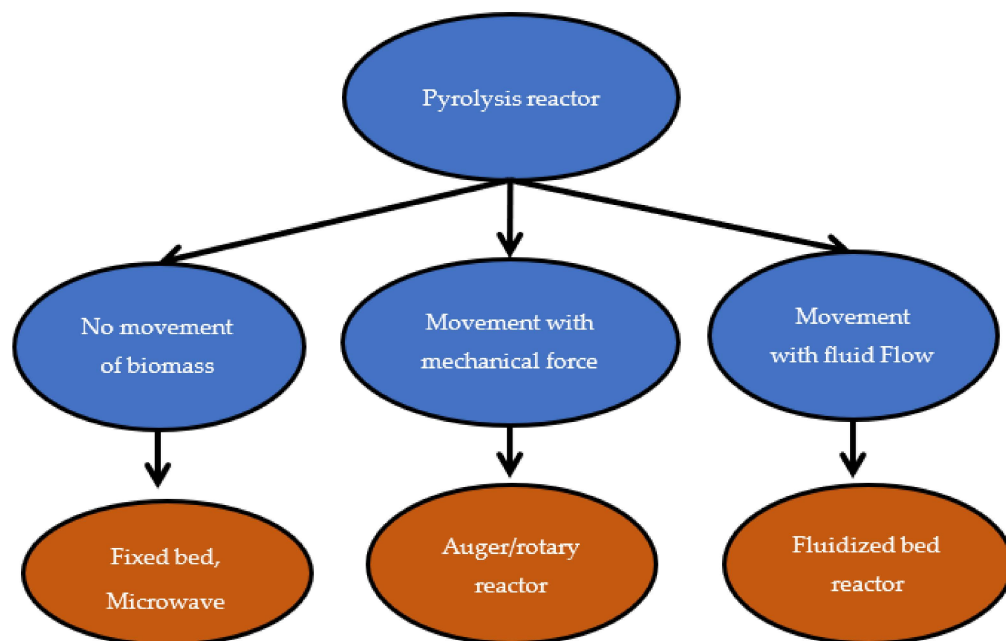
### 3.1.4. Flash Pyrolysis

With a heating rate of more than 1000 °C/s and a dwell time of under 0.5 s, flash pyrolysis takes place at temperatures that are comparatively high (900–1300 °C) [80]. The major product from flash pyrolysis is bio-oil (>75 wt%) [81]. It is a complex process, as with an upper heating rate and a smaller residence period, the biomass must be pre-treated and made into a fine powder (105–250 µm) before pyrolysis to ensure efficient heat transfer [82].

## 3.2. Reactors for the Pyrolysis Processes

Several types of pyrolysis technologies are available depending on the required end products (syngas, bio-oil, or biochar) [81]. The design of the pyrolysis reactor is the most important factor influencing product distribution and quality. Each technology contains specific working principles and an experimental setup [83]. According to the mobility of the biomass inside the reactor, the technologies are classified as fixed-bed reactors, auger/screw reactors, and fluidized bed reactors. Figure 5 depicts the available pyrolysis

technologies. The benefits and drawbacks of adopting various pyrolysis technologies are listed in Table S2, with a fixed-bed reactor being the most efficient and practical reactor on a lab size [84–87].



**Figure 5.** The pyrolysis processes, according to the movement of feedstock (regenerated from Jahirul et al. 2012 and Campuzano et al., 2019) [86,88].

### 3.2.1. Fixed-Bed Reactor

The reactor is positioned in a vertical or horizontal position in the fixed-bed reactor. Vertically, the solid particles move down via a shaft and contact the gas of the product stream, whereas horizontally, the particle is fixed inside the reactor [89]. Biochar production via slow pyrolysis using a fixed-bed reactor is simple to perform. During carbonization, the biomass is put into a reactor for many hours or even days to produce charcoal as the major product. This is the simplest form of carbonization, where only a chimney is required to combust the biomass. It is low in costs and simple to perform [90].

### 3.2.2. Auger/Screw Reactor

The auger reactor, sometimes referred to as a screw reactor, is made up of a revolving helical screw that serves as a conveyor to transport the feedstock through the heated reactor [91]. A rotating screw ensures uniform mixing of the feedstock, which increases heat-transfer efficiency [86]. An auger reactor can be made up of single or twin screws. A twin-screw auger reactor provides agitation of the biomass and simple conveyance, allowing better mixing and, hence, better heat transfer [92]. It is a continuous pyrolysis technology and can be used for biomass of different sizes and shapes [86].

### 3.2.3. Fluidized Bed reactor

One of the most widely used and commercially accessible methods for creating bio-oil is the fluidized bed reactor, which is well suited for fast pyrolysis [93]. The existence of turbulent gas flow and quick circulation in the reactor allows it to have excellent heat-transfer efficiency and superior temperature control, making it a better alternative than a fixed-bed reactor [94]. The batch-dense fluidized bed reactor, which is typically comprised of a refractory steel cylinder tube and a set of electric furnaces, is one of the most often used fluidized bed reactors [95]. The process is highly reactive and has a lower residence time [84].



### 3.2.4. Microwave Reactor

One of the most current research topics in the pyrolysis process is a microwave reactor, which eventually transfers energy to molecules or atoms through microwave heat. Normally, microwave cavity ovens are used to pyrolyze the biomass in this process. Inert gas is used as the carrier gas, which needs to flow continuously through the reactor to maintain an oxygen-free environment [88]. For the slow pyrolysis process, microwave reactors are a successful way to produce valuable compounds from biomass because they have several benefits, including effective heat transmission, enhanced chemical reactivity, and control of the heating process exponentially [96]. As a result, microwave reactors can process a variety of biomasses and industrial wastes with high yields of syngas and bio-oil [97].

### 3.2.5. Other Reactors

In addition, a number of other reactors were used to study the catalytic pyrolysis of biomass, including dual fluidized bed reactors [98], conical-spouted bed reactors [99], circulating fluidized bed reactors [100], drop-tube quartz reactors [101], and V-shaped downer reactors [102].

### 3.2.6. Impacts of Pyrolysis and Reactors on the Enhancement of Bio-Oil Quality

Ignited earlier, numerous studies have already demonstrated that the most affordable, easiest, and most scalable process for converting biomass and other feedstock into energy and other useful byproducts is pyrolysis [103]. The physicochemical characteristics, quality, and yield of pyrolyzed products (e.g., bio-oil) can all be greatly impacted by pyrolysis process parameters [104,105]. The performance and quality of the product are significantly influenced by several factors, including raw materials, reactor type, temperature, additives, catalysts, residence time, and pressure [106]. Bio-oil has a particularly difficult set of physicochemical characteristics due to the abundance of oxygenated organic functionalities that are present in it, and this bio-oil is transformed through extreme secondary upgrading into, for example, transportation fuels [107].

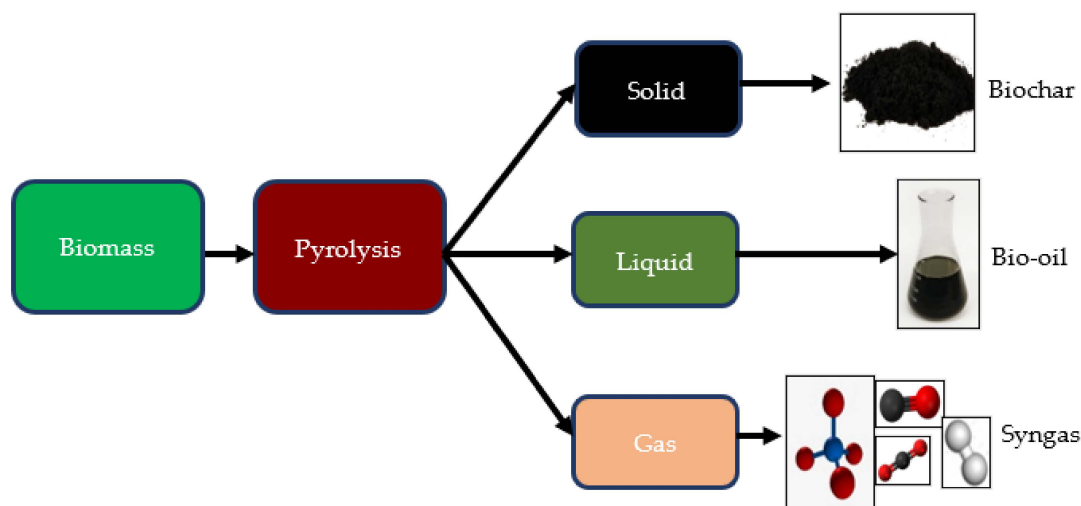
Fast pyrolysis is thought to be the most effective method of all these thermal conversion techniques for producing liquid fuel, such as bio-oil, at its highest potential. This pyrolysis is capable of producing up to 75% of bio-oil, which may be utilized immediately in a variety of applications or upgraded to become an energy carrier [108]. With a brief dwelling period of around 2–10 s and higher heating rates, fast pyrolysis is an effective method for turning biomass into bio-oil in an inert environment at medium temperatures between 400 and 600 °C. It emerged that this system could generate a maximum output of bio-oil of 78.07 wt% at the bed temperature of 480 °C by employing a circulating fluidized bed reactor via low-cost bio-oil fast pyrolysis [109]. Another study revealed that the fast pyrolysis of *S. japonica* in a fixed-bed reactor yielded a maximum bio-oil output of 40.91 wt% at 350 °C and a sweeping-gas velocity of 300 mL/min [110]. From the foregoing considerations, it can be inferred that although the fixed-bed reactor is more frequently employed, fast pyrolysis with a fluidized bed reactor produces the highest quantity of bio-oil output.

However, compared to bio-oil produced by fast pyrolysis, intermediate pyrolysis-produced bio-oil has better physical and chemical characteristics, including a low oxygen concentration, greater oil miscibility with fossil fuels, and a high calorific value [111]. Fast pyrolysis yields more bio-oil (60–75%) than intermediate pyrolysis (35–50%) in terms of yield [71,75,112–114]. Compared to fast pyrolysis oil (35–40%), intermediate pyrolysis bio-oil contains less oxygen (8–33%). Bio-oil with a high oxygen concentration is unstable and contains lower energy content [115]. In comparison to fast pyrolysis oil, intermediate pyrolysis oil has lower viscosity and miscibility due to the low oxygen level, making it easier to blend with biodiesel and hence easier to use in conventional engines. Consequently, intermediate pyrolysis is a viable choice for processing waste with little to no pretreatment while still producing high-quality products. It also has the potential to co-produce adsorp-

tion bio-oil, demonstrating that waste conversion is a technology that is both resource- and environment-friendly.

### 3.3. Products from the Pyrolysis Process

The main outcomes of the pyrolysis process are shown in Figure 6, where the solid is biochar, the liquid is bio-oil, and the gas is syngas.



**Figure 6.** Major products from the pyrolysis process (regenerated from Chen and Lin 2016 and Reza et al., 2023) [15,66].

#### 3.3.1. Biochar

Biochar, also known as charcoal or biocharcoal, is a carbonaceous substance with a higher carbon content [116]. The breakdown of lignin, which breaks weak bonds and forms more dense, stable structures from primary and secondary pyrolysis events, results in the formation of biochar [117]. It can be used to produce heat energy by containing more carbon (63–91%) and less oxygen [118]. Biochar production is aided by the higher content of ash due to inorganic substances [119]. Devolatilization assists in the formation of biochar with improved porosity and reactivity as biomass is pyrolyzed at high temperatures [66]. Biochar is used to diversify the arena due to its available functional groups, inert nature, and capability to repossess liquid or gaseous particles [120]. Biochar has recently demonstrated remarkable potential in the manufacture of activated carbon, which is one of the most adaptable adsorbents for a wide range of specialized applications [121]. Biochar is also useful as a solid fuel and fertilizer [114].

#### 3.3.2. Bio-Oil

Pyrolysis is one of the most efficient processes for producing bio-oils from biomass, with up to 70% efficiency [122]. It is a solvent derived from the condensable vapors of a complex mixture of acids, phenols, ketones, alcohols, aromatic hydrocarbons, carbohydrates, esters, ethers, amines, oxygenated compounds, and water [123]. Typically, bio-oils from the pyrolysis process mostly appear dark brown, are viscous/non-viscous, and have a strong, distinctive smell [124]. The production of bio-oils is mostly determined by the heat breakdown of cellulose [125]. After refining, bio-oils can be utilized directly as fuel for boilers, furnaces, or engines [126]. They are regarded as an acceptable fuel for energy savings, environmental support, and rural socioeconomic concerns [127]. Bio-oils can also be used for wood flavorings, preservatives, lubricants, resins, and adhesive synthesis, in addition to biofuels [128].

The two stages of bio-oil production are the organic phase and the aqueous phase, with the organic phase usually having greater energy levels than the aqueous phase [129].

The viscosity, acidity, and thermal stability of pyrolytic bio-oil are greater, resulting in bio-oil deterioration over time [130]. For appropriate applications, it is crucial to improve the quality of bio-oil. Currently, three forms of bio-oil upgrading processes are available:

- Physical methods with solvents;
- Catalytic methods with catalysts;
- Non-catalytic methods without catalysts.

Among the above processes, the catalytic methods show higher performance due to the better quality of the bio-oils [114].

### 3.3.3. Syngas

Depending on the feedstock, the gases produced during the pyrolysis process are referred to as syngas, biogas, or bio-syngas.  $H_2$ ,  $CH_4$ ,  $CO_2$ ,  $CO$ , and hydrocarbons are the principal constituents of the non-condensable gases. The production of gas grows with rising temperature as a result of the secondary breaking of the vapors [66]. Syngas can be utilized as a direct fuel in fuel cells, especially in microtubular solid oxide fuel cells, as a combustion fuel in manufacturing, as a heat source in the pyrolysis process, or as fuel in gas turbines to produce electricity [121,131]. The gas products from the pyrolysis process offer benefits over charcoal and bio-oil since they do not need any pricey upgrading operations [114].

### 3.4. Factors Influencing the Pyrolysis Process and Products

Both the pyrolysis procedure and the pyrolysis yields were significantly influenced by a number of different variables: temperature, heating rate, residence time, biomass particle size, presence of the catalyst, etc. [132].

#### 3.4.1. Temperature

The temperature has a significant impact on the yield and effectiveness of the pyrolysis processes and the products [133]. Normally, if the pyrolysis temperature increases, the production of biochar decreases by enhancing the pyrolytic vapors [134]. In general, the yield of bio-oils was achieved for the pyrolysis temperature of 400 to 550 °C; after that (>550 °C), the production is reduced by converting the tars and vapors into non-condensable gases via secondary cracking reactions, such as decarboxylation, deoxygenation, and dehydrogenation [135,136].

#### 3.4.2. Heating Rate

The product yield in the pyrolysis process is significantly influenced by the heating rate. The pyrolytic vapors from biomass rise due to a greater rate of breakdown and produce more gases than charcoal as a result of the increased heating rate [137]. For the pyrolysis of 14 plants (Wiregrass, Inkberry, Yaupon, Fetterbush, Swamp bay, Wax Myrtle, Longleaf Pine Foliage, Water Oak, Little Bluestem, Live Oak, Dwarf Palmetto, Saw Palmetto, Sparkleberry, Darrow's Blueberry), an escalation of the heating rate from 0.5 °C/s to 180 °C/s increases the tar and light gas yield and decreases the biochar yield [138]. Increasing heating rates leads to higher secondary reactions, which produce more gaseous products [139]. When the heating rate increased from 500 to 700 °C/min for the pyrolysis of sawdust, it was discovered that the yield of bio-oil increased by 8%, but when the rate increased from 700 °C/min to 1000 °C/min, there was no discernible difference in the production of bio-oil [140]. Similar outcomes were obtained while pyrolyzing cottonseed cake, where the bio-oil yield ranged from 26 wt% for a heating rate of 5 °C/min and 35 wt% for a heating rate of 300 °C/min. There was little change in the yield of bio-oils for the increase in heating rate from 300 to 700 °C/min [141].

#### 3.4.3. Vapor Residence Time

The length of stay, which significantly affects output yield, is the length of time that a substance persists in a medium or location. The amount of time it takes for the vaporized

gas inside the reactor to escape is known as the vapor residence time [142]. Since preventive secondary reactions take place in the reactors by eliminating organic vapors during shorter residence durations, more bio-oil is produced [143]. The intermediate pyrolysis process produced bio-oil with greater quality for a short residence time than the fast pyrolysis technique in terms of physical and chemical attributes [144]. On the other hand, with a long vapor residence time, the slow pyrolysis process provides a lower yield of bio-oils [145]. It was found that the yield of syngas increased with a higher residence time [146]. In the pyrolysis (at 525 °C) of raw sorghum bagasse, the bio-oil yields were reduced from 75 to 57% with an increase in vapor residence time from 0.2 s to 0.9 s, increasing the yield of biochar and syngas [136].

#### 3.4.4. Biomass Particle Size

Particle size influences product yield; as particle size increases, gas yield decreases, while char and tar yields rise due to the lower surface area and higher thermal resistance [147]. In the pyrolysis of smaller particles, the temperature is constant throughout each particle, which produces more liquids and gases by full conversion. On the other hand, for bigger particles, the inside is heated slowly, resulting in a stay in the solid phase due to lower temperatures producing higher amounts of solids. For a higher amount of bio-oils, smaller particles are highly preferable [148]. As a consequence, the production of biochar and syngas decreases, but the output of bio-oil increases due to the moderate particle size. The Chinese tallow tree produced the highest amount of bio-oil (46.20%) when the biomass particles were between 1.4 and 2.4 mm in size and the pyrolysis temperature was 550 °C [149].

#### 3.4.5. Presence of Catalysts

The liquids, gases, and solids generated during pyrolysis are greatly influenced by the presence of a catalyst. Few catalysts were achieved to increase the solid products, whereas others enhanced the liquids and gaseous products [71]. In comparison to the non-catalytic process, the production of bio-oil reduced from 36.70 to 34.72% in the ex situ catalytic pyrolysis of invasive *Pennisetum purpureum* grass with activated carbon, whereas the output of syngas increased from 35.90 to 37.52%. This was because of the catalytic effect of the catalytic and pyrolytic vapors [26].

The pyrolysis procedure can be accomplished either thermally (traditionally) or catalytically. It is an endothermic procedure [150]. In contrast to the catalytic approach, which involves using an external agent to help the pyrolysis process, the thermal route involves the process occurring without the aid of any external agents [151]. Conventional pyrolysis produces liquid byproducts that have long carbon chains with low octane values, wax, other residues, and impurities, necessitating additional refining to transform them into useful fuel products [152]. To address such challenges, catalytic pyrolysis of biomass is a powerful thermochemical conversion technique that may be utilized to enhance the quality of the liquid or bio-oil by boosting the number of lighter fractions in the oil and lowering the impurity concentration.

## 4. Catalytic Pyrolysis of Biomass

### 4.1. Catalytic Pyrolysis

Catalysts are substances that accelerate chemical processes without undergoing permanent chemical changes. They can open up new pathways by decreasing the energy required for a chemical reaction to happen under particular circumstances, such as pressure and temperature [153]. At the operating temperature range of 400 to 650 °C, catalysts are added to catalytic pyrolysis to increase the yield of the products [154]. When related to non-catalytic pyrolysis, the heavy components are broken down into smaller and lighter components, such as hydrocarbons, overall reducing oxygenated compounds during the cracking reaction [155]. There are two classifications of catalysts used in pyrolysis, namely

primary and secondary catalysts [156]. The types of catalysts and the pyrolysis setup for the catalytic pyrolysis of biomass are described in Table 1.

**Table 1.** Type of catalysts and pyrolysis setup used for catalytic pyrolysis of biomass.

Feedstocks	Catalysts	Pyrolyzer Type	Ref.
Pine sawdust	ZSM-5	Fluidized bed	[157]
Rice husk	ZSM-5	Fixed bed	[158]
Aspen wood	ZSM-5	Tubular bed	[159]
Pinewood chip	ZSM-5	Fixed bed	[160]
Pine barks	ZSM-5	Fixed bed	[161]
Sawdust	ZSM-5	Fluidized bed	[162]
Beechwood	ZSM-5	Fixed bed	[163]
<i>Nannochloropsis</i> sp.	ZSM-5	Fixed bed	[164]
Corn cob	ZSM-5	Fluidized bed	[165]
Pine sawdust oak	Mordenite	Packed bed	[166]
Beechwood	FeO, Al <sub>2</sub> O <sub>3</sub>	Fixed bed	[163]
Hazelnut bagasse	FeO, Al <sub>2</sub> O <sub>3</sub>	Fixed bed	[167]
Sewage sludge	La <sub>2</sub> O <sub>3</sub>	Fluidized bed	[168]
Rice husk	ZnO	Fixed bed	[169]
Rice husk	Al-MSU-F, Al-MCM-41, Rice husk ash	Fixed bed	[158]
Microalgae	Na <sub>2</sub> CO <sub>3</sub>	Fixed bed	[170]
Cellulose	K <sub>2</sub> CO <sub>3</sub>	Fixed bed	[171]
Reed	K <sub>2</sub> CO <sub>3</sub>	Fixed bed	[172]

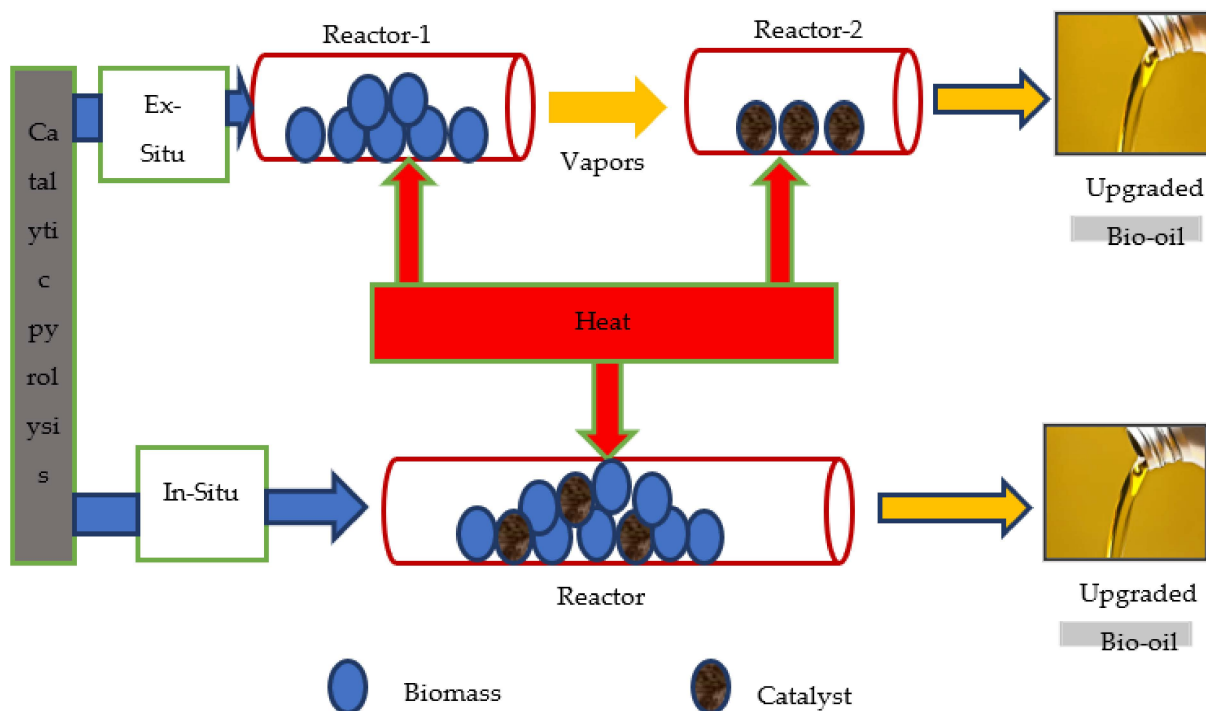
The prime catalysts are those that are combined with the biomass in the primary chamber before the pyrolysis process (in situ), while the secondary catalysts are those that are located in the secondary chamber after the pyrolysis process (ex situ). In the secondary process, the combustion of syngas or bio-oil takes place for energy or heat generation [173]. Sometimes, catalytic pyrolysis can also take place in the reactor chamber without mixing biomass and the catalyst [174].

#### 4.1.1. Arrangement of Catalysts

In situ or ex situ catalytic pyrolysis can be categorized according to where the catalysts are located inside the reactor [175]. The thermochemical conversion of biomass is carried out by in situ (primary) and ex situ (secondary) catalytic processes, as shown in Figure 7 [176,177]. By choosing the right catalysts and operating conditions, both procedures are necessary to transform oxygenated and heavy substances into chemically stable molecular products.

##### In Situ

In the in situ catalytic pyrolysis procedure, catalysts and biomass particles are mixed during the pyrolysis procedure to enhance the reactions. Catalysts not only participate in reactions but also serve as a heating medium. After being released from the biomass particles, the pyrolysis vapors directly react with the nearby catalysts in the in situ phase. This proximity between the biomass and catalyst speeds up the conversion of larger molecules. To provide effective deoxygenation of the vapors, there is a need for a large catalyst-to-biomass ratio [22]. The disadvantage of this process is that the biomass and catalyst have to operate under the same pyrolysis conditions. It is also tough to separate the biochar from the catalyst after pyrolysis [178]. The yield and quality of bio-oil were negatively impacted by the catalyst surface's abnormally high coke generation, according to research [96].



**Figure 7.** Arrangement of the catalytic pyrolysis processes (reproduced from Luo and Resende 2016; Muneer et al. 2019; Zadeh et al., 2020) [175–177].

#### Ex Situ

Catalysts are positioned in the same or other reactors in the ex situ catalytic pyrolysis process, downstream of the biomass. With various configurations of catalysts, it can be set up in a single bed, two phases, or more in sequence [179]. This method provides more stability and controllability for having various reaction conditions (combinations of catalysts, different temperatures, and variations in the gaseous condition), which can be dissimilar from the main biomass reactor. In addition, the ex situ process makes it possible to recover and recycle catalysts without the difficult isolation of catalysts that occurs in the in situ process [180]. As a consequence, both the end product and the intermediate product may be accurately tracked and tailored in line with research and industry demands after each procedure [22]. Ex situ pyrolysis is constrained by financial constraints due to the need for an extra catalytic reactor. Lower oxygen concentrations in bio-oils were discovered in an earlier investigation utilizing ex situ pyrolysis, even though deoxygenating activities were not seen during the in situ process [181].

#### 4.1.2. Affecting Factors of Catalyst Catalyst Position

The position of the catalyst (in situ and ex situ setups) plays an important role in the catalytic pyrolysis of biomass. When utilizing bubbling fluidized bed (BFB), auger, or pyro probe reactors, better yields of bio-oil, aromatics, phenols, gas, and CO are obtained in in situ mode with ZSM-5 (Zeolite Socony Mobil-5) compared to ex situ results. For the auger reactor, an in situ arrangement is preferable to an ex situ one for removing oxygen. When the BFB reactor was utilized, however, the opposite tendency was noted. Ex situ mode seems to yield better results for the deoxygenation of bio-oils in a fixed-bed catalytic pyrolysis reactor. Ex situ arrangements are preferred because they stop coking or metal accumulation from deactivating the catalyst by preventing it from happening on the surface of the catalyst. As a result, it is tough to conclude that the mode is superior because the findings are inconclusive [54].

### Ratio of Catalyst and Biomass

The “biomass-to-catalyst ratio”, also known as “weight turnover”, is the proportion of biomass or feed weight to catalyst weight. In the realm of catalytic pyrolysis, it is well known that catalysts can lose their activation properties when exposed to prolonged reactions or large amounts of feed materials because coke can build up on the catalyst’s surface and in its micropores, blocking the active sites [54]. The product yield is increased by a larger catalyst-to-feed ratio by preventing undesirable heat breakdown processes in the homogeneous phase. According to the research, increasing the catalyst ratio increased liquid yield while decreasing solid yield [182]. More than half of the Brønsted acidity and microporosity was lost during a weight turnover of 2.0 for catalytic pyrolysis of cellulose in a bubbling fluidized bed with ZSM-5. As a result, the aromatase-producing activity was significantly reduced [183]. Because the weight of the catalyst utilized is frequently significantly larger than that of the biomass feedstock, the inverse of this parameter, namely the catalyst-to-feed ratio, is occasionally used. Research suggests that increasing the catalyst-to-feed ratio might increase the generation of aromatic hydrocarbons [184].

### Catalyst Deactivation

The decrease in catalytic activity over time is known as catalyst deactivation. All catalysts are deactivated for poisoning, coking, and sintering [185]. Chemisorption of substances that block the active sites of catalysts cause poisoning to occur. Chemical and physical therapy are both effective ways to remove poisons. The active sites of the catalyst are blocked or altered by vapors that are deposited on its surface, leading to coking or fouling. By keeping the higher heating rate of the process constant and raising the catalyst-to-biomass ratio, it is easier to reduce it [186]. To decrease the surface area of the catalyst sites, tiny crystals start to form inside the catalyst, which then start the process of sintering. The amount of time the catalyst is exposed to is determined by the high-temperature stream [187]. The deactivation of the catalysts is the primary downside of the catalytic pyrolysis method [188].

### Catalyst Bed Temperature

In the process of catalytic pyrolysis of biomass, the temperature of the catalyst influences the rates of thermal and catalytic reactions like cracking, dehydration, decarbonylation, decarboxylation, and aromatization. These reactions affect the yields of bio-oil and gas, the productivity and selectivity of aromatic hydrocarbons and coke, as well as the deoxygenation pathways. It is possible to synthesize aromatic hydrocarbons with good selectivity and yields by raising the catalyst temperature [189]. The catalytic pyrolysis procedure is also impacted by the temperature of the catalysts. It was found that increasing the catalyst bed temperature from 450 to 600 °C caused the bio-oil production to drop as the amount of syngas increased [190]. The catalyst temperature also influences coke formation or catalyst deactivation. As catalyst temperature rises, the coke yield falls [191]. The output of coke decreased from 12.0 wt% at 400 °C to 7.8 wt% at a 600 °C catalyst temperature when rice husk was catalytically pyrolyzed in a fluidized bed reactor with a downstream fixed bed of an HZSM-5 catalyst [192].

## 5. Effect of Catalyst on the Catalytic Pyrolysis Process

### 5.1. Catalysts

There are several advantages to using a catalyst, but there are two main ones. First, the product benefits because the catalyst may increase the amount and quality of the desired end product by enhancing the formation of aromatics in the oil, which is accomplished by altering the process parameters. Additionally, the process is improved by adding a catalyst, which increases the overall process efficiency of the pyrolysis and energy performance. Next, the process is improved by lowering process temperatures and residency times, enhancing cracking and decomposition reactions, promoting isomerization reactions, and enhancing product selectivity [193]. Several catalysts are used in the catalytic pyrolysis

process: zeolite, natural catalysts (dolomite and clay), activated carbon, metal oxides, etc. [194].

### 5.1.1. Zeolite

Zeolite is a defined microporous form of crystalline aluminosilicates. It has a tetrahedral shape and is acidic, with channels and cavities connecting it to form a porous structure. Tetrahedral zeolites have a Si or Al central configuration with oxygen at the corners [195]. It has various acidities and an amorphous structure generated from the Brønsted and Lewis acid sites [196]. However, zeolite-based catalysts are ineffective against macromolecules in the procedure and have a slight denitrogenation effect [197]. Whilst synthetic zeolites like H-MFI, H-ZSM-5, H-BEA, and H-FAU (or H-X and H-Y single bond), and their modified forms are often used for industrial chemical processes, zeolites like chabazite and mordenite may be found naturally in rocks [198]. The petroleum industry has used ZSM-5 widely as a catalyst because of its shape selectivity, good pore size with steric hindrance, heat stability, and solid acidity [199].

Zeolite can be used as a hydrocracking catalyst due to the following: (i) greater acidity resulting in greater cracking activity; (ii) better thermal/hydrothermal stability; (iii) better naphtha selectivity; (iv) better resistance to nitrogen and sulfur compounds; (v) low coke-forming tendency; and (vi) easy renewability [200]. Nevertheless, when artificial zeolite is utilized as the catalyst, bio-oil production is reduced. Although the bio-oil output is reduced, it enhances the aromatic component of the bio-oil; as a result, once it is refined, it may be utilized as energy [201].

In Table 2, along with the results, the yield of the products from the catalytic pyrolysis of rice husk is shown. Compared to non-catalytic pyrolysis, the production of bio-oil drops from 39.61% to 38.29%, while the output of charcoal and syngas rises from 18.47% to 21.62% using a Brunei rice husk ash (BRHA) catalyst. In Table 2, aromatic hydrocarbons increase in zeolite but decrease in other catalysts. Phenol components also increase in zeolite and BRHA but decrease in other catalysts. It was found that each catalyst has its chemical selectivity, and zeolite has an influence on producing more aromatic hydrocarbons and phenols, which can be converted into biofuels after they are refined [158].

**Table 2.** Effects of a catalyst on the pyrolysis of rice husk [158].

Sample	Catalyst	Products Yield/wt%					Major Components in Bio-Oil				
		Biochar	Syngas	Bio-Oil	Organic Acids	Aromatic Hydrocarbon	Ketones	Furans	Heavy Phenols	Light Phenols	ANHYDR OSUGARS
Rice husk	--	41.92	18.47	39.61	16.06	1.51	14.75	8.99	13.57	12.77	3.65
	ZSM-5	42.27	19.45	38.29	15.49	2.24	12.96	9.63	13.48	14.44	2.04
	Al-MSU-F	43.31	19.18	39.59	15.51	1.57	13.82	9.57	14.24	12.56	2.34
	Al-MCM-41	43.15	18.80	39.98	14.17	1.42	13.65	9.57	14.99	12.60	2.88
	BRHA	42.27	21.62	38.29	16.16	1.53	14.76	9.48	12.84	12.66	2.75

### 5.1.2. Natural Catalyst

Clay and dolomite are examples of natural catalysts. Clay is mostly composed of alumina, silica, and magnesia [202,203]. The chemical compound dolomite, with the formula  $\text{CaMg}(\text{CO}_3)_2$ , is composed of calcium, magnesium, and carbonate [204]. Dolomite is used in the catalytic pyrolysis of biomass to increase the quality of the bio-oil by oxygenating oxygenates or catalytically splitting heavy organic materials into lighter fractions [205]. It was demonstrated that dolomite is effective in removing oxygen from bio-oil, resulting in a decreased O concentration and O/C ratio in the improved bio-oil [206]. It was shown that mineral clays can accelerate the catalytic cracking of heavy compounds present in the pyrolysis liquid [202].

By breaking down and reforming the high-molecular-weight organic components during the catalytic pyrolysis of biomass, dolomite demonstrated remarkable effectiveness as a catalyst [207]. When using dolomite as a catalyst in the pyrolysis process of the tulip tree, the bio-oil components  $\text{C}_5\text{-C}_{11}$  increase, and the ratio of  $\text{H}_2/\text{CO}$  produced



in syngas also increases, where it can be further treated and used as a liquid fuel [203]. Table 3 illustrates the effects of using natural catalysts (sand and dolomite) as catalysts in the pyrolysis of tulip trees. It was found that the catalytic pyrolysis of biomass using sepiolite (clay) could improve the yield of bio-oil by up to 46% regarding the non-catalytic method [208]. Another type of clay, named bentonite (aluminum phyllosilicate), showed an increase in bio-oil production of 48% in the pyrolysis of peat [209].

**Table 3.** Effects of natural catalysts in pyrolysis.

Sample	Catalyst	Temperature, °C	Products, wt%			Reference
			Biochar	Bio-Oil	Syngas	
Tulip tree	Sand	450	17.95	49.03	21.84	[203]
	Dolomite	450	26.04	34.26	39.70	

The literature reported that the utilization of dolomite as a catalyst would result in less bio-oil (34.26%) compared to the utilization of sand as a catalyst (49.03%) being produced during the pyrolysis process of tulip tree biomass. With a rise in syngas output, bio-oil likewise falls. Dolomite, which further breaks down the heavy components, might nevertheless enhance the quality of the oil. When the temperature rises, the breakdown of the heavier components accelerates [203].

### 5.1.3. Activated Carbon

Activated carbon is a substance that contains rich carbon and has a high degree of porosity and a high surface area. Due to its strong structure and surface area, it can be used to adsorb gas and further crack the components into smaller components. Both physical and chemical-activation processes can be used to transform the biochar product, which is produced during the pyrolysis of biomass, into activated carbon [26]. Activated carbon is a substance that contains a high amount of carbon and can be used as a catalyst to crack the bigger components into smaller components [210]. Utilizing activated carbon as a catalyst decreased bio-oil output while enhancing syngas yield, while biochar yield remained nearly unchanged. This is due to the reforming mechanism that occurs when a sample degrades with the AC catalyst, which causes additional cracking reactions [211]. Bio-oil production decreases as the temperatures rise due to components cracking into low-molecular-weight compounds [212].

From Table 4, it can be seen that using a catalyst decreases the bio-oil production while increasing the syngas yield and the biochar yield remains almost the same. Further reducing bio-oil output and increasing syngas yield are achieved by increasing the catalyst-to-cellulose ratio. However, it is also illustrated that the class of bio-oil was upgraded, while phenol production was increased when using a catalyst and increasing the catalyst-to-cellulose ratio. The author suggested that the reduction in bio-oil production was due to the reforming process, in which the sample underwent degradation and the volatile materials that flowed through the activated carbon led to further cracking reactions [211].

In Table 4, it is shown that an experiment was conducted on Douglas fir sawdust pellets in the pyrolysis procedure to engage in a different type of activated carbon, whose source was bituminous coal, wood, and lignite coal. In the absence of a catalyst, bio-oil yield was 45.20 wt%, syngas was 11.80 wt%, biochar was 43.00 wt%, and phenol components were 2.540 wt%. When activated carbon was introduced, the bio-oil yield and biochar production declined, while syngas production increased. However, the phenolic components were increasing significantly. This was because other components were further broken down into smaller components, where they were mostly converted into phenolic components [213].

**Table 4.** Catalyst effects of activated carbon on the pyrolysis process [213].

Sample	Catalyst	Products, wt%				Major Components, wt%			Ref.
		Bio-Oil	Syngas	Biochar	Phenols	Guaiacols	Furans	Ketones/Aldehydes	
Douglas fir sawdust pellets	No catalyst	45.20	11.80	43.00	2.540	48.78	3.90	10.36	[213]
	GAC 830 PLUS (Bituminous coal)	31.00	44.60	24.40	25.74	15.65	14.24	16.85	
	DARCO MRX (Wood)	26.50	52.67	20.83	71.87	1.33	-	3.03	
	DARCO 830 (Lignite coal)	28.97	47.53	23.5	74.77	-	-	2.02	
	Catalyst/Biomass				Phenol	Levoglucosenone	2-Furancarboxaldehyde, 5-methyl-		
Glucose	0	63.3	18.8	17.6	-	29.9		6.8	[211]
	0.28	52.8	18.7	24.0	4.7	18.8		8.8	
	0.4	49.5	18.9	25.6	10.9	20.5		10.8	
	0.7	45.8	18.8	29.1	34.5	-		24.4	
	1.13	44.6	18.7	29.6	88.4	-		-	

According to the latest research, the yield of the final products during the pyrolysis process can be increased by employing activated carbon as a catalyst. Furans, ketones, ethers, and phenols, for example, can be increased in bio-oil by up to 87% when activated carbon is used as a catalyst. Activated carbon can also increase the development of hydrocarbon or aromatic composites, where a rise in pH value and high heating value can upgrade the class of bio-oil [214]. Furthermore, the breakdown of components into low-molecular-mass compounds also results in a decrease in bio-oil production as a consequence of temperature increases [212].

The co-pyrolysis of the lignin and soapstock was studied, and non-catalytic co-pyrolysis showed higher yields of bio-oil and biochar with lower gas production. The major components showed low aromatics, phenolics, and other oxygenates with high aliphatic content. While activated carbon as a catalyst was introduced, it decreased the bio-oil yields and increased the gas yield, and the major components showed an improvement in aromatics and aliphatic compounds, with very few phenolic and other oxygenated compounds. Increases in the feedstock-to-catalyst ratio will, however, result in higher yields of bio-oil and lower yields of gas, which will result in a reduction in aromatic components and an increase in aliphatic components [212].

#### 5.1.4. Metal Oxide

Metal oxides are crystalline solids composed of a metal cation and an oxide anion [215]. Several types of metal oxides were used in catalytic pyrolyses, like magnesium oxides (MgO), aluminum oxides ( $\text{Al}_2\text{O}_3$ ), zinc oxides (ZnO), calcium oxides (CaO), titanium oxides ( $\text{TiO}_2$ ), and others [152,216]. Most of the time, metal oxides are frequently utilized in a variety of processes as heterogeneous catalysts. Metal oxides display redox qualities as a result of their polyvalent characteristics or specific acid-base characteristics, which may be useful for the catalytic pyrolysis of biomass to yield more stable products [217]. By using catalytic deoxygenation, oxygen from pyrolytic vapor is removed as  $\text{CO}_2$ , CO, and  $\text{H}_2\text{O}$ . Because of the carbon transfer for the gas product, the formation of water, and the carbon on the surface of the catalyst, the total yield of the liquid and organic phases is lower [163]. Metal oxides can be classified as acidic ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ), alkaline (salts of potassium, sodium, magnesium, and calcium), or transitional ( $\text{MnO}_2$ ,  $\text{CeO}_2$ ,  $\text{Fe}_2\text{O}_3$ , ZnO, and MgO) metal oxides depending on their properties [152].

Metal oxides typically react with water to form bases or with acids to form salts [218]. By keeping volatiles in tar, these catalysts can prevent their further breakdown into gaseous products [219]. Oxides of acidic metals also have an impact on oxygenate synthesis.  $\text{Al}_2\text{O}_3$ , for instance, facilitates the breakdown of macromolecular methoxyphenol and sugar during the catalytic pyrolysis of sawdust [220]. Alkaline metal oxides are inexpensive and available in huge numbers, and they are extensively employed in the catalytic pyrolysis of biomass. Alkaline metal oxides may concurrently remove acidic functional groups from bio-oil by ketylation and aldol condensation to reduce corrosivity and effectively lower the oxygen content in bio-oil [152]. In the catalytic pyrolysis of biomass, the output of both bio-oil and compound composition is enhanced by the use of transition metal oxides. It was found that the levels of carboxylic acid and oxygen decreased in the bio-oil produced by catalyzing the pyrolysis of various oxides [221].

Table 5 explains the effects of non-catalytic and catalytic pyrolysis and was converted to graphics for easy visualization. Once the catalyst was added, the production of bio-oil and bio-gas increased, but the yield of solids declined. The job of the catalyst during the pyrolysis of biomass is to lower the number of oxygenated molecules in the bio-oil. The catalyst then further cracks the oxygenated substance through a dehydration and decarboxylation process, which produces water and carbon dioxide [222].

**Table 5.** Effects of metal oxide as a catalyst on the pyrolysis process.

Sample	Catalyst	Products, wt%			Major Components, wt%				Ref.
		Bio-Oil	Biochar	Syngas	Acetic Acid	Anhydrosugar	Furan	Phenol	
Palm empty fruit bunches	No catalyst	42.3	27.2	30.5	1.95	0.22	0.38	1.54	[223]
	CaO, 5%	39.9	29.4	30.7	1.53	0.07	0.39	1.17	
	CaO, 10%	40.4	30.7	28.9	0.9	0.1	0.38	0.64	
	MgO, 5%	39.3	29	31.6	2.32	0.06	0.49	1.11	
	MgO, 10%	42.3	25.7	32	2.08	0.04	0.46	0.85	
	ZnO, 5%	44.7	27	28.2	2.29	0.07	0.41	1.2	
	ZnO, 10%	42.2	26.8	31	2.23	0.1	0.52	1.2	
Isochrysis Microalgae	No catalyst	16.82	37.86	45.32					[222]
		20.13	33.96	45.91					
		18.07	30.76	51.17					
	CeO <sub>2</sub>	20.82	34.83	44.35					
		22.97	31.08	45.95					
		19.91	28.48	51.61					
		22.41	33.18	44.41					
	TiO <sub>2</sub>	24.30	29.53	46.17					
		21.10	26.39	52.51					
		19.36	36.47	44.17					
	Al <sub>2</sub> O <sub>3</sub>	22.10	34.34	43.56					
20.03		31.80	48.17						

In Table 5, it is seen that the use of the catalyst in palm empty fruit bunches affects the product yield, where bio-oil and syngas yields decrease for CaO and MgO while ZnO increases. However, as the loading catalyst increases, the bio-oil yield in CaO decreases, while that in ZnO and MgO increases. The phenolic compounds decrease as the catalyst is used and with increases in catalyst loading. However, in ZnO, an increase in the loading effect of the catalyst does not change the phenol component. The anhydrosugar components decrease by breaking down into smaller components that increase the furan components. The acetic acid in CaO as a catalyst decreases, while it increases in ZnO and MgO since CaO is a basic oxide [223].

In the pyrolysis of rice husk, ZnO is utilized as a catalyst; the effect of temperature is that the production of biochar decreases while the yield of bio-oil and syngas increases. It also describes how the loading catalyst affects yields, showing how a rise in the loading catalyst enhances syngas production while reducing bio-oil output and slightly lowering biochar yield. In the pyrolysis of rice husk, the quality of bio-oil shows that non-catalytic bio-oil was 14.479%, while in catalytic bio-oil with zinc oxide, the bio-oil quality was 27.412%, consisting of light components with <120 g/mol, including alkanes, alkenes, styrene, and alkyl phenol [169].

Hence, from these studies, it can be deduced that different catalysts have different effects on the yield of the product, depending on the chemical selectivity of the catalysts.

#### 5.1.5. Mixture of Catalysts

Some researchers conduct pyrolysis experiments with a mixture of catalysts to find the compatibility needed to generate a high yield of bio-oil. The purpose of this research is to find synergistic effects. Some of the mixture catalysts that were investigated are Ni/C, Ce/AC, MgO/ZSM-5, and SiC/ZSM-5 [224,225].

The co-pyrolysis of soybean straw and soapstock was investigated using SiC-ZSM-5 as the catalyst, and it was found that bio-oil decreases when using SiC and ZSM-5 individually as catalysts compared to no catalysts, but when the catalysts of SiC and ZSM-5 are mixed, the bio-oil increases slightly compared to when using the catalysts individually. When utilizing a catalyst or a catalyst combination in comparison to not using a catalyst, the phenoxy compound in the chemical composites of the bio-oil drops. When ZSM-5 is used as

a catalyst, especially when compared with no catalyst, aromatic compounds considerably rise and somewhat decrease when ZSM-5 and SiC are combined [226].

Catalytic pyrolysis of *Jatropha curcas* residue was conducted by Kaewpengkrow et al. [227] and found that in the non-catalytic reaction, most of the constituents are the carboxylic acid group, while the acid group significantly decreases by introducing the catalysts. By using activated carbon as the catalyst, around 59.55% of aliphatic hydrocarbons are produced. When activated carbon was mixed with other metals, the aliphatic hydrocarbon components were decreased by increasing the aromatic hydrocarbons and N-compounds. For the biomass-to-catalyst ratio of 1:5, the aromatic hydrocarbon was significantly increased, and the oxygenating and acid components were decreased. For the feedstock-to-catalyst ratio of 1:10, the catalyst further decreased the mixture of oxygenating and acid components and increased the aliphatic and aromatic hydrocarbons.

Pyrolysis of acid-washed *Cladophora glomerata* was conducted, and Table 6 describes the comparison of non-catalytic and catalytic pyrolysis by using Zn/activated carbon. Biochar and syngas yields increased in catalytic pyrolysis from 34% to 37% and 20% to 28%, respectively, while bio-oil yields decreased from 46% to 35%. Oxygenates and acid compounds in bio-oil decreased when Zn/activated carbon was introduced, while nitrogenates, aromatics, and aromatic nitrogenates increased. It can be assumed that using Zn/activated carbon as a catalyst has selectivity for aromatics and nitrogenates [228]. A combination of  $K_3PO_4$  and clinoptilolite or bentonite enhanced bio-oil output during the catalytic pyrolysis of switch grass in comparison to using a single catalyst [229].

**Table 6.** Catalytic Pyrolysis of Acid-washed *Cladophora glomerata* [228].

Sample	Catalyst	Products Yield (wt%)		
		Biochar	Bio-Oil	Syngas
Acid-washed <i>Cladophora</i> Glomerata (ACG)	No catalyst	34	46	20
	Zn/Activated Carbon	37	35	28

## 5.2. Catalytic Effect on Bio-Oil

Before being employed in biofuels or other applications, the generated bio-oil has to be defined. It is characterized by following standards such as those of the American Society of Testing and Materials methods. The pH, water content, density, elemental analysis (CHNSO), ash content, higher heating value, viscosity, and other properties of bio-oil are being examined [230].

### 5.2.1. pH of the Bio-Oil

As bio-oil cannot be utilized as a transportation fuel if it is acidic, the pH of the bio-oil must be determined. As the pyrolytic temperature increases during the non-catalytic pyrolysis of pine wood chips, the pH level of the bio-oil increases [231]. Table 7 demonstrates that adding a catalyst reduces the pH of the bio-oil produced from pyrolyzing Brunei rice husk, whereas using a higher temperature raises the pH of the bio-oil produced from the pyrolyzing cotton stalk, where the pH of ZSM-5 is 2.74 at 450 °C and 3.9 at 600 °C. The pyrolysis of *Pinus halepensis* using CaO and a mixture of CaO and MgO, when their pH value is greater than non-catalytic bio-oil and compared to CaO, also increases the pH of the bio-oil from 2.8 (non-catalytic) to 4.8 (CaO). The loading effect of the calcium oxide catalyst was observed, where increasing the loading effect increased the pH value of the bio-oil. These results show that using basic oxide may increase the pH of the bio-oil [158,232–234].

**Table 7.** pH of bio-oil for catalysts and non-catalysts [232].

Sample	Catalyst	Temperature (°C)	pH	Reference
Cotton stalk	No catalyst	600	2.8 (±0.1)	[232]
	CaO		4.8 (±0.1)	
	MgO		3.9 (±0.2)	
	Al <sub>2</sub> O <sub>3</sub>		4.1 (±0.1)	
	ZSM-5		3.9 (±0.2)	
	MCM-41		2.8 (±0.1)	
	CuO		4.1 (±0.2)	
	Fe <sub>2</sub> O <sub>3</sub>		3.5 (±0.1)	
	NiO		3.9 (±0.1)	
	ZnO		4.3 (±0.1)	
	ZrO <sub>2</sub>		4.0 (±0.2)	
Brunei rice husk	TiO <sub>2</sub>	4.0 (±0.1)		
	No catalyst	450	3	[158]
	ZSM-5		2.74	
	Al-MCM-41		2.83	
	Al-MSU-F		2.69	
BRHA	2.79			
Pinus halepensis	Sand	450	2.9	[233]
	Sand-CaO		4.3	
Empty fruit bunch (EFB)	Sand-CaO.MgO	550	4.6	[234]
	No catalyst		3.8 ± 0.2	
	1% CaO		3.9 ± 0.2	
	5% CaO		3.92 ± 0.2	
	10% CaO	4.16 ± 0.3		

The temperature has also an impact on the pH value, and temperature increases can raise the pH value of bio-oil. When catalysts are used, the pH can be increased or decreased, but with the help of temperature, the pH can increase due to the breakdown of acid components into smaller components. Utilizing basic oxide can also raise the pH of bio-oil.

### 5.2.2. Water Content

Water content refers to how much water is present in bio-oil; the lower the water content, the better the bio-oil is for use as a fuel for transportation. Table 8 illustrates that as the temperature rises, the water content of bio-oil produced by non-catalytic pyrolysis remains constant at 20–21% [231].

**Table 8.** Water content in bio-oil for catalytic and nonanalytic pyrolysis [231].

Sample	Catalyst	Temperature (°C)	Water (wt%)	Reference
Pinewood chips	No catalyst	425	20.8 ± 3.9	[231]
		450	21.0 ± 4.6	
		475	20.3 ± 3.9	
		500	20.6 ± 3.9	
Brunei rice husk	No catalyst	450 (°C)	52.60	[158].
	ZSM-5		55.56	
	Al-MCM-41		54.66	
	Al-MSU-F		54.64	
	BRHA		55.43	
Pinus halepensis	Sand	450	3.5	[233].
	Sand-CaO		5.9	
	Sand-CaO.MgO		6.3	

As per Table 8, the trend in water content is the same: using a catalyst results in more water being present in the bio-oil than not using one. This is because using a catalyst improves bio-oil by eliminating oxygen from oxygenating compounds in the form of water,

carbon dioxide, and carbon monoxide [158,233,235]. It can be concluded that using catalysts can increase the water content of bio-oil due to the breakdown of oxygenated components into water and carbon dioxide.

### 5.2.3. High Heating Value (HHV)

The quantity of heat produced by the full combustion of a fuel is its heating value. The high heating value is the heat released from the fuel combustion with the original and generated water in a condensed state [236]. The higher the heating value, the more energy is formed and the more suitable it is to be used as a transportation fuel.

Bio-oil produced from the non-catalytic pyrolysis of pine wood chips is shown in Table 9, where an escalation in temperature slightly raises the HHV of the bio-oil. The HHV increased from 18.6 to 19.7 MJ/kg with the increase in temperature from 425 to 500 °C, indicating that the temperature has a minor role while catalyst and loading effects have a major role in increasing the high heating value [231].

**Table 9.** HHV of bio-oil from the pyrolysis of different feedstocks with various catalyst loading effects [22,180,231].

Sample	Catalyst	Primary Reactor Temperature, °C	HHV-Wet Basis, MJ/kg	HHV-Dry Basis, MJ/kg
Pinewood chips	No catalyst	425	18.6 ± 0.8	
		450	19.1 ± 1.3	
		475	18.4 ± 0.5	
		500	19.7 ± 1.2	
Brunei Rice husk	No catalyst		13.61	28.71
	ZSM-5		13.33	30.01
	Al-MCM-41	450	14.41	31.79
	Al-MSU-F		14.98	33.02
Empty Fruit Bunch (EFB)	BRHA		17.17	38.53
	No catalyst		13.46 ± 1.98	
	1% CaO	550	14.95 ± 0.58	
	5% CaO		15.80 ± 0.21	
	10% CaO		17.61 ± 1.94	

The type of catalyst has an impact on the HHV values of biomass in the pyrolysis of Brunei rice husk. About 30% of the HHV value was increased with the change in catalyst type. The highest HHV was obtained at 17.17 MJ/kg for the BRHA catalyst. Moreover, an increase in the loading of the CaO catalyst increased the HHV value by 30% compared to the non-catalytic process, indicating the impact of catalyst loading on the increase in the HHV of the biomass in the pyrolysis process [158,234].

### 5.2.4. Elemental Analysis

The elemental or ultimate analysis is the measurement of the carbon-hydrogen-nitrogen-sulfur-oxygen-ash contained in the bio-oil. It can be used as an alternative method to determine the HHV of the bio-oil using the following formula, for example [237]:

$$\text{HHV} = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{A}$$

The bio-oil quality is better when it has a greater H/C and a lower O/C ratio.

From Table S3, as temperature increases, the carbon (C)% increases while hydrogen (H)%, and nitrogen (N)% decrease at 500 °C, then increases at 600 °C while oxygen (O)% increases, vice versa for the pyrolysis of raw pine bark in a non-catalytic process [238].

As shown in Table 10, the elemental analysis of the bio-oil manufactured by non-catalytic and catalytic pyrolysis with the increase in temperature was obtained, where utilizing a catalyst results in higher C% and N% in the catalytic process than without one at 350 °C, while for O%, it is further decreased in the catalytic process. While the temperature

is augmented to 550 °C, C% is increasing and N% and O% are decreasing. Meanwhile, H% is fluctuating between 350 °C and 550 °C [239].

**Table 10.** Elements of bio-oil from the pyrolysis of *Anchusa azurea* [239].

Temperature, °C	Components	No catalyst	Na <sub>2</sub> CO <sub>3</sub>	ZnCl <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Ca(OH) <sub>2</sub>
350	C, wt%	45.68	56.00	46.52	49.82	50.76
	H, wt%	7.15	7.48	8.19	6.96	7.16
	N, wt%	1.57	3.37	1.74	2.28	2.64
	O, wt%	45.60	33.15	43.55	40.94	39.44
	H/C molar ratio	1.87	1.60	2.11	1.67	1.69
	O/C molar ratio	0.74	0.44	0.70	0.61	0.58
550	C, wt%	45.59	57.06	47.41	49.90	57.01
	H, wt%	7.11	7.48	7.21	7.43	7.05
	N, wt%	1.58	2.71	2.14	1.44	2.89
	O, wt%	45.72	32.75	43.24	41.23	33.05
	H/C molar ratio	1.87	1.57	1.82	1.78	1.48
	O/C molar ratio	0.75	0.43	0.68	0.62	0.43

Hence, from Table 10, it can be concluded that increases in temperature with the help of a catalyst can increase the C% and decrease the O%, in which this change is due to the reactions that occur within the catalyst, such as dehydration and decarboxylation.

#### 5.2.5. Stability of Bio-Oil

Biofuels are not as chemically or thermally stable as fossil fuels since they include a lot of oxygenated compounds. According to theory, the chemical interactions between components like ketones and aldehydes cause molecules with a high molecular weight to form, increasing the viscosity of bio-oil when temperatures are higher than 40 °C or when it is being stored for an extended period of time [240]. As a result, it is anticipated that bio-oil with a reduced carbonyl group concentration is more stable. Increased heavy-molecule-breaking processes and the removal of oxygenated chemicals result from the use of catalysts in the transportation and storage of bio-oil, producing bio-oil with a high degree of stability [241]. ZnO was used as a catalyst in a study by Nokkosmaki et al. [242] to pyrolyze pine sawdust. The stability test, which lasted 24 h at 80 °C, showed that the addition of ZnO changed the viscosity. The 55% change in viscosity was significantly smaller than the 129% change in non-catalytic bio-oil. Mante and Agblevor [243] examined the stability of the hybrid poplar wood-derived catalytic bio-oils (low and high bio-synchrude oils). A gravity oven was used for stability and aging evaluations, which lasted for 24 h at 90 °C. Moreover, the viscosities of the bio-oil samples stored at 40 °C for more than 10 months were analyzed. According to research, low bio-synchrude oil has a viscosity difference of 5%, whereas high bio-synchrude oil has a difference of 27.9%. It was discovered that catalytic bio-oils have excellent thermal stability and could be stored at room temperature for more than 10 months without viscosity appreciably rising.

When carbon dioxide (CO<sub>2</sub>) and water undergo catalytic pyrolysis, deoxygenation processes, such as dehydration, decarbonylation, and decarboxylation, release oxygen as a byproduct, regulating yield and quality [28]. By turning the oxygenated compounds into aromatic hydrocarbons, bio-oil produced by the pyrolysis of biomass is suited for upgraded bio-oil qualities. The bio-oils from catalytic pyrolysis are related to superior quality and greater output compared to non-catalytic pyrolysis due to the considerably larger proportions of aromatic hydrocarbons and pH. The quality of produced bio-oil often increases when a simple thermal process is switched to catalytic pyrolysis because of subsequent catalytic upgrading reactions.

To assess the economic viability of the pyrolysis process, a full grasp of cost concepts and their analysis is necessary. The outcomes of this investigation can help direct and influence future research and developments to boost efficacy and cost-effectiveness. We may make wise choices regarding the potential for commercialization and future expansion of



pyrolysis as a promising alternative energy source by taking into account its technological, financial, and environmental ramifications.

Though pyrolysis has a lot of promise, commercialization is still difficult to achieve, and it is necessary to thoroughly comprehend its dynamics in order to scale up the process. Although difficult, time consuming, and expensive, waste biomass pyrolysis is still a viable option. If these challenges can be resolved, using machine learning as a potential tool for assisting and expediting pyrolysis research would make biomass pyrolysis an attractive choice.

## 6. Machine Learning and Techno-Economic Analysis of Catalytic Pyrolysis

### 6.1. Machine Learning

Computer programs may predict outcomes more correctly thanks to machine learning, a type of artificial intelligence (AI) that does not require any explicit training. In order to forecast new output values, machine learning algorithms use previous data as input. ML-based models just need an experimental data set and do not require a great deal of process understanding and information. Most often, artificial neural networks (ANNs) have been employed in the gasification and pyrolysis sectors [244]. A variety of machine learning algorithms are crucial in the data science sector. These machine learning methods are crucial for creating predictive models and performing categorization and prediction. For performing prediction and classification in both supervised and unsupervised contexts, these ML methods are the most beneficial. The most popular artificial intelligence algorithms are listed below [245]:

- Artificial neural network;
- Linear regression;
- Decision trees;
- Logistic regression;
- Gaussian mixture model;
- Naive Bayes;
- K-means clustering;
- Anomaly detection;
- Principal component analysis;
- K-nearest neighbors algorithm;
- Support vector machines

Pyrolysis and gasification can be precisely modeled by machine learning models. To increase the production of renewable energy and meet national priorities like energy security and environmental sustainability, one of the numerous processes with optimization potential that may effectively use ML approaches is the thermal conversion of biomass [246]. More heed is being paid to the engineering applications that can benefit from process optimization by using the new knowledge that machine learning offers for managing the yields of pyrolytic products via the algorithm [247].

ANNs are a specific class of machine learning algorithms that mimic the human brain and function on the same fundamental principles as the neurons in our nervous system. The majority of recent research on the use of ML in pyrolysis is on traditional pyrolysis in fixed-bed reactors. The use of ML must be broadened, nevertheless, to include processes like catalytic pyrolysis and other types of reactors [248]. ML methods can forecast the yield and oxygen content of bio-oil depending on the properties of the biomass and the pyrolysis process [249], and the models based on artificial neural networks are also created to forecast biomass pyrolysis kinetics [250].

Four models, namely ANN-1 for proximal analysis; ANN-2 for ultimate analysis; ANN-3 for combined proximate and ultimate analysis; and ANN-4 for combined proximate, ultimate, and biochemical analysis, were employed by Balsora et al. [250]. With regression coefficient values of  $R^2 \sim 0.99$ , relative root-mean-squared error  $<10.0\%$ , and mean absolute error  $<0.071$ , it was discovered that the ANN-3 and ANN-4 models were highly useful in appropriately predicting the kinetic variables. The kinetic parameters discovered by

ANN-3 and ANN-4 are in good agreement with the kinetics established using the analytical approach, which can be inferred from the discussion above.

ANN prediction was also shown to be superior to optimized response surface methodology for producing bio-oil from the pyrolysis of *Mangifera indica* wood sawdust. Based on average absolute relative deviation percentage = 0.25945, mean squared error = 0.00001, and  $R^2 = 0.99711$ , the ANN-FFBP [3-9-1] model demonstrated good agreement with experimental bio-oil yield, and the MIW bio-oil has a flash point of 70 °C, a kinematic viscosity of 3.97 cSt, a high heat capacity of 25.10 MJ/kg, a pH value of 2.78, a mass density of 1058.7 kg/m<sup>3</sup>, and a high heat index of 25.10 MJ/kg [251]. This finding implies that to help plant operators make judgments on process improvement, machine learning techniques might be applied more often.

## 6.2. Techno-Economic Analysis

Pyrolysis, gasification, and biochemical processes were subjected to techno-economic evaluations in order to assess their relevance in the conversion of biomass to liquid fuels [252]. The price of feedstock, the cost of transportation, the cost of utilities, and the cost of waste disposal systems are all variables that affect the cost of producing bio-oils from biomass by catalytic pyrolysis. Other constant costs include labor costs for installation and depreciation, labor costs for maintenance, and investment costs. The commercialization of bio-oil is dependent on plant capacity, feedstock availability, and government subsidies [253,254]. Depending on the sources, manufacturing processes, collection, processing, and transportation distance, feedstock expenses can range from USD 50 to USD 97 per ton, or between 30 and 54% of the cost of generating liquid fuels [255]. An investigation of the profitability of both slow and fast pyrolysis of common wood discovered that fast pyrolysis was economical as a result of increased production of bio-oil, which is highly valuable in the production of energy [256]. To assess the techno-economic performance, such as production costs and profitability, machine learning models may be trained using data on process parameters, feedstock characteristics, and other pertinent factors.

Cost is a crucial component in determining if a pyrolysis process is economically feasible, and both capital and operational expenses must be examined [257]. Operating expenses may be divided into fixed and variable costs. Utility bills, payroll taxes, rent or mortgage payments, and insurance are a few examples of fixed operating expenditures. A variable operating cost is the cost of supplies like byproducts, feedstock, and raw materials [258,259]. To assess the economic viability of the pyrolysis process, it is crucial to have a solid grasp of cost concepts and their analysis.

Rice straw collection is far less expensive than energy crop production [260]. About 17.7 wt% of fuel is produced by the mild catalytic pyrolysis of woody biomass, and 39% of the energy is converted to fuel. While the pyrolysis liquid needs 2.7 wt% hydrogens to be deoxygenated, it also needs 6.4 wt% hydrogens to be saturated with aromatic rings. For a plant that can process 2000 metric tons per day, the total project expenditure is USD 457 million, with operational expenses of USD 142 million per year. On the basis of a 10% internal rate of return, a minimum fuel selling price (MFSP) of USD 3.69 per gallon is predicted [261]. The techno-economic study of the catalytic pyrolysis of olive mill wastewater sludge using two distinct cooling techniques was conducted by Khan et al. [262], in which a vapor compression refrigeration machine (type-1) and an absorption refrigeration machine (type-2) were used. The production cost of bio-oil was achieved in the range of 2.16 EUR/GGE to 6.19 EUR/GGE for type-1 and 1.78 EUR/GGE and 5.01 EUR/GGE for type-2, where the cost parameters are adjusted within an industrially applicable range.

Fast pyrolysis had the largest yields and lowest production costs, the exact reverse of what happened with biological methods. From each liquid fuel plant, product values ranging from USD 0.53 to USD 1.45 per liter (USD 2.0 to USD 5.5 per gallon) were anticipated. For a facility processing 2000 tons of feedstock per day, product values were calculated using a maize stover costing USD 75 per ton and plant starting costs [252]. Fast

pyrolysis analyses showed that power and biomass prices account for roughly 75% of production expenses. Selling the char generated by pyrolysis can lower the cost by around 18%. Production costs will rise from 6.8 GBP/GJ to 8.3 GBP/GJ with an 800-ton/day pyrolysis facility [263]. In the techno-economic analysis of catalytic pyrolysis for bio-oil production using ZSM-5, around 615 USD/ton was spent on making pyrolysis oil with 18% oxygen. When bio-oil yields rose by 20% (1000 tons/day), production costs dropped by up to 43 USD/ton. Pricing for biomass range from USD 57 to USD 114 per ton, and production expenses increased to as much as USD 841 per ton [264]. The economics of bio-oil production varies depending on the size, source, biomass, and catalyst expenses. As a result, the key to catalytic pyrolysis is the employment of affordable catalysts and close biomass sources [265].

## 7. Conclusions and Recommendations

### 7.1. Conclusions

In light of all the research results discussed in this review, it is noteworthy that the distinctive method for energy production from biomass is the catalytic pyrolysis process. This method can effectively transform waste materials into fuels and bioenergy with the support of catalysts. In the catalytic pyrolysis process, the quality of bio-oils is significantly increased by the formation of stable chemical compounds (phenolic, alcoholic, and aromatic compounds) and a reduction in unstable chemical compounds (acidic, oxygenated, and nitrogenous compounds) compared to the non-catalytic pyrolysis process. In the catalysts, zeolites are used mostly as a hydrocracking catalyst to increase the aromatic compounds in the bio-oil with higher thermal stability and better resistance to nitrogen and sulfur compounds. Among dolomite and sand as natural catalysts, the production of bio-oil was decreased in the catalytic pyrolysis process as the dolomite has the capability to break down heavy components. The activated carbon contained a huge number of active functional groups, which effectively increased the catalytic activity. The phenol components were significantly increased for breakdown into smaller components using activated carbon as catalysts. The mixture of catalysts is also effective for desirable outcomes in bio-oils. The quantity and purity of bio-oils generated by catalytic pyrolysis are significantly influenced by the structure of the biomass, the biomass-to-catalyst ratio, the operating temperature, and other process factors.

Catalytic fast pyrolysis is one of the most advantageous and affordable ways to extract upgraded bio-oil products from biomass feedstock. In the commercialization of bio-oils, the production costs are the key consideration in comparison to other biofuels, as the costs depend on the pretreatment, upgrading, and recycling methods. Techno-economic analysis, combined with the machine learning process, can effectively reduce production costs by enhancing the quality of the bio-oils. This process can also help direct the development of catalytic pyrolysis procedures that are both environmentally friendly and profitable. Finally, the catalytic pyrolysis process is one of the best methods to convert biomass into upgraded bioenergy, and techno-economic analysis with machine learning can enhance the viability of the process.

### 7.2. Recommendations for Future Works

The results of this study contribute significantly to the field of renewable energy science. The concept presented here may be applied to the pyrolysis process design and development of other biomass samples for energy generation. According to the experiments and findings, the study has met the expectations within the framework, and it can now be advanced for the future as follows:

- The catalytic effect can be observed with different biomass-to-catalyst ratios with in situ and ex situ arrangements in the future;
- Inexpensive materials can be studied as catalysts for catalytic pyrolysis;
- The experiment can be optimized with higher accuracy by changing the operating parameters like heating rate, nitrogen flow rate, etc.;

- The use of regenerated catalysts can be continued several times until satisfactory results are achieved;
- Different mixture ratios can be applied with activated carbon and other low-cost metal oxides to obtain upgraded bio-oils
- The syngas can be analyzed for further applications in the fuel cell to obtain clean energy;
- The bio-oils produced from catalytic pyrolysis can be used as fuel in real-world applications to achieve practical performance;
- A gap between lab-scale studies and the real industrial situation can be thoroughly discussed;
- Standardization of raw materials and process designs for the catalytic pyrolysis process should be performed with optimum techno-economic solutions;
- In order to expedite catalytic pyrolysis research, extensive machine learning processes can be explored due to their capacity to learn nonlinear input and output correlations;
- Future models for process optimization and control ought to strike a balance between determining load and precision. However, ML is not a universal fix for all issues in pyrolysis research; nevertheless, it may work in conjunction with current technologies and provide a great tool for pyrolysis process monitoring, control, and product yield optimization.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en16145547/s1>, Table S1: Conditions of operation and product yields of several pyrolysis processes; Table S2: Advantages and disadvantages of various pyrolysis technologies; Table S3: Elements of the bio-oil produced by the pyrolysis of raw pine bark.

**Author Contributions:** Conceptualization M.S.R., S.A. and A.K.A.; writing—original draft preparation, M.S.R., S.A., A.K., K.Z.B., M.M.K., H.R. and M.S.I.; writing—review and editing, Z.B.I., M.S.A.B., A.K.A. and M.S.I.; supervision, Z.B.I., M.S.A.B., A.K.A. and K.K.; funding acquisition, K.K. and M.S.I. All authors have read and agreed to the published version of the manuscript.

**Funding:** The research was completed as part of Project No. AP09261208 supported by the Ministry of Science and Higher Education, Kazakhstan.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors highly acknowledge L.N. Gumilyov Eurasian National University, Kazakhstan, Universiti Brunei Darussalam, Brunei, and Bangladesh University of Engineering and Technology for facilitating this work.

**Conflicts of Interest:** The authors declare no conflict of interest.

## Glossary

### Nomenclature

Al	Aluminum
Al <sub>2</sub> O <sub>3</sub>	Aluminum oxides
Ca	Calcium
CaMg(CO <sub>3</sub> ) <sub>2</sub>	Dolomite
CaO	Calcium oxide
CeO <sub>2</sub>	Cerium dioxide
CO <sub>2</sub>	Carbon dioxide
CO <sub>x</sub>	Carbon oxides
CO	Carbon monoxide
(C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>n</sub>	Cellulose
(C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> ) <sub>n</sub>	Hemicellulose
CH <sub>4</sub>	Methane
Cr	Chromium
Fe	Iron
Fe <sub>2</sub> O <sub>3</sub>	Ferric oxide
H <sub>2</sub>	Hydrogen

H <sub>2</sub> O	Water
HCl	Hydrogen chloride
K	Potassium
KCl	Potassium chloride
K <sub>2</sub> Cl <sub>2</sub>	Potassium chloride
K <sub>3</sub> PO <sub>4</sub>	Tripotassium phosphate
Mg	Magnesium
MgO	Magnesium oxide
Mn	Manganese
MnO <sub>2</sub>	Manganese dioxide
N <sub>2</sub>	Nitrogen
Na	Sodium
NaCl	Sodium chloride
P	Phosphorus
R <sup>2</sup>	Regression coefficient
Si	Silicon
SiC	Silicon carbide
SiO <sub>2</sub>	Silicon dioxide
TiO <sub>2</sub>	Titanium dioxide
ZSM-5	Zeolite Socony Mobil-5
Zn	Zinc
ZnO	Zinc oxide
Abbreviations	
3D	Three dimensional
AC	Activated carbon
AI	Artificial intelligence
ANN	Artificial neural network
Bentonite	Aluminum phyllosilicate
BRHA	Brunei rice husk ash
HHV	High heating value
ML	Machine learning
TEA	Techno-economic analysis

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