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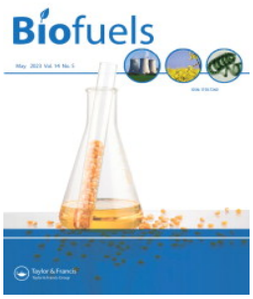

Biofuels

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/tbfu20

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To cite this article: Denzel C. Makepa, Chido H. Chihobo & Downmore Musademba (2023) Advances in sustainable biofuel production from fast pyrolysis of lignocellulosic biomass, Biofuels, 14:5, 529-550, DOI: 10.1080/17597269.2022.2151459

To link to this article: https://doi.org/10.1080/17597269.2022.2151459

BIOFUELS
2023, VOL. 14, NO. 5, 529–550
https://doi.org/10.1080/17597269.2022.2151459

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Advances in sustainable biofuel production from fast pyrolysis of lignocellulosic biomass

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ABSTRACT

The review provides a thorough assessment of current developments in biomass pyrolysis research, including both basic research and technological applications. Recent advances in pyrolysis-characterization methods, particularly on the online characterization of biomass pyrolytic intermediates and spectroscopic and microscopic imaging methods for biochar and bio-oil are discussed. Then, relevant optimization and regulation approaches for the biomass pyrolysis process are discussed in light of the demands made to enhance the physicochemical features of the relevant pyrolysis products. Previous studies have shown that co-pyrolyzing biomass with another feedstock can improve the physicochemical characteristics of the pyrolysis products and efficiently realize waste recycling. As a result, this study includes a thorough assessment of current developments in biomass co-pyrolysis using four different feedstocks (coal, plastics, tyres, and sludge). Recent activities of catalytic biomass pyrolysis, or catalytic co-pyrolysis, are also described as an essential part of general biomass pyrolysis. Reactor design aspects and economic evaluation of pyrolysis technologies have been reviewed. Additionally, two cutting-edge heating techniques (microwave heating and solar heating) for biomass pyrolysis are discussed, and their advantages and disadvantages are contrasted with those of the traditional heating approach. This review is concluded with some predictions for the development of biomass pyrolysis in the future.

ARTICLE HISTORY
Received 4 August 2022
Accepted 21 November 2022

KEYWORDS
Biomass pyrolysis; bio-oil; biochar; characterization; co-pyrolysis; biofuel production

Introduction

Biofuels are a form of energy fuel made from organic substances (often referred to as biomass) produced by plants and other living things that may be continuously grown and collected. Agricultural and critical harvesting, woods, and residual streams are the main sources of the biofuels used to replace nonrenewable energy fuels [1]. Biofuels typically take the form of biodiesel, which is made from vegetable oils, recycled wax, or animal fats, and bioethanol, which is distilled from plants that contain sugar and starch, such as corn, or biogas. One of the most significant energy sources in the world is petroleum oil. More than 70% of all petroleum fuel is used by the transportation industry. According to estimates, the world will run out of petroleum oil by 2070–2080 due to the substantial increase in petroleum consumption [2]. Due to greenhouse gas emissions (GHG), which include CO_2 and other harmful gases including methane, carbon monoxide, and chlorofluorocarbons, petroleum excessive use has raised worries about human health and global warming. By 2040, it is expected that greenhouse gas emissions will reach an estimated 43 billion metric tonnes. Consequently, it is vital to have additional power sources that are quickly available, renewable, and easy to access [3].

As a result of its nontoxic, sulfur-free, biodegradable, and renewable source origins, biofuels are being explored as a replacement for petroleum. In addition to farm waste, crops, and junk from manufacturing facilities, lignocellulose also comes from forests. A nutritional and environmental crisis can be lessened with the development of lignocellulosic biofuels. The three components lignin (26–31%), hemicellulose (25–32%), and cellulose (41–46%) are typically combined in the formation of lignocellulosic biomass [4].

Biofuels are divided into four categories based on the feedstock: first, second, third, and fourth generation biofuels. First-generation (1 G) biofuels raise serious financial, environmental, and political issues since their large-scale production of feedstock necessitates more fertile farmland, which reduces the amount of land available for growing crops for consumption. Researchers focused on second-generation (2 G) biofuels, which are derived from various non-food products including cellulosic biomass, inedible plant parts, straw, manure, waste cooking oil, wood, and sawdust, as the first-generation (1 G) biomass is not viable. However, because the production process necessitates expensive and cutting-edge technology, producing ethanol from 2 G biomass feedstocks is not commercially viable [5]. Following this, research focused on the creation of third-generation (3 G) biomass from microalgae, which is now believed to be a viable alternative for a sustainable source of energy for biofuel production by addressing the drawbacks of both 1 G and 2 G biofuel sources [6]. Bioethanol and biodiesel, for example, may both be produced from microalgae. A novel and fast developing field employing engineered cyanobacteria, is being used to generate fourth generation biofuels [4].

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There are two major conversion pathways in the process of transforming lignocellulosic biomass into hydrocarbon biofuels to generate upgradeable gaseous or liquid products, and the whole biomass is fragmented. Typically, this phase is carried out using thermochemical techniques to create syngas (through gasification) or bio-oils (through pyrolysis or liquefaction), alternatively it can be accomplished using hydrolysis to make sugar monomers that are subsequently deoxygenated to create improved intermediates. A key technique for upgrading biomass for the generation of biofuels is the thermochemical conversion process, which offers a variety of possible technologies [7].

The desire to create biofuel from vegetable oil, particularly palm oil, has grown during the past few years. The aim to lower greenhouse gas emissions is the key motivator for this. The production of biofuel from palm oil has several drawbacks, including the following: (i) it is insufficient to offset global fuel consumption; (ii) it increases food and fuel price competition; and (iii) it causes environmental degradation as a result of the conversion of forests to oil palm plantations to increase oil production [8]. As a result, a plan has been made to make biofuel from waste lignocellulosic biomass. To manufacture biofuel from lignocellulosic biomass wastes, multiple studies have been undertaken and a variety of techniques have been suggested [9–11]. The approaches described change depending on the type of waste utilized as a feedstock for making biofuel. Depending on the process and feedstock employed, the properties of the produced biofuel also change. So, it is crucial to review and discuss the key findings of these research studies.

A well-planned biomass garbage collection and repository system is crucial for the development of a large-scale biofuel system for managing organic waste. To enhance the waste collection and repository system, effective regulatory procedures must be established [12]. Government grants to establish biofuel facilities and incentives for application will aid in managing the biofuels produced from waste [13]. One can significantly improve the development process by adding cutting-edge methods [14]. However, cutting-edge technologies are essential for the efficient production of biofuels to reduce the use of nonrenewable fuel in global economies and achieve sustainable energy stability in the future. Therefore, it is essential to make quick progress to produce enough biofuel to meet the world's energy needs. Therefore, a novel strategy is required to address the continuous issues with waste administration, including increased area and water usage [15].

This review discusses the improvements made in the production of biofuels using organic waste and innovative technology. The best source of renewable energy that can perform better than other fuels in the transit industry is biodiesel. By using biodiesel, the brown haze will be reduced by 40%, and the CO percentage will be greatly reduced. With just a slight loss in power, the combustion of a mixture of biodiesel and mineral diesel lowers the emission levels of CO, hydrocarbons, and particulate matter. Given how effective and desirable using biodiesel is, the primary obstacle to starting a profitable business is the rising cost of raw materials [16].

Emerging technologies' potential economic efficiency may be adequately estimated, allowing for the selection of the most efficient conversion path depending on the type of raw biomass needed and the desired product [17]. Therefore, this study seeks to provide a wide-ranging and thorough account of current developments in both fundamental mechanisms and technological applications of biomass pyrolysis. Notably, this work analyses relevant research on the biomass pyrolysis process from the molecule to the reactor size, leading to a more thorough and complete understanding of biomass pyrolysis. Additionally, there have been engaged combined uses of various pyrolysis methods. In this regard, this study starts with the mechanisms of the biomass pyrolysis process, followed by the properties and applications of pyrolysis products. The parameters influencing the biomass pyrolysis process and the co-pyrolysis of biomass are also discussed. The last section reviews the two pyrolysis methods, namely, microwave pyrolysis and solar pyrolysis are introduced. In the end, future development directions of biomass pyrolysis are presented.

Pyrolysis mechanism

The complexity of biomass pyrolysis results from the diversity in reaction mechanisms and rates that occur during the degradation of the various components of the biomass, which is also partially dependent on the thermal processing settings and reactor designs. Prior research has established interactions between the main components of woody biomass, such as cellulose, hemicelluloses, and lignin, during pyrolysis [18], which makes the prediction of biomass pyrolysis characteristics simply based on the thermal behavior of the three individual components very difficult. For instance, the interaction between lignin and hemicellulose encourages the development of phenols generated from lignin while inhibiting the production of hydrocarbons [19]. While cellulose-hemicellulose contact has a lesser impact on the synthesis and dispersion of pyrolysis products, lignin and cellulose interact extensively during pyrolysis since lignin prevents the polymerization of levoglucosan from cellulose and hence reduces biochar formation [20].

Dehydration, depolymerization, isomerization, aromatization, decarboxylation, and charring are only a few of the numerous parallel and series reactions that occur during biomass pyrolysis [21]. It is generally accepted that the pyrolysis of biomass consists of three main stages: (i) initial evaporation of free moisture, (ii) primary decomposition followed by (iii) secondary reactions (oil cracking and depolymerization) [22]. These stages coexist, and thermal analysis can be used to observe how they transition between one another. Through the use of computer-aided thermal analysis at various heating rates, the apparent specific heat of biomass during pyrolysis and the associated temperatures of reactions throughout various pyrolysis stages have been thoroughly researched in the past [23,24].

The main decomposition of biomass, which results in solid char at temperatures between 200 and 400 °C, often causes the most decomposition of biomass. The solid

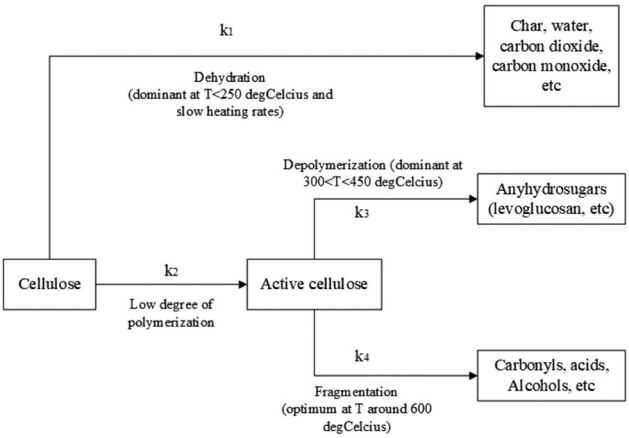

Figure 1. Waterloo mechanism of primary decomposition of cellulose.

matrix continues to experience secondary reactions as the temperature continues to rise [25].

The primary biomass constituents' individual degrading routes have each been studied. After cellulose, which largely decomposes between 325 and 400 °C with levoglucosan as the main pyrolysis product, hemicellulose, which is typically represented by xylan, decomposes mostly between 250 and 350 °C [26]. Lignin is the most stable component which decomposes at a higher temperature range of 300–550 °C [27].

Among the three major biomass constituents of cellulose, hemicelluloses, and lignin, the decomposition of cellulose has been most widely analyzed and best comprehended [28]. The widely accepted Waterloo mechanism, represented in Figure 1, shows the cellulose pyrolysis reaction route in a simplified form. The key competitive processes that predominate at various temperature ranges are dehydrogenation, depolymerization, and fragmentation.

Properties and applications of pyrolysis products

Bio-oil

Fast or flash pyrolysis is the method of choice to maximize bio-oil yields when producing bio-oil is the main product of interest. The key elements of fast pyrolysis typically include moderate pyrolysis temperatures (450–650 °C), biomass particle sizes of less than 2 mm, extremely high heating rates (103–105 °C/s), extremely short vapor residence times (2 s), and rapid quenching of pyrolytic vapors to suppress secondary reactions [29]. Primary char must be removed quickly because it catalyzes the formation of secondary char, gas, and water from primary organic vapors, which reduces the yield of bio-oil. Based on the dry biomass feed weight, the fast pyrolysis process typically generates bio-oil, gas, and char yields of 60–70 wt%, 13–25 wt%, and 12–15 wt% respectively [30]. With typical feed particle sizes of not more than 200 mm and higher temperatures of about 800–1000 °C, flash pyrolysis produces bio-oil yields that are typically 75 wt% and gas and char yields that are 12–13 wt% [31]. Typically, slow pyrolysis takes place at low temperatures with a prolonged residence time and slow heating rate. Due to the primary product cracking, which may have a negative impact on the yield and quality of the bio-oil, this method of pyrolysis can yield more char when the operating conditions are controlled than fast and flash pyrolysis [32].

Bio-oil, also known as 'pyrolysis oil, pyrolysis liquid, pyrolysis tar, bio-crude, wood liquid, wood oil or wood distillate' [33], is a dark brown, freely flowing organic liquid mixture that typically contains a significant amount of water (15–35 wt% on average) and a large number of organic compounds, including acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, alkenes, nitrogen compounds, and various oxygenates, as well as solid particles [34]. The initial moisture content of the feedstock and water generation during pyrolysis in relation to the reaction parameters determines the ultimate water content of the bio-oils. Due to the presence of pyrolytic lignin with molecular weights as high as 5000 amu or even more, it is exceedingly difficult to accomplish chemically accurate identification of some individual components in the bio-oils [35].

The normal range of the bio-oils' higher heating value (HHV) is between 15 and 20 MJ/kg, which is only 40–50% of the HHV of conventional petroleum fuels (42–45 MJ/kg) [36]. This is a result of the significant oxygen content, which ranges from 30 to 35wt% on a dry basis weight.

The low pH value of 2–3.7 caused by the presence of carboxylic acids is one of the negative properties of pyrolysis bio-oils in addition to their high oxygen content. As a result, bio-oils have the potential to be destructive to common structures, have high instability during storage due to ongoing chemical reactions that result in larger molecules (primarily polymerization, etherification, and esterification) [35], and retain solids to the extent of 0.01–1 wt% of their weight. Concerning moisture content (15–30 wt% vs. 0.1 wt%), specific gravity (1.2 vs. 0.94), elemental makeup, and a few additional fuel indices, such as pour point (−33 °C vs. −18 °C), extensive comparisons between bio-oil and heavy fuel oil were offered [37].

Bio-oils have undergone considerable testing as potential fuels for gas turbines, diesel engines, boilers, furnaces, and combustors [38]. Long-term operation is not possible due to the poor quality of the bio-oils, which include weak volatility, high viscosity, high corrosiveness, and coking. Bio-oils were successfully burnt in a diesel test engine with limited operation time [29]. It is well acknowledged that bio-oils need to be upgraded further before they may be used in engines through hydrogenation [39], hydrodeoxygenation [40], catalytic pyrolysis [41], catalytic cracking [42], steam reforming [43], molecular distillation [44], use of supercritical fluids [45], esterification [46], or emulsification [47]. Additionally, bio-oils can be utilized as a feedstock for the manufacturing of chemicals, including phenols for resin manufacture, additives in the fertilizing and pharmaceutical sectors, flavoring agents (like glycolaldehyde) in the food industry, and other specialized chemicals [38, 48].

Biochar

The main solid product, known as biochar or charcoal, is composed primarily of unconverted organic solids, carbonaceous wastes, and a mineral fraction that results from the partial or total breakdown of biomass components. The kind of feedstock and pyrolysis working conditions affect the chars' physical, chemical, and mechanical characteristics. Slow pyrolysis at pyrolysis temperatures between 300 and 800 °C favors the production of biochar by reducing

the yields of bio-oil (typical product yields: bio-oil 30 wt%, biochar 35 wt%, and gas 35 wt%). The elemental composition (carbon content varying from 53 to 96%), HHVs (20–36 MJ/kg), and yields (30–90 wt%) of biochar from the pyrolysis of various biomass feedstock, as well as pyrolysis at varied heating rates and temperatures, were summarized by Demirbas [36]. Char is a desirable coal alternative in several fuel applications due to their high HHV.

The microscopic surface structure of biochar produced during pyrolysis gives them the ability to filter and adsorb organic and inorganic contaminants [49,50], especially after the chars are physically or chemically activated. The ideal biochar qualities for filtration (surface area of 1400 m^2/g and micropore volume of 0.7 cm^3/g) were produced from coconut shells using a fluidized bed reactor at reaction temperatures of 850 °C and 1.5 h under steam. Olive seed waste was pyrolyzed in a fixed-bed heated under N_2 at 800 °C for 1 h to form biochar, which was then activated with KOH to produce biochar with similar qualities (surface area of 1690 m^2/g and micropore volume of 0.7 cm^3/g) [51]. Manyà [52] has provided more information regarding the properties of several activated biochars, including BET surface area, micropore volume, and the ratio of micropore volume to total pore volume, as well as the activation conditions (reaction atmosphere, temperature, and retention time).

Biochar contains a range of plant nutrients, making them valuable as soil amendments [23] and they can also contribute to carbon sequestration to mitigate atmospheric carbon [53]. The type of biomass and the pyrolysis conditions have a significant impact on the concentration of the various nutritional components. Due to the loss of biomass bulk at higher temperatures during pyrolysis, the concentrations of nutritional components are increased in the biochar. The concentrations of nitrogen might vary based on the type of biomass and the chemistry of the nitrogen in the feedstock because it is more volatile than the other nutrients.

Syngas

CO_2, CO, hydrogen (H_2), low carbon number hydrocarbons like methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4), as well as trace amounts of other gases like propane (C_3H_8), ammonia (NH_3), nitrogen oxides (NO_x), sulfur oxides (SO_x), and low carbon number alcohols, can all be released during the pyrolysis of biomass. Depending on their actual composition, the usual LHVs of the syngas range from 10 to 20 MJ/Nm^3. As the primary products of biomass pyrolysis, CO_2 and CO mainly originate from the decomposition and reforming of carbonyl (C = O) and carboxyl (COO) groups [54,55]. Light hydrocarbons (primarily CH_4) are primarily attributed to the decomposition of weakly bonded methoxyl (-O-CH3) and methylene (-CH2-) groups as well as the secondary decomposition of the oxygenated compounds, while H_2 results from secondary decomposition and reforming of the aromatic C = C and C–H groups at high temperatures [56].

Biomass pyrolysis can result in the production of hydrogen-rich gas or synthetic gas. Wet biomass could give up to 40% higher H_2 yield and content in the gas, compared to dried biomass [57]. Temperature and catalysts can further enhance the hydrogen production from biomass [58]. Catalysts which can promote H_2 production and adjust the gas composition for downstream applications (e.g. Fischer–Tropsch synthesis) include $ZnCl_2$, dolomite, K_2CO_3, Na_2CO_3, Ni/Al, Ni/Fe, CaO, Fe_2O_3, Cr_2O_3 and Rh/CeO_2 [59,60]. Before the syngas can be used in practice, it must undergo several treatments to decrease or remove the undesirable constituents, which may include dust/aerosols, tars, steam, evaporated heavy metals, HCN, H_2S, and NH_3.

The syngas has multiple potential applications, such as direct use for the production of heat or electricity (e.g. gas combustion in spark ignition and compression ignition engines [61]), either directly or co-fired with coal, production of individual gas components, including CH_4, H_2 or other volatiles, or in production of liquid biofuels through synthesis. In some situations, the hot pyrolytic gas can be recycled into the pyrolysis reactor as a carrier gas or utilized to pre-heat the inert sweeping gas.

Analysis of pyrolysis products

The bio-oil, char, and gaseous by-products of pyrolysis have been chemically and physically characterized using a variety of analysis techniques. The characteristics of these products and the relevant analysis techniques are summarized in Table 1.

In situ characterization of biomass pyrolysis

Pyrolysis–GC and mass spectrometry (Py-GC/MS)

Py-GC/MS is employed to identify the chemical composition and structure of the pyrolysis vapors that emerge during the pyrolysis of biomass. During the pyrolysis process, the biomass sample is heated at elevated temperatures, in an inert environment, and the pyrolysis volatiles that emerge are transferred to the GC column, where they are chemically identified by mass spectrometry. Flame ionization or a thermal conductivity detector then quantifies the pyrolysis volatiles. A typical schematic of a Py-GC/MS system is illustrated in Figure 2. In a study by Ye et al. [83], this technique was employed to analyze the products of biomass fast pyrolysis. In their study, the pyrolysis volatiles were first observed at 400 °C, and high yields were observed at temperatures as high as 600–700 °C. The pyrolysis volatiles constituted mainly levoglucosan, anhydrosugar derivatives, furans, phenols, aromatic hydrocarbons and light linear carbonyls. The pyrolysis volatiles increased at the temperature and feedstock residence time increased. Mullen & Boateng [84] employed the same technique to quantify the aromatic hydrocarbons produced from catalytic fast pyrolysis of biomass. Fe-Modified HZSM-5 zeolites were employed as catalysts, and the results showed that around 18% of selected aromatic hydrocarbons, including benzene, toluene, and ethylbenzene, can be obtained. The aromatic yield of switchgrass was 17% and cellobiose 25%. With this information and technique, a possible pyrolysis mechanism can be developed depending on the required product characteristics. The only drawback with this technique is that Py-GC/MS can only allow non-continuous analysis; therefore, it cannot give evolution characteristics over a wide range of temperatures. However, TG-based techniques (TG-MS, TG-FTIR, and TG-FTIR-MS) counter all these problems.

Table 1. Biomass and pyrolysis products analysis techniques.

Pyrolysis Products	Properties	Analysis Methods	Reference
Bio-oil	Water content	Water content ASTM E203 or ASTM D-1744 by Karl–Fischer titration	(62)
	Carbon residue	ASTM E203 by destructive distillation method	(62)
	Qualitative and quantitative identification of bio-oil compounds	Gas chromatography-mass spectrometry (GC–MS), high-performance liquid chromatography (HPLC)	(62)
	Molecular weight distributions	Gel permeation spectroscopy (GPC), Matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy	(63)
	Gross calorific value (GCV)	ASTM D4809	(62)
	HHV	Theoretical calculation	(64)
	Elemental composition (C, H, N and O by difference)	ASTM D5373	(62)
	Sulfur content	ASTM D4294 by Energy dispersive X-ray fluorescence (EDXRF) spectrometry, or ASTM D4239 by Infrared measurement of SOx after combustion of bio-oils	(62)
	Functional groups	Infrared techniques including near-IR (NIR) and Fourier transform infrared (FTIR) spectroscopy	(65)
	Types of hydrogens or carbons in specific structures	Nuclear magnetic resonance (NMR) spectroscopy	(66)
	Acid number	ASTM D664 by potentiometric titration method, or ASTM D974 by colour-indicator titration	(62)
	Density at 15 °C (kg/m^3)	ASTM D4052 by digital density meter	(62)
	Kinematic viscosity(mm^2/s)	ASTMD445–03	(62)
	Flash point, pour point and boiling range (°C)	ASTM D93, D97, and D2887, respectively	(62)
	Water insolubles	FTIR, ^{13}C NMR, and column chromatography	(65)
Biomass/Char	Proximate analysis (moisture, ash, volatile matter, and fixed carbon contents)	ASTM D1762-84,2007	(66)
	Ultimate analysis (elemental analysis of CHN, and O by difference)	ASTM D3176-89,2002	(66)
	Metal content	X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES)	(67)
	Elemental surface distribution	Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)	(68)
	Functional groups	FTIR	(69)
	Aromaticity	^{13}C NMR	(70)
	Mass/heat change during heating in different atmospheres (N_2, O_2, air, etc.)	Thermogravimetric analysis with differential scanning calorimetry (TGA/DSC)	(71)
	Crystalline phases, and their qualitative and semi-quantitative data	X-ray diffraction (XRD)	(72)
	Brunauer–Emmet–Teller (BET) surface area, porous structure	Nitrogen gas sorption	(73)
	Surface morphology	SEM	(70)
	Particle size distribution	Laser sizing equipment	(74)
	Electrical conductivity (EC)	Conductivity meter	(75)
	Particle size distribution	Microscopy, particle counter laser sizing equipment	(74)
	Surface acidity and alkalinity	Boehm titration	(73)
	Organic carbon	DPI in-house method 236	(76)
	Cation exchange capacity	Ion chromatography (IC)	(77)
Gas	Gases species and concentrations	Gas chromatography (GC); mass spectrometry (MS); non-dispersive infrared (NDIR) analysis	(78)
	Functional groups	FTIR	(19)
	Lower heating value (LHV)	Calculation from gas composition: LHV(MJ/m^3)=(107.98*H_2 + 126.36*CO + 358.18*CH_4 + 59.036*C_2H_4 + 63.772xC_2H_6)/1000, where gas species represent the respective volumetric fractions	(79)
	H_2S content	Lead sulfur precipitate through a reaction between H_2S and lead nitrate	(80)
	Tar content and composition	Cold trapping; solid-phase adsorption (SPA)	(81)
	Size distribution of particles	Scanning mobility particle sizer (SMPS)	(82)

TG-based techniques

TG-MS

TG-MS can identify the pyrolysis volatiles that evolve during the biomass pyrolysis process. A research study by Sanchez-Silva [85] employed this technique for thermochemical degradation characteristics of lignocellulosic biomass. It was found that biomass pyrolysis takes place in four distinct stages: (i) moisture evaporation, (ii) hemicellulose degradation, (iii) cellulose and lignin degradation and (iv) carbonization of lignin. At temperatures between 200 °C and 450 °C, light hydrocarbons, CO_2 and H_2O were produced, and at temperatures above 700 °C, secondary reactions known as char self-gasification took place,

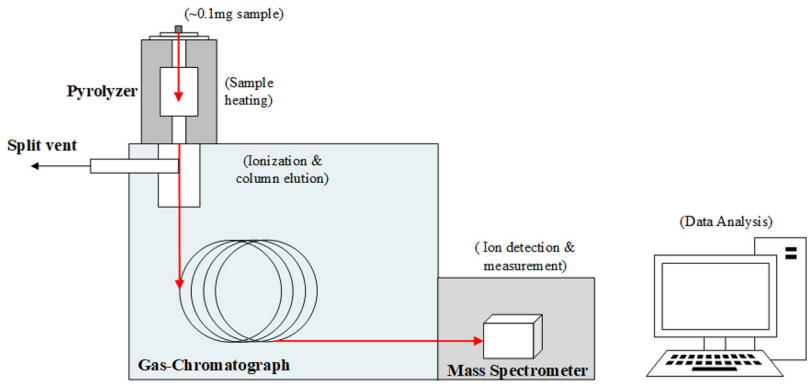

Figure 2. A typical schematic of a Py-GC/MS system.

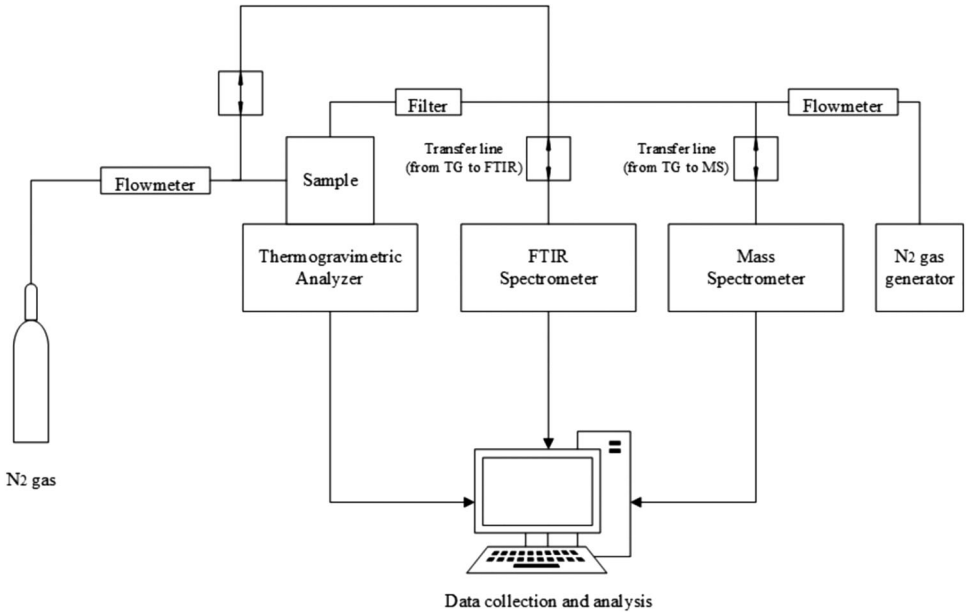

Figure 3. Illustration of the principle of the TG-FTIR-MS.

liberating H_2 as a product. A research study by Magdziarz [86] discovered that biomass devolatilization takes place at 200–540 °C, and pyrolysis volatiles constituted H_2, CO_2, CO, and CH_4.

TG-FTIR

TG-FTIR technique can detect numerous volatile compounds in the gaseous mixture of the pyrolysis products and offers real-time and nondestructive measurements. The FTIR spectrometer can *in situ* detects the functional groups of the pyrolysis volatiles that evolve from the TG. A research study by Gao et al. [87] employed this technique to assess the pyrolysis characteristics of pine sawdust. They discovered that the second stage of the pyrolysis process produced most of the pyrolysis volatiles, and CO, CO_2, CH_4, H_2O, phenolic compounds, and paraffin gas were detected as the main constituents. Chen et al. [88] observed similar results in the pyrolysis of bamboo over a temperature range of 300–700 °C. The results of their study have shown at elevated temperatures, pyrolysis vapor yields increased and biochar yields decreased. According to their study, the gaseous products (CH_4, CO, H_2O, alkane, and aldehydes compounds) were liberated at 240–400 °C. CH_4 was formed as a result of the high binding energy of methylene groups and the weakly bound methoxy groups (-OCH_3-). The production of CO resulted from the breakdown of ether groups, which were generated from ether compounds found in pyrolysis vapors and/or lignin. H_2O was primarily liberated at temperatures between 100 and 500 °C mostly from the crystallization of water and moisture bound in the biomass. H_2O is also produced at temperatures exceeding 500 °C due to secondary reactions of oxygen functional groups created during pyrolysis process. The amount of CO_2 released grew as the temperature increased and peaked at 360 °C. It subsequently reduced between 360 and 400 °C and then spiked again when the temperature was raised to 700 °C. The primary reaction in the pyrolysis process, known as solid-phase polymerization, occurs as the temperature rises and releases low amounts of CO_2.

TG-FTIR-MS

Even though TG-FTIR is a useful tool for analyzing the pyrolysis behaviors and the evolution of pyrolysis vapors from biomass, there is frequently overlap between the spectrum bands of several groups. As a result, it was challenging to reliably determine complicated molecular structures that are present in the pyrolysis vapors. The MS technique is used as an efficient supplement for TG-FTIR to solve this limitation, and it has become more widely used in the pyrolysis of biomass feedstocks (Figure 3) [89]. The fundamental mechanisms of the pyrolysis of sewage sludge were first studied by Tian et al. [90] using the TG-FTIR-MS online

approach, particularly the migration and modification of N-containing constituents. The TG results revealed that there were primarily two processes involved in the degradation of sludge. The initial weight loss (15 wt%), which took place between 150–350 °C, was attributable to the breakdown of biodegradable materials. The subsequent weight loss (25 wt%) was caused by the breakdown of dead bacterial biomass between 350 and 550 °C. By using TG-FTIR-MS, it was possible to pinpoint the precursors of NO_x and N_2O, N-containing substances, and short-chain hydrocarbons that were produced during the pyrolysis of sludge. The mechanisms of nitrogen migrations and alterations in the biomass feedstock during the pyrolysis process can be established based on the TG-FTIR-MS study of the intermediates. Qian et al. [91] also employed the TG-FTIR-MS technique to investigate the production of P-containing substances during the co-pyrolysis of biomass and plastic. Results showed that butyl propionate, 2-butoxyethanol, and 1, 2-dibutoxyethaneare were the primary chemicals produced at temperatures between 220 and 390 °C, which were caused by the cleavage of the side chain of TBEP. P-containing substances, such as dimethyl hydrogen phosphate and diethyl hydrogen phosphate, were found to exist between 370 and 620 °C. These substances could be a result of breaking down of TBEP that has vaporized at low temperatures. Recent research by Nan et al. [92] used TG-FTIR-MS to examine how the minerals in cow dung interacted with biomass carbon and pyrolysis. Small molecules (such acetic acid and butane) as well as middle- and large-molecular compounds (such as furfural, furan, and pyrazole, D-glucopyranoside, cortisol and cholestane) made up the majority of the gaseous by-products of the pyrolysis of cow manure. According to the findings, less oxygen containing material was liberated from the original cow manure than from the demineralized cow manure. According to this finding, the pyrolysis process was affected by minerals, which led to a greater release of aromatized compounds.

Photoionization mass spectrometry (PI-MS)

The molecules of analytes can only be detected at the ionized level by mass spectra, not at a molecular scale. The 'hard' ionization approach known as electron impact ionization is the most frequently utilized in mass spectra. It may be challenging to interpret the mass spectra because the ionization fragments from the collision of electrons may overlap. 'Soft' ionization methods, such as chemical, electrospray, photon (PI), and matrix-assisted laser desorption/ionizations [93], can produce fragment-free ions, which can avoid misleading the mass spectra. The advancement of optical technology, particularly the vacuum UV (VUV) light sources, has caused the PI, one of those ionization techniques, to gain more attention [94]. The synchrotron VUV PI-MS technique was first employed by Weng et al. [95] to examine the pyrolysis behavior of poplar biomass. When compared to mass spectra obtained using the electron ionization method, the recorded mass spectra displayed less fragmentation and greater sensitivity. Coniferyl, p-coumaryl, and sinapyl alcohol made up the majority of the pyrolysis products produced by poplar, and with higher temperatures, all of these compounds' spectrum intensities decreased. Zhou et al. [96] recently integrated the TG with PI-MS to explore the co-pyrolysis behavior of kraft lignin and lignite and the synergistic influence on the yield and quality of gaseous products. According to PI-MS findings, the synergetic impact can promote the production of aromatics like phenol, cresol, and syringol. At low temperatures, the guaiacol product yield was increased; while, at high temperatures, it was inhibited. The PI-MS can identify solitary radicals in addition to stable products during pyrolysis, which is useful for understanding the theory behind biomass pyrolysis. Jarvis et al. [97] pyrolyzed $C_6H_5C_2H_4OC_6H_5$, a model compound in lignin, and examined the radicals that were produced. The existence of the radicals of cyclopentadienyl, phenoxy, phenyl, and benzyl demonstrated the homolysis of $C_6H_5C_2H_4$-OC_6H_5 and $C_6H_5CH_2$-$CH_2OC_6H_5$. As a result, PI-MS generated consolidated data for developing the biomass pyrolysis mechanism.

In situ solid characterization

X-ray diffraction (XRD) and FTIR are the *in situ* technologies that are most frequently utilized to characterize solid products of pyrolysis. Zickler et al. [98] used synchrotron radiation to conduct *in situ* XRD research to examine the kinetics of thermal degradation of crystalline cellulose. They discovered that when the temperature was raised, the Scherrer size in the equatorial 0 0 2 direction dropped. The outcomes showed that the fibril diameter reduction and breaking during the thermal treatment procedure are the key contributors to the thermal degradation of crystalline cellulose. However, because the wood cellulose barely deteriorated below 300 °C and the reaction kinetics moved too quickly to allow for *in situ* measurements beyond 360 °C, the temperature in the study was solely restricted to the range between 300 and 360 °C. *In situ* FTIR was utilized by Uchimiya et al. [99] to examine how biochar's surface functionality changed over time as it underwent pyrolysis. The pyrolysis parameters included a heating rate of 10 °C per minute, a pyrolysis temperature of 500 °C, and an hour of residence time. According to the findings, the majority of the spectral transition took place prior to the temperature peak. The most noticeable modifications were between 325 and 500 °C, and once 500 °C had been achieved for 20 min, no more changes were seen. Aliphatic functional groups' O–H and C–H stretching bands diminished over time and vanished after 70 min. When the temperature was increased to 500 °C, the carboxyl vibrational band was visible. It reached its peak strength after the temperature was held at 500 °C for 15 min, and then it vanished after 40 min. We can achieve the desired characteristics of biochar and improve the understanding of biomass pyrolysis by analyzing the biochar *in situ* during the pyrolysis process.

Parameters influencing biomass pyrolysis

Biomass type

Lignocellulosic biomass is composed of cellulose (25–50 wt%), hemicellulose (15–40 wt%), lignin (10–40 wt%), extractives (0–15 wt%), and generally a small fraction of inorganic mineral matter [26]. The process of pyrolysis and

the products produced depend on the kind of biomass in several different ways. First, depending on the kind of biomass feedstock used, the climate where it originated, and the time of harvesting, different organic and inorganic components relative mass ratios exist. Each constituent's pyrolysis has its specific reaction routes, and thermochemical properties, and results in a variety of products [26]. The output of bio-oil is enhanced by the presence of cellulose and hemicelluloses, whereas lignin produces a higher percentage of solid char [100]. The molecular mass and viscosity of the bio-oils may increase with higher lignin content, while their water content may drop. The nonstructural components of lignocellulosic biomass known as extractives, including saturated fats, simple sugars, waxes, and sterols, can be extracted using solvents such as water, ethanol, acetone, benzene, and toluene [101]. Wang et al. [102] found that the extractives may boost the bio-oil yield and decrease the production of char and gas when utilizing maize stalks and wheat straw during the pyrolysis process.

Additionally, the bio-oils from the enhanced extracted samples exhibited more oxygen and fewer alkane contents than the initial samples. In a different investigation, it was established that the extractives reduced the activation energy and yields of CO_2, CO, and aldehydes while increasing acid formation during the pyrolysis of pine [103]. The structural arrangement of the components varies from biomass to biomass, changing the interactions between components as a result. The effectiveness of pyrolysis is significantly changed by this. Additionally, due to its catalytic action during biomass pyrolysis, the mineral matter composition in the various biomass types might potentially be variables that affect the distribution and characteristics of products [101].

Biomass pretreatment

It is usually essential to pre-treat the biomass feedstock before pyrolysis. To improve pyrolysis efficiency, the lignocellulosic structure of the biomass is altered or even destroyed during the pretreatment. There are five main categories in which biomass pretreatment technologies can be categorized: (1) physical (such as milling/grinding and extrusion); (2) thermal (such as torrefaction, steam explosion/liquid hot water pretreatment, and ultrasound/microwave irradiation); (3) chemical (such as treatment with acids, bases, and ionic liquids); (4) biological (such as fungal, microbial consortium, and enzymatic); and (5) above combined pretreatments [104].

Physical pretreatment

The process of milling or grinding biomass feedstock into tiny particles can simplify the biomass input into reactors and improve pyrolysis performance. Because biomass is often a poor heat conductor, the biomass pyrolysis process will be influenced by the temperature differential across the particle [105]. Smaller particles often facilitate heat and mass transfer to create constant temperature within particles during pyrolysis, which increases the production of bio-oil by limiting char formation and secondary vapor cracking. This boosts the production of bio-oil by reducing biochar formation and subsequent vapor cracking. However, particle size reduction can be quite costly and significantly increase the overall cost of the process.

Biomass is extruded at greater pressures to create biomass pellets, which often resemble compact cylinders and have a higher volumetric energy density while having a lower moisture content [106]. Bigger particle sizes improved biochar and syngas output as well as biochar density [107], but they lowered bio-oil output. Erlich et al. [106] also documented instances of similar circumstances.

Thermal pretreatment

Prior to pyrolysis, biomass is dried, which improves the process' energy efficiency and raises the quality of the bio-oil output. According to Isaksson et al. [108], several industrial dryers may be used to dry biomass. These dryers are created to recycle the fugitive heat emitted during the heated pyrolysis process and extract the moisture in the biomass. The water content of the biomass is eliminated and the oxygen content is slightly decreased when the thermal pretreatment is carried out at temperatures between 200 and 300 °C, a procedure known as torrefaction [109]. Torrefied biomass provides several advantages versus untreated biomass. It has a greater energy density, better grindability, reduced hygroscopicity when kept outdoors, reduces the chance of biological deterioration and self-ignition, and enhances reactor feeding [110]. Some disintegration reactions start to occur during torrefaction, producing CO_2, CO, acetic acid, and levoglucosan [111]. According to Boateng & Mullen [111], torrefied biomass generates bio-oils with lower acidity and better energy density as compared to untreated biomass. Other studies validated the results, which showed a higher quality and lesser output of bio-oils from the pyrolysis of torrefied biomass [112]. It was discovered that torrefaction increases the H_2 and CH_4 concentrations of generated syngas while decreasing their CO_2 level [113].

To 'break up' the biomass structure, steam explosion (SE) involves exposing biomass to saturated steam for a brief period at a pressure of 1.5 to 5 MPa and a temperature of 150 to 260 °C in a sealed vessel [114]. SE changes the physical characteristics of lignocellulose and breaks down carbohydrate connections, altering the behavior of biomass pyrolysis and the qualities of the final product. By using thermogravimetric analysis at 10 °C/min to evaluate the pyrolysis of willow chips following SE pretreatment at 205 °C, Biswas et al. [115] found that the cellulose crystallinity was higher than in the untreated material. Hemicellulose breakdown became more active and migrated to a lower temperature region during this process, although cellulose and lignin experienced an increase in thermal stability. Loblolly pine chips were pretreated by SE (1.3 MPa and 173–193 °C) [116]. The raw materials and the pretreated components were subsequently pyrolyzed separately in a customized auger reactor. The findings revealed that the chips after SE pretreatment had greater cellulose and lignin contents and reduced hemicellulose contents when compared to the untreated feedstock. A bio-oil with a variation of viscosities (from 6.5 to 3.9 cSt at 40 °C), acid values (from 90.1 to 64.2), and water contents (from 20.8 to 29.3%) was also obtained by the SE pretreatment. Similar to this, hot liquid water is occasionally used

to partly dissolve the hemicellulose in biomass feedstock, which helps to lower the amount of acetic acid present and stabilize bio-oils [117].

For the pretreatment of biomass, unconventional thermal methods including ultrasound and microwave irradiation are used. The primary purpose of ultrasonography is to increase the generation of biogas, primarily methane, from the anaerobic digestion of sludge [118]. Furthermore, there have been several studies conducted on lignocellulosic biomass. Yachmenev et al. [119] used ultrasonic to effectively speed up the enzymatic hydrolysis of cellulose in maize stover and sugarcane bagasse to produce sugars because the cavitation effects might improve the mobility of enzyme molecules and the opening up of the substrate's surface. To extract hemicellulose from wheat straw, Sun & Tomkinson [120] utilized a KOH solution and ultrasonic irradiation. They discovered that the ultrasound assistance generated hemicellulose with more linearity and less acidity than those obtained from traditional KOH extraction. The impact of ultrasonic pretreatment on biomass pyrolysis has to be studied further. Nowadays, lignocellulosic biomass is frequently heated *via* microwave irradiation, which can cause 'hotspots' in the biomass [118, 121]. Although biomass pyrolysis with microwave assistance has received much research [122], research on the pretreatment of biomass with microwave radiation is lacking [123]. Due to the inhibition of secondary reactions during pyrolysis following biomass drying in a microwave oven, microwave drying at 600 W and six min were proposed to increase the bio-oil and char yields with a performance exhibiting better yields than traditional electric oven drying [123].

Chemical pretreatment

The process of biomass pyrolysis is thought to be affected by the presence of inorganic minerals, particularly alkaline-earth (Mg, Ca, etc.) metal salts and alkali (K, Na, etc.). For instance, during the first pyrolysis of cellulose, potassium in the biomass mineral matter catalytically promotes the synthesis of lower molecular weight molecules and inhibits the creation of levoglucosan [124]. As catalysts, the cations cause the biomass monomers to fragment rather than depolymerize, which favors char production and reduces bio-oil yields [21]. The build-up of salts on the inside walls of the reactor and pipeline also leads to corrosion and engineering challenges [125]. Ash in bio-oils influences their later uses and speeds up the aging process, in addition to other effects.

The aforementioned flaws can be eliminated by decreasing the ash concentration with water or acid cleaning. Water washing is used to wash away dirt and minerals from the surface of the biomass particles during harvesting, transportation, and storage. However, the structural minerals will still be present in the biomass matrix. Acid washing using HNO_3 and HF can further lower the ash concentration [126]. Blasi et al. [127] investigated how water washing affected the pyrolysis properties of straw and discovered that while char production is lowered, bio-oil yields are increased. To increase the generation of levoglucosan and levoglucosenone in the bio-oils, phosphoric acid was used to pre-treat the cellulose feedstock. In certain instances, concentrated acids (such as H_2SO_4) were used to hydrolyze and solubilize carbohydrates in biomass to extract lignin [128], while alkaline solutions (such as NaOH) were used to eliminate lignin, hemicellulose, and/or cellulose [104].

Ionic liquids are a class of recently discovered chemicals that, at temperatures below 100 °C, may assume the form of or transform into liquids. They mostly consist of organic cations and inorganic/organic anions [129]. They are seen as environmentally friendly solvents because of their distinctive physical and chemical properties, which include low vapor pressure, high chemical stability, and non-flammability. Ionic liquids are used in several industrial processes, including catalysis, chemical synthesis, and the production of engineering fluids. They are also used in the breakdown and dissolving of cellulose, hemicellulose, and lignin [130]. Ionic liquids have been used to pre-treat lignocellulosic biomass for the production of sugars from enhanced enzymatic hydrolysis of oil palm fronds [131], renewable chemicals of vanillin, syringyl and allyl guaiacol from eucalyptus, switchgrass and pine respectively [132], levulinic acid from cellulose [133], and biogas from improved anaerobic digestion of water hyacinth, rice straw, mango leaves and spruce [134]. Following their pretreatment with ionic liquids, biomass materials' thermal behavior can also be altered. Zhang et al. [135] discovered that the Avicel and switchgrass samples had greater heat resistance following the pretreatment with 1-butyl-3-methylimidazoliumacetate as a result of the cellulose's alteration in crystal structure and the removal of minerals, respectively.

Biological pretreatment

When compared to physical and chemical pretreatment techniques, biological techniques are slower but use less energy and have a better impact on the environment [136]. It has been demonstrated that pyrolysis performance is enhanced by fungal pretreatment of lignocellulose. White-rot fungus has been selected to pre-treat the natural lignocellulose as it could selectively decompose the refractory lignin component during pyrolysis [6]. Yang et al. [137] bio-pretreated maize stover with three different white-rot fungus species (Pleurotus ostreatus BP2, Echinodontium taxodii 2538, and Irpex lacteus CD2) before studying the corn stover's thermal properties as it was being pyrolyzed in a TGA instrument. As a result of reducing the sulfur content of the feedstock by 30–45%, the results indicated that this bio-pretreatment may successfully lower the pyrolysis temperature by 1–35 °C and reduce the emission of harmful SO_x. Yu et al. [136] explored the rapid pyrolysis of maize stover pre-treated by I. lacteus CD2 white-rot fungus in the presence of ZSM-5 zeolite and found that yields of important aromatics products were improved by 10%, and coke deposition on catalysts was reduced by 20%.

Pre-treating lignocellulosic biomass with a microbial consortium has often been employed to increase the production of biogas. It uses specific bacteria drawn from the environment that primarily break down the cellulose and hemicellulose components [104]. The procedure can raise the methane output by 25% to almost 100% and lasts up to many days [104]. It has been suggested that using enzymes to hydrolyze lignin before it is pyrolyzed will increase the number of aromatic phenols and hydrocarbons that are produced [138]. The chars that were created also seem to have vesicles and to be quite porous.

Effects of reaction conditions

Reaction atmosphere

Usually, N_2 gas is used to provide an inert environment needed for biomass pyrolysis. To change the pyrolysis process conditions, other gases might be utilized. For instance, steam can partially gasify the biomass and slightly oxidize it. The steam is employed as the carrier gas and may also participate in the processes in a recently developed pyrolysis procedure known as steam pyrolysis. For biomass pyrolysis, steam has several benefits. Primarily, it can upgrade the yield of organic oxygenated products by preventing to some extent the secondary cracking reactions in the gas phase [139]. The effects of N_2, CO_2, CO, CH_4, and H_2 atmospheres on biomass pyrolysis in a fluidized bed reactor were examined by Zhang et al. [140]. The highest bio-oil yields were discovered to be in the CH_4 environment (58.7%), whereas the lowest yields were in the CO atmosphere (49.6%). When CO and CO_2 were used as the sweeping gases, it resulted in the detection of bigger monofunctional phenols and lower methoxy-containing compounds in the bio-oils. When compared to other atmospheres, the HHV of bio-oils under H_2 could reach a maximum of 24.4 MJ/kg, and more oxygen in biomass was transformed into H_2O. The char obtained in the CO_2-containing atmosphere had increased surface area and different chemical composition [141] compared to the chars produced under an inert atmosphere.

Temperature

Pyrolysis temperature significantly influences the distribution and properties of products. The bio-oil yields typically reach their peak concentrations between 400 and 550 °C and then start to fall as the heating process continues. At temperatures higher than 600 °C, the bio-oils and char products are converted into gas due to the dominant secondary cracking reactions [142]. The polar, aliphatic and aromatic fractions in the bio-oils enhance with increased temperatures from 300–500 °C to 600–800 °C [143]. Generally, temperatures exceeding 700 °C increase the carbon content of the bio-oils in the form of polycyclic aromatic hydrocarbons (PAHs), such as pyrene and phenanthrene, due to the decarboxylation and dehydration reactions [100]. Uddin et al. [56] have studied how the pyrolysis temperature affects the yields and composition of gases (CO, CO_2, CH_4, H_2, etc.). Previous research has also looked at the physicochemical properties of biochar produced by biomass rapid pyrolysis at various temperatures, including its surface area, electrical conductivity, the concentration of inorganic components, carbon content, aromatic structure, and HHV [144,145].

Heating rate

The primary factor that distinguishes between flash, fast, and slow pyrolysis of biomass is the heating rate. Fast heating rates encourage the biomass to break down rapidly, producing more gases and less char in the process. Fast heating rates also increase bio-oil production because mass and heat transfer constraints are reduced and secondary reactions have less time to complete [100]. Prior research has revealed how heating rate affects product yields and attributes [146,147]. Salehi et al. [148] found that increasing the heating rate from 500 °C/min to 700 °C/min results in increased bio-oil yields from wood shavings by 8%. However, when the heating rate was increased further from 700 to 1000 °C/min, no discernible change in the bio-oil yields was found because mass and heat transfer constraints had been overcome. Similar to this, pyrolysis of cotton seed cake showed a rapid increase in liquid yield when heating rate was increased from 5 °C/min (26 wt%) to 300 °C/min (35 wt %), but there was no discernible change in liquid yield when heating rate was increased further from 300 °C/min to 700 °C/min [149].

Vapor residence time

Shorter residence times favor the synthesis of bio-oil because organic vapors are removed from reactors quickly and reduce secondary reactions. Scott et al. [150] found that for the pyrolysis of raw sorghum bagasse at 525 °C, changing the residence time from 0.2 to 0.9 s led to a drop in the bio-oil yields from 75% to 57% and an increase in the char and gas yields. Similarly, by extending the vapor residence time from 0.7 s to 1.7 s during the pyrolysis of sweetgum hardwood at 700 °C, the bio-oil output decreased from 22 wt.% to 15 wt.%. Although the impact of vapor residence time on product distribution has been extensively investigated, further research is necessary to understand the impact of the relationship between vapor residence time and pyrolysis temperature on product yields as well as product quality [56].

Co-pyrolysis of biomass

As an effective alternative method to improve the quality of pyrolysis products, the co-pyrolysis of biomass has attracted more and more interest [151]. In contrast to the conventional biomass fast pyrolysis, co-pyrolysis concurrently adds various raw materials as fuel, such as plastics, coal, sludge, etc. [78]. The recent research on the co-pyrolysis of biomass with various raw materials is discussed in sections to follow.

The unique feature of co-pyrolysis is that the synergistic effect among the chemical reactions between different feedstocks plays an important role in co-pyrolysis [152]. Nevertheless, the synergistic effect varies dramatically with the added raw materials of co-pyrolysis.

Co-pyrolysis behavior of biomass with coal

Because of its advantages like high energy density and low price, coal is a good material for biomass co-pyrolysis. Zhu et al. [153] analyzed the composition of liquid bio-oil from the fast co-pyrolysis of cedar sawdust with low-rank coal. Their results showed that there were more generations of single-ring and two-ring aromatic compounds and less formation of three-ring and four-ring aromatic compounds. They ascribed this to the hydrogen supply by the pyrolysis of cedar sawdust, thereby restraining the secondary polymerization of volatile in fast co-pyrolysis. Alkali and alkaline-earth metals in biomass have an impact on the co-pyrolysis process in addition to their function as hydrogen donors. Li et al. [154] studied the co-pyrolysis of Xilinhot

lignite and rice husk, and they revealed that the secondary cracking of volatiles from both feedstocks was promoted by alkali and alkaline-earth metals in biomass.

However, the interactions of biomass and coal, especially the synergistic effect, still need to be explored. Ferrara et al. [155] evaluated the co-pyrolysis process of the mixtures of biomass and coal and argued that the synergistic effect was negligible, which was consistent with the study of Montiano et al. [156]. In contrast, the synergistic effect was captured and emphasized in many other studies [157, 153]. Zhao et al. [157] carried out a thermogravimetric analysis of cellulose and lignite blends, where a strong synergistic effect between the feedstocks was observed between 300 and 400 °C and the decomposition of lignite was accelerated by the increasing content of cellulose during co-pyrolysis. Qiu et al. [158] identified the existence of a synergistic effect, by the apparent activation energy, and the lower frequency factor of the poplar and fat coal blends, compared with the pyrolysis of pure polar compounds. According to Chen et al. [159], the occurrence of the interactions, including the positive and the negative (the inhibitory effect) synergistic effects, is dependent on the operating parameters of the co-pyrolysis process of biomass with coal, such as the type of coal feedstock and the blend ratio.

Besides, some previous studies have shown that co-pyrolysis with biomass can reduce or prevent the emission of harmful substances in coal. Guo et al. [160] studied the co-pyrolysis of biomass with several different low-rank coals with high sulfur contents. They found that, during co-pyrolysis with biomass under a CO_2 atmosphere, large amounts of sulfur elements in coals were transferred to thiophenes contained in the char, rather than along with gas emissions.

Co-pyrolysis behavior of biomass and plastics

To efficiently extract energy from used plastics, Garcia & Robertson [161] suggested that the pyrolysis of plastics would be a potential chemical recycling process. In addition, the low oxygen concentration and high carbon and hydrogen content of plastics make co-pyrolysis of waste plastics and biomass potentially valuable for upgrading bio-oil.

Many related studies have focused on the co-pyrolysis behavior of biomass and plastics wastes, several of which have indicated the significance of the synergistic effect [72, 152]. Van Nguyen et al. [162] examined the characteristics and yields of bio-oil produced from the co-pyrolysis of waste polystyrene foam and pure pine sawdust. The results revealed that co-pyrolysis of pine sawdust and used polystyrene foam provided a greater yield of bio-oil and enhanced the HHV of the produced bio-oil from 17.81 MJ/kg to 39.65 MJ/kg. Yuan et al. [163] discovered that when cellulose and high-density polyethene (HDPE) was pyrolyzed together, the production of compounds containing oxygen was inhibited while the development of alkane and alkene groups was supported. It has been noted that the synergistic effect may cause the quality of the bio-oil to improve. The interaction between various free radicals generated by the biomass and plastics, respectively, is primarily responsible for the synergistic effect [72]. The pyrolysis behaviors of sugarcane bagasse, HDPE, and their blends in a fixed-bed reactor were examined by Hassan et al. [152]. According to their hypothesis, the generation of co-pyrolysis products was significantly influenced by the hydroxyl radical produced from sugar cane bagasse at various mixed feedstock ratios.

Co-pyrolysis behavior of biomass and tyres

Similar to waste plastics, waste tyre is another high hydrogen and carbon-containing waste-derived fuel; the major components of waste tyres are rubber compounds including natural or synthetic rubber, and carbon blacks, making it practical to utilize waste tyres in pyrolysis [164]. Waste tyres can be introduced into biomass co-pyrolysis as raw materials to enhance the quality and yield of bio-oil. Slightly different from waste plastics, the components in waste tyres are relatively complex, which might result in some differences in the co-pyrolysis bio-oil.

Positive effects on the quality of final products have been shown by introducing waste tyres into co-pyrolysis with biomass. According to Ahmed et al. [165], when sugarcane bagasse and tyres were co-pyrolyzed, the bio-oil yields increased as the ratio of tyres increased. Furthermore, the HHV of bio-oil produced by co-pyrolysis of sugarcane bagasse and tyres could reach as high as 41 MJ/kg. In the co-pyrolysis of biomass with waste tyres, Wang et al. [166] demonstrated that the production of PAHs was reduced while the formation of olefin components was increased. Alvarez et al. [151] asserted that the co-pyrolysis bio-oil includes less moisture and oxygen than the bio-oil produced by the pyrolysis of pure pinewood sawdust due to the synergistic effect of pinewood sawdust and waste tyres. Shah et al. [167] reported that, at the optimal blend ratio (3:2), the yield of liquid products from the co-pyrolysis of cotton stalk and waste tyres could increase by 10%, compared with that from cotton stalk pyrolysis. Additionally, the outcomes demonstrated that the synergetic effect during co-pyrolysis led to the formation of additional alkanes, demonstrating that the bio-oil from co-pyrolysis was more suitable for use in vehicles [167]. Besides, additives in tyres have a certain influence on the properties of the co-pyrolysis products. Shah et al. [167] also observed that the co-pyrolysis bio-oil had a relatively high sulfur content, leading to the requirement for desulfurization of such bio-oil.

Co-pyrolysis behavior of biomass and sludge

The sludge used as raw material for biomass co-pyrolysis mainly includes sewage sludge and oily sludge. The former is mainly generated as the by-products of numerous municipal sewage plants, while the latter is a form of a complex waste emulsion that accumulates during particular stages of the petroleum industry [168, 169]. These two different types of sludge both contain several various organic chemicals that are acceptable as raw materials for co-pyrolysis, while they also contained some harmful compositions, such as heavy metals, etc. [168, 170]. Various researchers examined the properties of the co-pyrolysis products made from biomass and sewage sludge. Wang et al. [171] discovered that when sewage sludge and wheat straw were co-pyrolyzed, the reaction rate increased, producing more bio-oil and less biochar. Lin et al. [169] proposed that the

compounds that have more than seven C atoms yielded more in the co-pyrolysis bio-oil of bagasse and sewage sludge. Chen et al. [172] reported that the yields of hydrocarbons and phenols were enhanced, while the yields of acids and nitrogenous chemicals production decreased in the co-pyrolysis of sewage sludge and coffee grounds. These researchers found that the synergetic effect significantly affected the co-pyrolysis of biomass and sewage sludge, changing the properties of the co-pyrolysis products. According to Xu et al. [69], interactions changed as temperature ranges varied during the co-pyrolysis of hazelnut shell and sewage sludge. Particularly, at lower temperatures (260–400 °C), the interactions were reduced, whereas at higher temperatures (450–900 °C), they were accelerated. The characteristics of biochar products for uses like soil amendments have been a major focus of other research on the co-pyrolysis of sewage sludge and biomass [89, 69, 173]. Wang et al. [174] found the biochar from biomass co-pyrolysis with sewage sludge to be more profitable, featuring a larger specific surface area, better pore size distribution, and lower risk of heavy metals. Yin et al. [173] studied the adsorption capacity of biochar from sewage sludge and walnut shell co-pyrolysis and found that the adsorption of NH_4^+ was improved by the mixture of feedstocks. Compared with sewage sludge, studies on biomass co-pyrolysis with oily sludge are relatively limited. However, because of its high concentration of various petroleum hydrocarbons (PHCs), high content of hydrogen and low content of oxygen is found in the oily sludge [168]; as a result, co-pyrolysis of biomass and oily sludge can increase the yield and quality of the liquid products while also lowering harmful pollution, notably heavy metal contamination. Hu et al. [168] compared the bio-oils produced from pure sawdust pyrolysis and co-pyrolysis of sawdust with oily sludge, respectively. Higher H/C ratio and higher HHV were found in the bio-oil from co-pyrolysis, which were increased by 0.5 and 5 MJ/kg, respectively. Meanwhile, the bio-oil yield was also increased by 4% due to the synergetic effect. Lin et al. [175] studied the properties of liquid products from co-pyrolysis of rice husk and oily sludge, and they suggested that more saturates and aromatics were generated while less oxygenated compounds were formed because of the synergetic effect.

Catalytic co-pyrolysis

A favorable synergy between biomass and plastics is present during catalytic pyrolysis of biomass and plastics, which increases hydrocarbon production while lowering biochar yield [176]. Two feedstocks interact with each other during pyrolysis to produce the synergistic effect. Yuan et al. [163] utilized hydrogen transfer to identify the synergetic breakdown between polymer and cellulose. Oxygen compounds derived from cellulose increase the cracking of HDPE, and hydrogen from HDPE can promote the breakdown of cellulose. However, the product distribution during the non-catalytic co-pyrolysis of cellulose and low-density polyethene (LDPE) was comparable to that of individual pyrolysis. This indicates that pyrolysis without a catalyst results in the absence of interaction between two pyrolysis intermediates [177]. As a result, to create mutual contact between two feedstocks, catalysts are required. A higher synergetic effect can be produced by utilizing acid/base catalysts through several processes, some of which are covered in the following sections.

Acid catalysts

Dehydration, decarbonylation, cracking, and aromatization processes are favored by acid catalysts such as zeolites [178]. Strong acid sites in zeolites have a major role in promoting the aromatization process, which produces high-value monocyclic aromatic hydrocarbons including benzene, toluene, ethylbenzene, and xylene, which are among the most significant petrochemicals [179]. Due to its distinct microporous structure and relatively high Bronsted acidity, zeolite ZSM-5 is regarded as the best acid catalyst for the synthesis of monocyclic aromatic hydrocarbons [180].

Base catalysts

In the residual ash of biomass, alkali and alkaline-earth metals (AAEMs) including Ca, K, Mg, and Na are typically present. These metals can be deposited on the acid sites of the catalyst easily, which immediately deactivates the acid catalyst [181]. On the other hand, catalysts with base sites, as opposed to acid sites, withstand deactivation by AAEMs much better. With acid sites, the base active sites display several reaction pathways, such as carbon coupling (C-C) reactions. Carbon coupling processes transform low molecular weight substances like organic acids, ketones, and aldehydes into gasoline and diesel range products. Base catalysts that produce CO_2 during the ketonization of acids, such as MgO [182] and CaO [183], facilitate the deoxygenation of pyrolysis products. With regard to preserving carbon, the deoxygenation pathway is more effective than the acid catalyst pathway since the latter encourages the creation of CO [184]. Base catalysts also reduce H_2O generation to preserve the hydrogen level in the bio-oil, hence improving the energy and quality of the bio-oil [181, 184].

However, a key mechanism of base catalyst-assisted catalytic pyrolysis has not yet been explored. A few processes of individual components, biomass, and plastic over base catalysts were studied in earlier investigations. Processes for biomass pyrolysis over base catalyst correspond to the ketonization of acids with simultaneous generation of CO_2 and aldol condensation of aldehydes and smaller ketones [185]. Alkali metal oxides can deoxygenate bulky oxygenates, linear aldehydes, and carboxylic acids during the catalytic pyrolysis of lignocellulosic biomass. Ketonization, fragmentation, and aldol condensation processes are used to create light hydrocarbon compounds and oxygenates with low molecular weight when alkali metal oxides deoxygenate a substance [174].

Pyrolysis reactor designs

In the process of pyrolysis, the reactor design and the heating system plays an important role. Several reactors have been developed during the last two decades to accomplish this aim, depending on the heating technique used. Figure 4

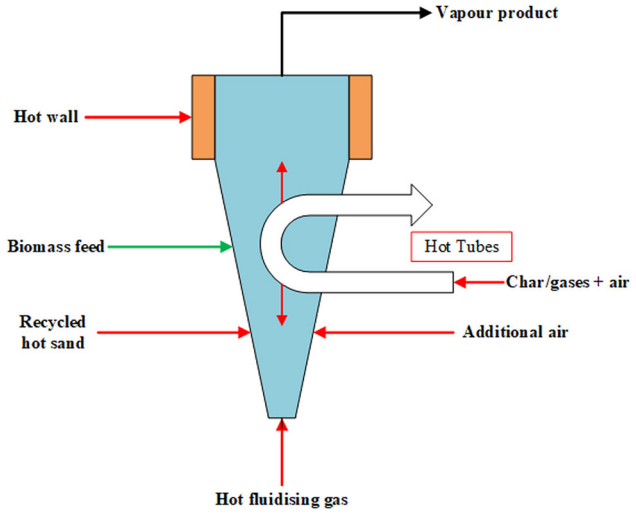

Figure 4. Various heating techniques are used in pyrolysis reactors.

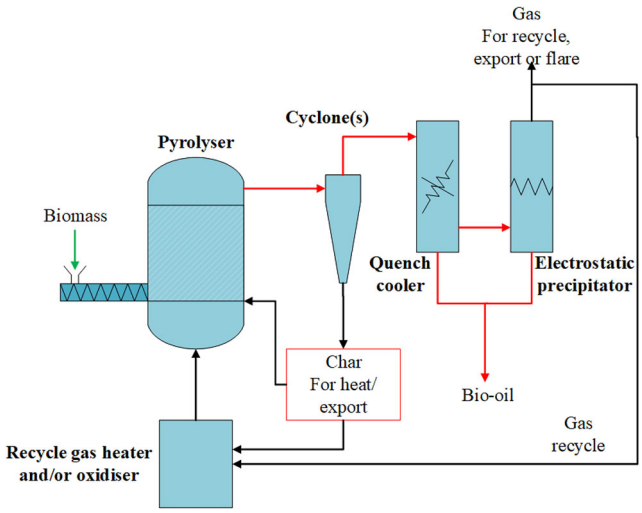

Figure 5. A typical schematic of a bubbling fluidized bed reactor.

illustrates the various heating techniques that are employed in pyrolysis reactors.

Bubbling fluidized beds

The performance of bubbling fluidized bed pyrolysers is associated with a high liquid production from biomass of approximately 70–75 wt.% on a dry basis. For high biomass heating rates, the feedstock particle sizes must be less than 2–3 mm. The heating rate of the particles is typically the limiting stage in fluidized bed reactors. The retention time of char and pyrolysis vapors is governed by the flow rate of the fluidizing gas. Char typically has a longer residence duration than vapors. Upon completion of the pyrolysis process, the char that is generated needs to be removed from the bio-oil since it works well as a catalyst for vapor cracking. An ejection and entrainment system is often constructed for this purpose, accompanied by segregation in cyclones [29]. Figure 5 illustrates a typical schematic of a bubbling fluidized bed reactor.

Circulating fluidized beds and transported beds

The operating principle of a circulating fluidized bed (CFB) and transporting bed reactor is similar to that of a bubbling bed reactor, with the exception that the residence period for char is nearly identical to that of vapors and gas. Additionally, the recovered bio-oil may have a larger char content than the fluidized bed reactor due to this. Despite having more complicated hydrodynamics, CFB has the advantage of being suited for very high throughputs. It is commonly employed in the oil and petrochemical industries at extremely high throughputs as a result of this property. The heat is provided by the recirculation of hot sand from a secondary char combustor [29, 186]. Figure 6 illustrates a typical schematic of a circulating fluidized bed reactor.

Rotating cone

The University of Twente developed a rotating cone reactor for the flash pyrolysis of biomass [29]. Since vigorous mixing of hot inert particles and biomass is the most efficient method of transferring heat to the biomass, this method is the foundation of the spinning cone reactor's design. In contrast, the heat transmission of a fluidized bed requires an excessive amount of unproductive inert carrier gas. The development of a rotating cone reactor eliminated the need for inert gases and simplified the design of the reactor's components and supporting machinery, such as the oil condenser and gas cleaning systems. The rotating cone reactor's first design from 1989 relied only on the ablative principle; no inert sand was employed. Later, the rotating cone reactor (RCR) with a transportable bed of sand was established. Upon completion of the pyrolysis process, the sand and char are then moved to a different fluidized bed where the char is burned [29, 186]. Figure 7 shows an illustration of the spinning cone reactor.

Ablative pyrolysis

With smaller equipment, lower costs, and better controllability, ablative reactors are utilized to produce bio-oil at high yields. When biomass moves across a hot surface, heat is transferred as a result (Figure 8). The rate of heat transmission through the biomass particle serves as the reaction's limiting factor in an ablative reactor. Temperature, relative feedstock velocity on the heat transfer surface, and pressure all influence how fast a reaction happens. The main characteristics of pyrolysis inside an ablative reactor are strong particle pressure on a heated reactor wall, relatively high movement between the particle and the reactor wall, and a hot reactor wall temperature. Additionally, inert gas is not necessary [29, 186].

Auger reactor

This kind of reactor consists of a hot, tubular, inert tube through which augers feed biomass. Figure 9 illustrates an auger reactor design. The feedstock temperature is raised to the pyrolysis temperature by the temperature within the tube. The volatiles are assumed to liquefy in a condenser. Both bio-oil and char outputs for the auger reactor's end products are comparable to those of the fluidized bed reactor [187,188]. Auger reactors can be categorized into four different types: single screw laboratory-scale reactors (1 kg/h), single screw laboratory-scale reactors with a large

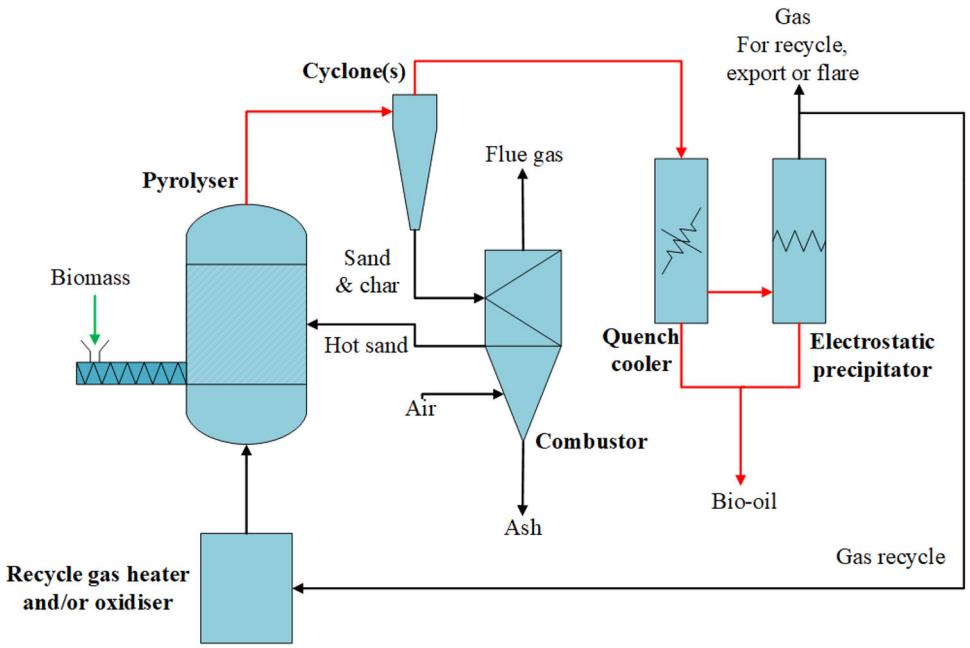

Figure 6. A typical schematic of a circulating fluidized bed reactor.

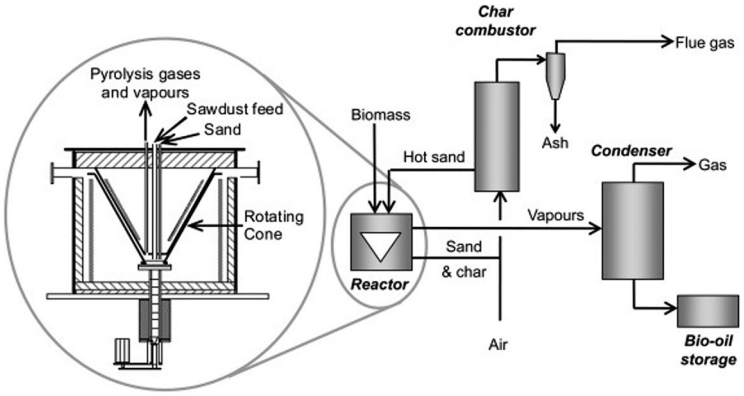

Figure 7. An illustration of the spinning cone reactor (29) Copyright 2012, Elsevier.

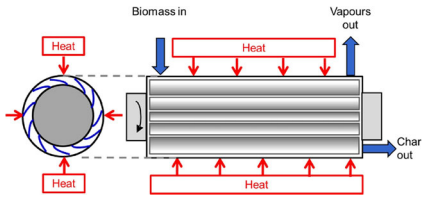

Figure 8. A typical schematic of an ablative pyrolysis reactor.

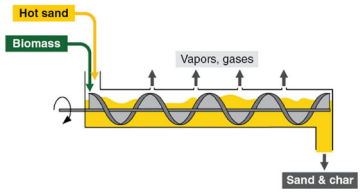

Figure 9. An illustration of an auger reactor.

capacity or pilot-scale (1–15 kg/h), single screw industrial-scale reactors (>15 kg/h), and twin-screw reactors [186].

Fixed-bed reactor

Fixed bed reactors are more appropriate in lab scale investigations because of their simplicity and simpler control mechanism. However, its deployment in large scales requires more research, particularly the homogenous heat energy distribution inside the reactor. Xiong et al. [189] employed a fixed-bed reactor to pyrolyze rice husk biomass. Their investigation used temperature variations between 300 and 800 °C to track the production of coke. Also modified was the heating rate. According to their findings, the coke produced at low temperatures and a slow heating rate was impervious and had a smooth surface. However, it became porous when the heating rate or pyrolysis temperature was increased. This was due to the fact that greater temperatures or faster heating rates produced more free radicals, which encouraged the condensation process of big molecules, particularly aromatics.

Recently developed pyrolysis methods

A wide range of biomass pyrolysis-related technologies has recently emerged. Due to their unique benefits over more traditional electrical heating-assisted biomass pyrolysis, microwave- and solar-assisted pyrolysis have received the most attention [190,191]. Hence, they were summarized with particular emphasis on the combination of existing related biomass pyrolysis technologies (such as co-pyrolysis, catalytic pyrolysis, etc.) with these new heating methods.

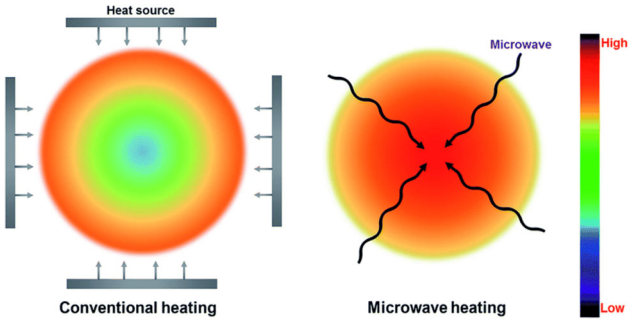

Figure 10. Comparison of microwave heating and conventional heating methods (192). Copyright 2016, Elsevier.

Microwave-assisted pyrolysis

The microwave heating method is the critical technology for biomass microwave-assisted pyrolysis systems. Different from the electrical or the combustion heating method of pyrolysis by-products, microwave heating does not use an external temperature field to heat biomass but converts microwave energy into heat energy through the agitation of molecules in the electromagnetic field and the generated heat will diffuse from the inside of the materials to their outside, as shown in Figure 10 [192–194].

Besides, a very important feature of microwave heating is that the microwave absorption rate of different materials might vary, leading to selective heating [195,196]. Biomass can only partially absorb or reflect microwaves; therefore, microwave absorbents such as SiC, activated carbon, graphite, CaO, $CaCO_3$, NiO, Ni_2O_3, TiO, Fe_2O_3 and charcoal are always added to improve the microwave heating efficiency [197]. Because of its special energy conversion mechanism, microwave heating has the following advantages: a high heating rate, uniform heating, instantaneous regulation, low energy dissipation, selective heating, and high energy conversion efficiency [191, 195, 197]. Huang et al. [198] noted that microwave heating was superior to conventional heating, in terms of heating rate, efficiency, and biomass weightlessness.

The microwave-assisted pyrolysis of various feedstocks has already been conducted [37, 194, 199–201, 202]. Gautam et al. [194] reported that a type of bio-oil with lower oxygen content and more aromatic hydrocarbons content than that from conventional fast pyrolysis was obtained from microwave-assisted pyrolysis of macroalgae. Borges et al. [200] investigated the bio-oil yields obtained from the microwave-assisted pyrolysis of wood sawdust and corn stover, respectively. Their results showed that the maximum bio-oil yields of these two raw materials were higher than those from conventional fast pyrolysis. Wang et al. [202] found that the temperature could affect the content of hydrocarbons in the microwave-assisted pyrolysis of soap stock and the optimal temperature for the formation of aromatics was 550 °C. However, product quality improvement is not prominent. According to Kostas et al. [201], olive pomace microwave-assisted pyrolysis generated bio-oil with a greater acetic acid concentration. Abas et al. [199] found a greater amount of water and different organic acids in the bio-oil generated *via* microwave-assisted pyrolysis of oil palm fiber. Although several strategies for commercializing microwave-assisted pyrolysis have been put forth, the majority of associated initiatives are now still in the laboratory research stage [203,204]. To produce more-favorable products, current biomass microwave-assisted pyrolysis methods still require optimization and modification. Microwave-assisted co-pyrolysis and catalytic pyrolysis might be a potential approach to upgrade the target products and give full play to the advantages of microwave-assisted pyrolysis [205,206].

A range of co-pyrolysis raw materials, including biomass and lignite, biomass and plastics, biomass and soap stock, etc., have been used in microwave-assisted co-pyrolysis experiments [70, 205, 207]. An et al. [205] found that microwave-assisted co-pyrolysis of biomass and lignite can produce more liquid oil and pyrolytic gas, because of the synergetic effect of biomass and lignite. Suriapparao et al. [207] revealed that the bio-oil from microwave-assisted co-pyrolysis of numerous types of biomass with polypropylene and polystyrene had a reduced water content and improved HHV, about 38–42 MJ/kg. Due to internal interactions, various raw materials have varying effects on the product quality of microwave-assisted co-pyrolysis. (208) investigated the composition of the by-products of oil sands and sawdust co-pyrolysis with microwave assistance. Their results showed that the yields of both liquid bio-oil and gas products were changed due to the synergetic effect, and the content of aromatic hydrocarbons in liquid bio-oil was improved, because of the microwave radiation.

Microwave-assisted catalytic pyrolysis not only has the advantages of microwave heating and can also promote the directional conversion of biomassW. (209) noted that the modified HZSM-5 could promote the formation of bio-oil and increase the selectivity of phenols during the microwave-assisted catalytic pyrolysis process of cellulose. According to Zhu et al. [210], the microwave-assisted catalytic pyrolysis of Douglas fir pellets in the presence of biochar as a catalyst resulted in a hydrocarbon content of bio-oil of 52.77%. However, Mohamed et al. [206] reported that coke deposition on the catalyst surface might affect the microwave heating rate, which could result in changes in product distribution. The performance of the catalyst and the prevention of coke deposition are still critical in microwave-assisted catalytic pyrolysis.

Solar-assisted pyrolysis

Solar-assisted pyrolysis is a relatively new research direction in the field of biomass pyrolysis. Compared with conventional biomass pyrolysis, solar-assisted pyrolysis directly converts solar energy to the thermal energy required for pyrolysis, achieving the clean utilization of the primary energy. Additionally, a unique method of solar pyrolysis has been developed for the disposal and improvement of biomass polluted with heavy metals [211,212]. As shown in Figure 11, the most notable feature of the solar-assisted pyrolysis system is the solar concentrator [213]. Some particular solar concentrators, such as Fresnel lenses and parabolic troughs, are used in solar-assisted pyrolysis systems to gather and concentrate solar energy [190, 214]. The biomass pyrolysis process is then aided by the concentrated solar radiation being converted to heat in the pyrolysis reactors. Li et al. [215] indicated that solar heating could meet the temperature requirements for biomass pyrolysis and have a wide adjustment range of heating temperature (up to 2000 °C) and heating rate (5 – 450 °C/s). Higher

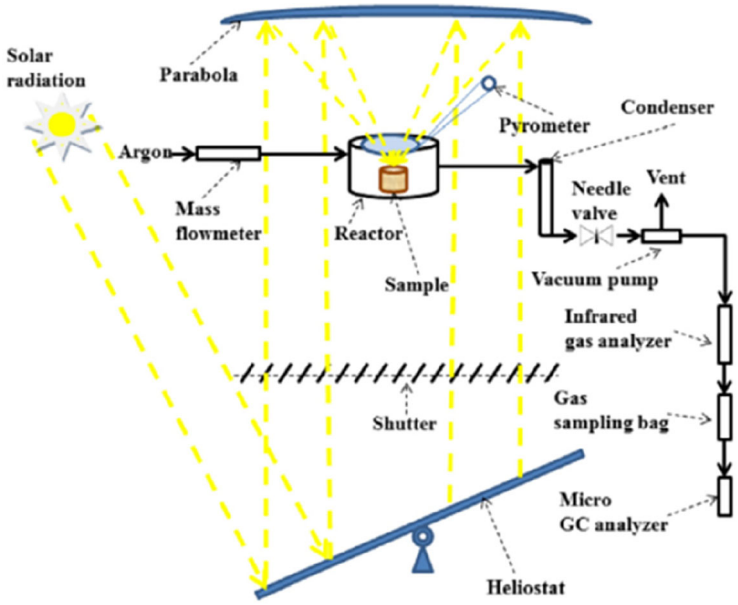

Figure 11. Solar-assisted pyrolysis experimental setup (211). Copyright 2019, Elsevier.

temperatures and faster heating rates will lead to the formation of more gaseous products. However, the adjustment range of solar heating mainly relies on the types of solar concentrators [71]. Hence, a specific solar heating technique should be selected reasonably, according to the requirements of the pyrolysis reactions.

Pyrolysis with solar assistance can store solar energy as chemical energy in the pyrolysis by-products. Recently, there have been some reports of biofuel production from solar-assisted pyrolysis [71, 213–216]. Rony at al. [216] reported that the bio-oil of corn stover obtained *via* solar-assisted pyrolysis had high contents of phenols (∼44%) and furans (∼13%), which indicated that solar-assisted pyrolysis of biomass had the potential to generate fuels and chemicals. Chintala et al. [71] evaluated the properties of bio-oil formed from the solar-assisted pyrolysis of non-edible Jatropha seeds and found that the bio-oil was rich in ester compounds, and it had the potential to be used as engine fuel. Besides, they also indicated that reducing the heat loss during the solar-assisted pyrolysis process could effectively improve the yield of the bio-oil. Bashir et al. [217] studied the solar-assisted pyrolysis of biomass *via* CFD simulation and found that the bio-oil yield could reach 51.5% under the simulated operating conditions. Zeng et al. [213] found that the temperature of solar heating can have a significant impact on the yields of pyrolysis products, and due to its high oxygen content, bio-oil produced from solar-assisted pyrolysis of beech wood still has to be improved in terms of its heating value. As a consequence, it is significant to regulate and control solar-assisted pyrolysis to enhance the quality of solar pyrolysis products.

Catalysts were used in the solar-assisted catalytic pyrolysis method to enhance the selective conversion of target products due to their effective performance in conventional catalytic pyrolysis. Weldekidan et al. [218] reported that the CaO catalyst significantly lowered the number of fatty acids in the bio-oil produced from chicken litter (decreased to 8% in the *in situ* catalytic process and 3% in the *ex situ* catalytic process). Barbosa et al. [219] identified that more microalgae bio-oil was formed in the solar-assisted pyrolysis and more hydrocarbons were detected in the bio-oil, because of the catalysis of hydrotalcite. Hijazi [220] found that the TiO_2 catalyst could increase the tendency of hydrocarbon chain cleavage during the solar-assisted catalytic pyrolysis of rubber tyres. However, research on the solar-assisted catalytic pyrolysis field is relatively scarce. The selection of excellent catalysts and the optimization of related operating parameters for the solar-assisted catalytic pyrolysis still need to be studied further.

Economic evaluation of pyrolysis technologies

The cost of production and the ability of the pyrolysis technologies to compete with conventional fossil fuel sources will determine their commercialization for the production of fuels and chemicals. Fuels produced by pyrolysis have different life cycle manufacturing costs depending on the type of feedstock, product output, plant capacity, plant lifetime, and discount rates. These factors, the price of the finished products, and the availability of renewable energy or biofuel subsidies all have a role in how profitable pyrolysis technologies are in the end [221,222].

About 30–54% of the price of producing liquid fuels is attributed to the cost of the feedstock. The cost varies based on the source or method of production of the feedstock, the amount and technique employed in processing the feedstock, and the distance traveled. Bhatia et al. [223] highlighted that the transportation costs of biomass resources can have a substantial impact on the production cost of biofuels, while Kung & Zhang [224] indicated that the acquisition cost of agricultural residues (rice straw) is significantly lower than the expenses of producing energy crops.

Differences in technology and their fuel production are probably another significant factor contributing to the diversity of life cycle costs, in addition to feedstock prices. The improved bio-oil production, the cost of the catalysts, and the catalyst's lifetime all have a significant impact on the process economics [225,226]. Michailos et al. [227] compared the production of bio-oil from sugarcane bagasse *via* the Fischer–Tropsch (FT) and the fast pyrolysis pathways. The authors reported that the FT synthesis is

slightly more profitable than the fast pyrolysis pathway. This agrees with the study by Ramirez & Rainey [228] which reported the highest yields of bio-oil through gasification as compared to other thermochemical conversion techniques. The hydro-processing unit's costs (both capital and operating) are the biggest obstacle in the fast pyrolysis process. The FT process has a higher thermodynamic efficiency than fast pyrolysis because of the higher fuel productivity. In fast pyrolysis, lignin is used in a steam cycle to generate power, but in FT, it is gasified and so contributes to the generation of liquid fuels.

The profitability of pyrolysis has been shown in some studies to increase with the conversion of co-products like biochar into more valuable products such as activated carbon [229], as well as pyrolysis chemicals. However, a study by Patel et al. [230] evaluated the economics of three production scenarios, (i) producing biofuels only, (ii) biofuels and potash fertilizer, and (iii) biofuels, potash fertilizer, and activated carbon. Negative values of NPV for only biofuel production and the biofuel and potash fertilizer scenario were obtained. This indicated that the production pathways were not economically feasible. The biofuels, potash fertilizer, and activated carbon production scenario was the only production pathway that proved to be profitable. The synthesis of activated carbon from spent char after potash fertilizer recovery has remarkably improved the profitability of the plant. However, biorefineries can produce value-added products from process waste to improve the economic feasibility of the process.

Scaling up production is another way to boost profitability [221, 231] since it lowers fixed costs due to longer product lifecycles while potentially raising variable costs, particularly transportation expenses. The economic feasibility of large-scale biorefineries would thus be enhanced by the production of energy-dense products (such as biochar and bio-oil) close to sources of biomass.

Conclusion and future directions

One of the most promising processes for the high-value use of biomass is pyrolysis, which effectively transforms biomass into liquid fuel. The development of biomass pyrolysis technology has raised concerns. In recent years, a lot of research has been done to better understand the process of biomass pyrolysis by investigating the pyrolysis characteristics of cellulose, hemicellulose, and lignin. The pyrolysis behavior of biomass is greatly influenced by a variety of additional components, such as inorganic chemicals, whose composition is quite complex. Furthermore, the complex interactions between the components of the biomass make the pyrolysis mechanism particularly difficult. Future studies on the mechanism of biomass pyrolysis should be integrated with the actual production process and genuine biomass samples to better understand the process of biomass pyrolysis. This work should be based on advanced measuring techniques and modeling methodologies. Further consideration should be given to the relationships between the pyrolysis behavior of biomass components and the heat and mass transport in the pyrolysis process. Additionally important is the development of more accurate CFD models and the optimization of associated algorithms for biomass pyrolysis.

Although biomass co-pyrolysis demonstrated some promising results in terms of oxygen removal and oil quality improvement, the liquid oil produced is still insufficient and cannot be used as a direct alternative for petroleum oil. Additionally, the synergistic effects between biomass and feedstock with a high hydrogen content are yet unknown; therefore, biomass pyrolysis still requires attention to how to improve the synergistic effects and produce higher quality products. The development of catalysts is essential for the advancement of catalytic fast pyrolysis technology and is an efficient way to generate liquid oil that is higher grade and aromatics enriched. Because of their strong aromatic selectivity, ZSM-5 catalysts have received a lot of attention. High coke and low liquid output, however, are two significant issues that are impeding the advancement of biomass catalyst fast pyrolysis. Therefore, it is important to continue designing new catalysts that are affordable, highly efficient, durable, and well-suited for biomass. To fully exploit the benefits of each approach, it is also worthwhile to consider applying co-pyrolysis and catalytic pyrolysis together.

Microwave pyrolysis and solar pyrolysis have drawn a lot of attention due to their distinctive heating properties when compared to traditional biomass pyrolysis by electrical heating. However, the resulting bio-oil is still of low quality. As a result, some research has been done to further improve the quality of products, such as the integration of current relevant biomass pyrolysis technologies (such as co-pyrolysis and catalytic pyrolysis) with these new heating methods. Despite this, there has not been much research done in this area; therefore, more work needs to be done in the future to optimize pertinent operational parameters, catalyst compositions, and pyrolysis reactors to produce cheaper higher quality liquid oil. An in-depth study of the mechanism is also necessary to comprehend the process completely.

Authors' contribution

Denzel Christopher Makepa-Conceptualization, Investigation, Writing-Original draft. Chido Hermes Chihobo-Conceptualization, Validation, Supervision, Writing-review and editing. Downmore Musademba-Conceptualization, Validation, Supervision, Writing-review and editing.

Disclosure statement

The authors declare no competing interests.

Funding

The authors would like to express their sincere gratitude to the Department of Fuels and Energy and Chinhoyi University of Technology, Vice Chancellors Scholarship of Excellence for rendering all the indispensable support and funds needed in this work.

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