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Research Article

Microwave-Assisted Pyrolysis and Co-Pyrolysis: Oil, Char, and Gases-A Technological Review

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Abstract : Microwave-Assisted Pyrolysis and Co-Pyrolysis: Oil, Char, and Gases is an in-depth exploration of the new field of microwave-assisted pyrolysis. Microwave-assisted pyrolysis allows the extraction of oil, char, and gases from biomass, waste, and other organic components. Microwave-assisted pyrolysis has several advantages compared to conventional pyrolysis, which are discussed in detail in this paper. The article covers various aspects of microwave-assisted pyrotechnics, including fundamentals of pyrolysis, thermal decomposition processes, factors affecting pyrolysis reactions, material distribution and yield, synergistic effects, and process parameter optimization Co- pyrolysis. It also looks at production processes, where multiple raw materials are used to produce multiple value-added products simultaneously through simultaneous co-pyrolysis. This paper is helpful for academics, engineers, and professionals in biomass conversion and renewable energy since the writers explore co-pyrolysis's synergistic effects and prospective applications. With its comprehensive coverage and in-depth analysis, Microwave-Assisted Pyrolysis and Co-Pyrolysis: Oil, Char, and Gases offers a unique perspective on the application of microwave technology in pyrolysis processes. It provides readers with a thorough understanding of the basic principles, experimental methods, and potential applications of MW-assisted pyrolysis and co-pyrolysis.

Keywords : Microwave-assisted Pyrolysis, Co-pyrolysis, Synergistic Effects, Bio-oil, Char

1 Introduction

Rising standards of living combined with a growing human population have resulted in a meteoric rise in garbage output. Untreated garbage poses serious risks to ecosystems and human health if not properly managed [1]. As global energy demand and population expand, fossil fuels are increasingly exploited and progressively consumed, exacerbating the energy crisis and other major environmental challenges. Therefore, more and more people are concentrating on developing long-term strategies for using renewable energy sources [2]. The potential for more effective heating and the production of higher quality fuel and chemical products than are currently attainable using traditional pyrolysis technologies have motivated researchers to examine microwave pyrolysis in recent years. Despite the interest, the mechanisms of microwave pyrolysis are largely unreported for several reasons, including the complexity of the pyrolysis chemistry, the difficulties surrounding bio-oil analysis and quantification, a shortage of knowledge concerning the fundamentals of microwave heating, and the intensity and poorly controlled electric fields that are typical of domestic-type microwave ovens that keep going to see significant usage within scientific research. Microwave heating of biomass presents additional difficulties for precise temperature measurement, as even the most advanced laboratory equipment can only take point readings from the sample's surface rather than a complete temperature distribution [3]. Pyrolysis is the heat degradation of organic molecules that produces oil, char, and gases when oxygen is absent. The possibility of using this technique to recycle biomass, plastic, and rubber has piqued the curiosity of researchers in recent years. The advantages of microwave heating over more conventional heating methods have piqued the public's attention. Microwaves have wavelengths between 0.01 and 1 meter, corresponding to frequencies between 0.3 and 300 gigahertz (GHz) in the electromagnetic spectrum. Most home microwave ovens operate at 2.45 GHz, while 915 MHz is widely used [4]. Pyrolysis is a controlled heating process in which the feedstock is heated to high temperatures, typically (300 to 800) degrees Celsius. Since oxygen isn't present, the organic materials can be heated without catching fire. The end products have several potential uses and can be refined for further uses [5]. Multiple feedstocks can be degraded simultaneously in a co-pyrolysis process. This approach improves individual pyrolysis regarding feedstock efficiency, product yields, and quality.

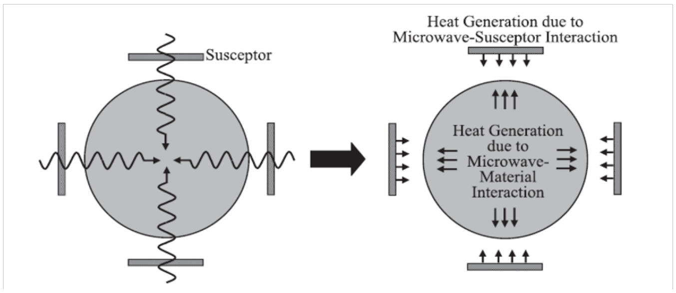

Figure 1: Two-way hybrid microwave heating with susceptors [10].

Plastic and rubber by-products and biomass are among the many organic resources that co-pyrolysis can treat [6]. It is possible to extract beneficial compounds from complex organic materials using pyrolysis and co-pyrolysis. Pyrolysis oil, sometimes called bio-oil, is a thick black liquid containing organic matter. It has many potential applications, such as fuel regeneration after processing [7]. Char, another carbon-rich product, is one of the products of pyrolysis. The high carbon content of char makes it a suitable solid fuel for heating purposes. Because of its adsorption properties, char may also purify water and air. Syngas, a by-product of pyrolysis that includes volatile organic molecules like methane, carbon dioxide, and carbon monoxide, can be utilized for heating and power generation and converted into chemicals. Conventional pyrolysis and microwave-assisted pyrolysis are different. If the former is correct, heating materials with microwaves makes the pyrolysis process go more quickly and evenly. Microwave heating is superior to older heating methods because it is more controlled, uses less energy, and is more efficient overall [5, 6]. Subjecting long-chain polymer molecules to heat and employing a catalyst makes it feasible to synthesize simpler compounds. The hydrocarbon solids (char), liquids, and gases produced during the subsequent breakdown of polymers are of fuel grade because of their petrochemical composition [8]. By utilizing microwave heating systems, pyrolysis, and co-pyrolysis processes can increase product yield, improve product quality, and decrease reaction speed. Product distribution and yield can be enhanced by microwaves controlling the pyrolysis processes. The commercialization of microwave-assisted pyrolysis technology is possible due to its rapid and effective heating capacity. This technology could completely transform pyrolysis by offering a more sustainable and economical option [5].

This review aims to equip researchers with all the necessary information regarding microwave-assisted pyrolysis and co-pyrolysis procedures for producing oil, char, and gas. The study's main objective is to find out how to employ microwave heating technology to make pyrolysis reactions more efficient and selective and then to use those products more effectively. The introduction and description of pyrolysis and co-pyrolysis are essential steps in generating renewable energy and disposing of waste. The basic concepts of pyrolysis are then covered, including how heat breaks down, what variables can influence the results of the reactions, product distribution, and yields.

2 Microwave-assisted pyrolysis Technology

The pyrolysis industry has recently extensively researched and implemented new MAP technology. Renewable energy generation is just one of several applications of microwave technology. Microwaves are electromagnetic waves with wavelengths between 1 millimeter and 1 meter (corresponding frequencies of 0.3 gigahertz GHz and 300 gigahertz GHz). The microwave is a dielectric heating method that may penetrate the biomass raw materials deeply, making it distinct from the conventional exterior heating methods of convection, conduction, and radiation. This type of heating can generate heat through molecules' strong collisions and friction. Thermogravimetric measurements using microwaves revealed that, compared to traditional Pyrolysis, MAP lowered the temperature at which biomass components began to decompose and moved the fastest weightless zone to reduce temperature intervals [9]. The microwave heat was "hybrid," meaning the susceptor helped it along. Two distinct types of heating occur during the lifetime of the susceptor, as depicted in (Fig 1). Surface heating is achieved by the susceptors, as opposed to the inside heating achieved by microwave ovens. Similarly, when compared to heating by direct microwaves, the material is heated more consistently, where the interior is often kept at a higher temperature than the exterior for a prolonged time. Reduced surface heat loss due to the presence of susceptors also aids in maintaining thermal consistency throughout the hybrid heating process [10].

Consequently, MAP has benefits, including a faster heating rate, higher energy utilization rate, quicker reaction time, and higher selectivity. Researchers in pyrolysis have increased the market value of liquid fuel, syngas, and solid carbon by using MAP technology [11, 12]. (Husam Talib Hamzah et al.) It was reported that pyrolysis was used to extract valuable materials from the tea powder. Chemical pre-treatment involved soaking the WTP and TWTP in benzene, acetone, and ethanol solvents. The FWTP was torrefied at 150 °C, resulting in a powder we call torrefied waste tea (TWTP) [5]. Researchers (Zhang et al.) found that microwave-assisted Pyrolysis (MAP) is more effective in turning low-grade lignite into bio-oil than electric heating pyrolysis [13]. Pyrolysis of bituminous coal heated in a microwave oven has been found to involve cyclization and aromatization processes. Changes in the structure of bituminous coal brought on by MAP can lead to the leakage of fluid and the subsequent release of volatiles and moisture [14]. Improved selectivity towards phenol-rich bio-oil from microwave-assisted pyrolysis of cellulose was achieved by modifying the HZSM-5 catalyst, as reported by (Wang et al.) [15]. To selectively recycle unwanted materials, however, MAPs allow for producing phenolic compounds [16]. Vacuum distillation with membrane adsorption/fractionation (MAP) in succession is a promising method for recovering and recycling used engine oil [17]. More significant molecular weight methyl esters were abundant in the biodiesel-distilled raffinate, and a more considerable recovery rate was achieved by using MAP to extract them [18]. Combustible gas produced by biomass pyrolysis can be heated using microwave technology, which has several benefits. For MAP, high-synthesis gas was prepared with the help of a catalyst comprised of iron (III) ions supported by activated carbon. H2/CO was 1.04, and 81.14 vol% were present [19]. High-value hydrogen-rich syngas can be produced from biomass by MAP and activated carbon reforming [20]. The phenolic chemicals in industrial effluent can be removed using biochar made from MAP biomass [21]. To increase the longevity of activated carbon and make it suitable for use as a fuel adsorbent, (Lam et al.) reported combining MAP technology with chemical impregnation activation to create activated carbon with a high percentage of fixed carbon (83 wt%) and a high BET surface area (1350 m2/g) [22]. Biochar produced via microwave-catalyzed pyrolysis is more porous and has a higher cation exchange capacity than traditional pyrolysis [23].

3 By-product yield calculation

It is useful to determine the bio-oil, biochar, and biogas yields in order to assess the outcomes of a microwave pyrolysis procedure. The values of these constants are given by Equations 1, 2, 3, and 4. The yield factor is defined as the ratio of the weight of the by-products from the conversion process to the weight of the raw biomass input [24].

$$\text{Liquid yield (wt\%)} = 100 \times \frac{\text{weight of condensed liquid}}{\text{weight of raw biomass}} \tag{1}$$

$$\text{Solid yield (wt\%)} = 100 \times \frac{\text{weight of char residue}}{\text{weight of raw biomass}} \tag{2}$$

$$\text{Gas yield (wt\%)} = 100 - (\text{liquid yield} + \text{solid yield}) \tag{3}$$

$$\text{General yield (wt\%)} = 100 \times \frac{\text{biochar weight} + \text{oil} + \text{gas}}{\text{biomass weight}} \tag{4}$$

As an alternative, the yields of by-products can be calculated using Equations 5, 6, and 7. The number connects the biomass's fiber composition and the end product's functionality. Without the fiber analysis, getting an accurate range for the discrepancy between expected and experimental yields is impossible. These aspects assess how the chosen operational parameters affect final product quality [24].

$$Solidyield(wt\%) = -0.167H - 0.239C + 0.007L + 34 \tag{5}$$

$$Liquidyield(wt\%) = 0.185H - 0.076C + 0.272L + 34 \tag{6}$$

$$Gasyield(wt\%) = -0.018H + 0.315C - 0.280L + 31.9 \tag{7}$$

4 Fundamentals of Pyrolysis

In order to start the process, no oxygen should be available for pyrolysis surrounding. Organic matter can be converted into gas, char, and oil. This section covers the basics of thermal decomposition, reactions, product distribution and yield, and pyrolysis [10].

4.1 Thermal Decomposition Mechanisms

In the absence of oxygen, it is a decomposing process that reduces complex organic compounds to simple connecting parts. Knowledge of the mechanisms of thermal degradation is essential to increase product yields from pyrolysis [5]. The production of oil, char, and syngas from organic materials in efficient pyrolysis is a multistep process. This process involves pre-treatment, such as drying through heating. It is important to remove water at low temperatures before starting pyrolysis reactions [25]. During MW pyrolysis, organic matter is heated into hot particles. The high temperature of the reaction causes the chemical degradation of the product. Methane, ethane, hydrogen gas, water, and solids vapures are formed. Pyrolysis produces char as a by-product. When the temperature increases, the solid decomposes, producing char. When pyrolyzed, char is stable and contains a high percentage of fixed carbon [5].

4.1.1 Homolytic and Heterolytic Bond Cleavage

During the initial pyrolysis, the links between feedstock molecules are broken. It is possible to cleave bonds by both homolytic and heterolytic mechanisms. During the process of homolytic bond cleavage, a bond is broken into two radicals by the presence of one electron that is not paired [10]. Microwave radiation or heat is typically the initiating factor in this process. Radicals have the potential to cause bond cleavage and radical generation after they have reacted with other molecules. One way to break an unequal electron distribution is through heterolytic bond breakdown. As a consequence, a cation and an anion are produced. In the presence of catalysts or polar materials, which prevent charged species from becoming unstable, heterolytic bonds are broken more quickly [26].

4.1.2 Primary and Secondary Reactions

Radicals generated by bond breaking can undergo additional reactions. Hydrogen abstraction, beta-scission, and intramolecular rearrangements are primary reactions that immediately convert radicals or charged species into smaller molecules [10, 27]. In the hydrogen abstraction process, a new radical and a hydrogen molecule are formed when a radical combines with a hydrogen atom from another molecule. Since biomass contains a lot of hydrogen, pyrolyzing produces lots of hydrogen-rich by-products; hence, this step is especially crucial in biomass pyrolysis. Two smaller molecules are created when a bond close to the radical site is broken, known as beta-scission. In this process, unsaturated chemicals like alkenes and aromatics are formed, which can be used as chemical feedstocks or fuel precursors. Rearranging the atoms within a molecule to create new isomers or more stable molecules is an example of an intramolecular rearrangement. Because of these shifts, the distribution and yield of pyrolysis products might be substantially changed. After the primary reaction, secondary reactions occur, involving yet more modification of the intermediate products. Some examples of possible reactions are condensation, polymerization, cracking, and gasification. The reaction time, temperature, and catalysts or other reactants all have a role in secondary reactions [5, 24].

4.2 Product Distribution and Yield

Depending on the feedstock utilized, pyrolysis products are dispersed and created differently. The by-products of pyrolysis include bio-oil, char, and gases [5, 25]. A thick fluid containing several organic components, oil made by pyrolysis is called bio-oil. Feedstock and pyrolysis process settings change the characteristics of the product after pyrolysis. Bio-oil can be used as a pollution-free fuel and can be used to generate energy. Char is a by-product after pyrolysis. Although other inorganic compounds and ash exist, carbon is the most important. Char is multipurpose; it can be used as a solid fuel, but it can also enhance soil quality and neutralize contaminants in the environment [28]. Hydrogen, carbon monoxide, methane, and carbon dioxide are all components of the syngas created when microwave-assisted pyrolysis of material starts. Chemicals, liquid fuels, and energy generation can be produced from this gas. During pyrolysis, reaction time, heating rate, and temperature affect products' distribution and yield. Optimizing the pyrolysis process can enhance product yields [29]. Microwave-assisted pyrolysis requires a thorough knowledge of the principles. Prepare to apply this method to oil, char, and gas recovery by examining thermal separation, pyrolysis reaction variables, product distribution, and yield.

4.3 Factors Affecting Pyrolysis Reactions

Several factors affect pyrolysis processes and final product distribution. Temperature, heating rate, reaction time, feedstock composition, and reactor design are all important parameters to consider. When it comes to pyrolysis, heat is important. Higher temperatures produce gas, but lower temperatures are better for bio-oil and char production [10]. Furthermore, pyrolysis processes are influenced by temperature. The heat accelerates the decomposition of the material, increasing the amount of gas produced. Secondary processes can produce high yields of bio-oil and char at low temperatures. One of the important parametars is the residence time of feedstock in a pyrolysis reactor. Longer residence times allow secondary reactions, resulting in higher bio-oil and char yields. The rate of pyrolysis and the distribution of products depend on the composition of the feed. The chemical composition of the waste materials used in the process, such as plastics, rubber, or biomass, can affect the quantity and quality of the product [5, 27]. Pollutants and inorganic contaminants can impact pyrolysis. The reactor layout matters for pyrolysis. The reactor must efficiently heat and maintain feedstock temperature. The reactor design affects residence time, product distribution, and heating uniformity [10].

4.4 Influence of Feed stock Composition

The composition of the feedstock has a significant impact on the pyrolysis approach to heat breakdown. Changes in reactions and products are possible since every feedstock possesses a distinct chemical structure and functional groups. There is a difference in the thermal stability and breakdown temperatures of cellulose, hemicellulose, and lignin found in wood and agricultural waste. The pyrolysis of biomass results in the breakdown of hemicellulose and lignin at high temperatures; Bio-oil, char, and gasses are all obtained through the multistage decomposition process. However, plastic waste feedstocks include polymers like polyethylene, polypropylene, and polystyrene [30, 31]. Plastic polymer chains are broken during pyrolysis, creating smaller hydrocarbon molecules. It is also possible for pyrolysis processes and product yields to be affected by the plastic waste's

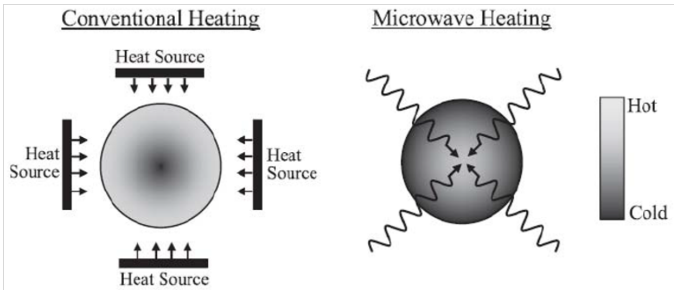

Figure 2: Conventional and Microwave-induced heating patterns [10].

composition, such as adding additives or impurities. Elastomers, found in rubber waste feedstocks like used tires and scrap rubber, have a highly intricate molecular structure. When rubber is heated to high enough temperatures, its polymer chains break down, releasing volatile gasses and leaving behind carbon black and other solid leftovers. During pyrolysis, sulfur in rubber can be converted into sulfur-rich compounds [32, 33]. Some examples of product output from microwave pyrolysis of various biomasses are shortened (Table 1).

Table 1: Microwave pyrolysis of various biomass types and product yield

Biomass	Reactor (g)	Temperature (°C)	Time (min)	Char yield (wt%)	Oil yield (wt%)	Gas yield (wt%)	Reference
Bamboo	Microwave oven	600	15	19	8	73	[34]
Pine	Microwave oven	800	15	18	4	79	[34]
Gumwood	Microwave oven	800	15	15	4	81	[34]
Rosewood	Microwave oven	700	15	22	6	72	[34]
Macroalgae	Microwave oven	750	60	28	35	37	[35]
Sugarcane bagasse	Microwave oven	550	30	62	22	16	[35]
Wood pellets	Microwave oven	800	16	22	26	52	[36]
Rubberwood	Microwave oven	550	16	21	19	60	[36]
Pinewood + lignite coal	Microwave oven	550	-	43	14	43	[37]

4.5 Residence Time

4.6 Temperature and Heating Rate Effects

Thermal degradation mechanisms during pyrolysis are susceptible to temperature and heating rate changes. In most cases, a temperature rise will cause pyrolysis reactions to proceed more quickly, resulting in increased product yields. Gasification is an example of unwanted side reactions that can occur at very high temperatures and diminish the yield of the desired products. In conventional heating, heat is transferred from an external source to an interior space using conduction and convection to transport a heating front from the surface to the interior space. The old-fashioned approach of Heating a sample always results in a higher surface temperature than an inside temperature, as seen in (Fig.2) [10].

The rate at which the temperature is increased (the heating rate) also affects the pyrolysis process. Faster reactions and shorter residence durations are two benefits of increasing the heating rate, especially in large-scale industrial pyrolysis processes. However, partial pyrolysis and the subsequent generation of char or tar residues are also possible outcomes of high heating rates [5]. The ideal temperature and heating rate are context-specific and change with the type of feedstock and the desired outcome. The optimal heating conditions, which optimize product yields while reducing undesired side reactions, can be determined by modeling and experimental research [10, 38].

4.7 Residence Time

A further factor that influences reactions is the residence of feedstock in the pyrolysis reactor. Longer residence times result in the completion of feedstock degradation, producing a greater quantity of gases and char. On the other hand, shorter residency times are more favorable for bio-oil creation. The feedstock's properties, the feedstock particles' size, and the reactor's geometry determine the residence time. Product dispersion and the efficiency of the process depend on the optimization of the residence period [10, 38].

4.8 Catalysts and Additives

Adding catalysts and additives can drastically alter the pyrolysis reactions and product yields. Cracking and reforming reactions can be boosted by catalysts, leading to more gas output and higher quality bio-oil. Pyrolysis has been modified for various uses by employing different catalysts such as zeolites, transition metals, acid catalysts, and Nano-catalysts. The pyrolysis reactions can be affected by additives like alkali metals and alkali earth metals by speeding up biomass degradation or increasing the catalytic activity. Suitable catalysts and additives must be chosen and optimized to get the targeted product yields and boost

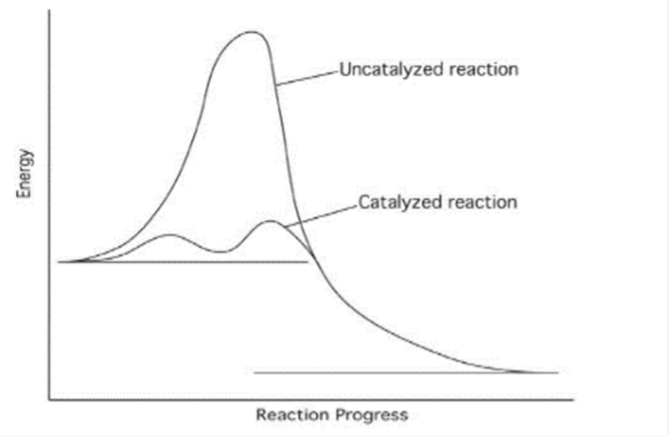

Figure 3: Conventional and Microwave-induced heating patterns.

the overall process efficiency [5]. (Figure 3) depicts catalyzed and uncatalyzed reactions, respectively. The catalytic approach has two steps, and an intermediate species is present [10]. Many catalysts function similarly, as seen in (Fig. 3), reducing the barriers for both phases relative to the uncatalyzed reaction.

4.9 Reactor Design and Configuration

The sensitivity of the pyrolysis reactions to the design and setting of the pyrolysis reactor is well-documented. The methods of heat transfer and the distribution of time of stay in a microwave reactor affect the final product's distribution. The heating uniformity and overall process efficiency can be affected by the reactor's geometry, size, and the arrangement of the heating elements. The reactor's insulation and construction can also affect heat transport and reaction kinetics. It is essential to optimize the reactor design and setup for effective heat transfer and management of the pyrolysis reactions [38, 39].

4.10 Moisture Content

The pyrolysis reactions are sensitive to the feedstock's moisture content. Since moisture is a heat sink, it takes more heat to evaporate before pyrolysis reactions occur. Due to increased moisture content, lower product yields may result from longer residence durations and less efficient heating. In addition, secondary processes such as water-gas shift reactions can be accelerated by moisture and change the chemical composition of the pyrolysis gases. Proper drying or pre-treatment of the feedstock to eliminate excess moisture is necessary to improve the pyrolysis process [10, 40, 41].

4.11 Pressure and Atmosphere

The distribution of products and their qualities are affected by the pressure and environment in which the pyrolysis events occur. Reaction kinetics and the generation of particular products can be affected by operating conditions such as atmospheric pressure, vacuum, or extreme pressures. The pyrolysis reactions can also be affected by the type of environment used (inert, reducing, or oxidizing). For instance, a reducing environment can boost syngas generation, whereas an inert atmosphere can dampen unintended reactions. Customizing the pyrolysis process for proper ends requires careful consideration of pressure and environment [28, 41, 42].

5 Co-pyrolysis Reactions

Pyrolysis of various feedstocks is called co-pyrolysis. This approach can enhance biomass and waste utilization and provide commercially viable products, including bio-oil, char, and gases. Many biomass, plastic, and rubber waste combinations can co-pyrolyze [28, 29]. Co-pyrolysis with LLDPE and HLDPE has also been the subject of substantial research. Pine pyrolysis proved to be expedited by MgCl2 and HZSM-5, while HDPE co-pyrolysis increased aromatic selectivity. Increased yields of aromatics are achieved through a reaction between furfural (made from the catalytic cracking of a pine sawdust/MgCl2 mixture) and short-chain olefins (made from the catalytic cracking of High-density polyethylene HDPE) [42]. Hydrocarbon fuel generation enhanced in waste vegetable oil and HDPE co-pyrolysis. Hydrocarbon fuels, in contrast to biodiesel, are of superior quality due to their reduced viscosity, higher heating value, and improved fluidity [43].

Co-pyrolysis of boxwood and High-density polyethylene (HDPE) synergistically produces aromatics like xylene and toluene. Increased Diels-Alder reaction between furan from biomass pyrolysis and olefins from HDPE pyrolysis accounts for the vast difference between the experimental and theoretical aromatic yields [44]. (Fig.4) shows a flow chart of this paper's subjects. The literature review provides a broad viewpoint for discussing issues and opportunities for conclusions. The findings demonstrate

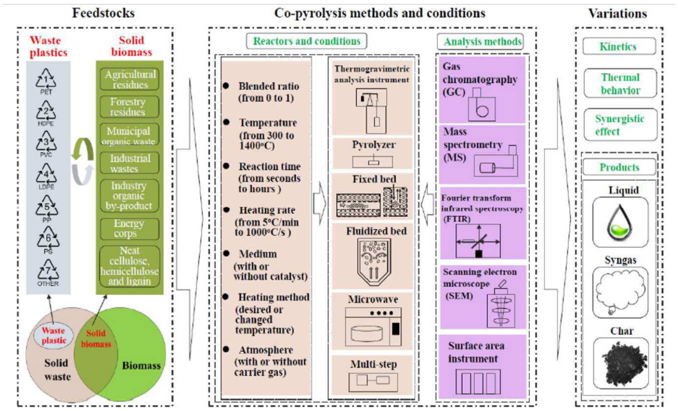

Figure 4: Diagnostic procedures for co-pyrolysis of mixed waste plastic and solid biomass are summarised in a flow diagram for laboratory studies [10].

the significance of co-pyrolysis investigation and suggest further study for sustainable and synergistic waste disposal. Co-pyrolysis has many advantages over separate pyrolysis processes for each feedstock. Synergistic effects between the various components can be realized, resulting in more productivity and better quality in the final product. Second, it allows us to get beyond the drawbacks of specific feedstocks, such as biomass's high oxygen content or plastic waste's poor energy density. The co-pyrolysis technique creates products with a more versatile composition by combining diverse feedstocks [5, 45]. Catalytic co-pyrolysis (CCP) of biomass with hydrogen-rich materials has been studied extensively, and some results are summarized in (Table 2).

Table 2: Microwave pyrolysis of various biomass types and product yield

Biomass	Co-Reactant	Catalyst	Biomass to Co-Reactant Ratio	Temp. (°C)	Reactor	Mainly Compounds	Ref.
Lignin	LDPE	MgO/HZSM-5	1:0	550	Microwave oven	Phenolic compounds	[46]
Lignin	LDPE	MgO/HZSM-5	2:1	550	Microwave oven	Phenolic compounds, aromatics	[46]
Lignin	LDPE	MgO/HZSM-5	1:1	550	Microwave oven	Aromatics, phenolic compounds	[46]
Lignin	LDPE	Zn/lignin-char	-	500	Microwave oven	Hydrocarbons, ketones, phenols	[47]
Lignin	PP	HZSM-5	1:1	200	Microwave reactor	Aromatics, alkenes, cycloalkanes	[48]
Lignin	PP	HZSM-5	1:1	250	Microwave reactor	Cycloalkanes, aromatics, alkenes	[48]
Lignin	PP	HZSM-5	1:1	300	Microwave reactor	Aromatics, cycloalkanes, alkenes	[48]
Lignin	PP	HZSM-5	1:1	350	Microwave reactor	Alkenes, aromatics, cycloalkanes	[48]
Bamboo	PP	HZSM-5	1:0	250	Microwave oven	Oxygen-cont., Aromatics, Oxygen-cont., aliphatics	[49]
Bamboo	PP	HZSM-5	2:1	250	Microwave oven	Aliphatics hydrocarbons, aromatics	[49]
Bamboo	PP	HZSM-5	1:1	250	Microwave oven	Aliphatics hydrocarbons, aromatics	[49]
Bamboo	PP	HZSM-5	1:2	250	Microwave oven	Aliphatics hydrocarbons	[49]
Bamboo	PP	HZSM-5	0:1	250	Microwave oven	Aliphatics hydrocarbons, aromatics	[49]
Rice straw	PP	HZSM-5	1:1	500	Microwave oven	Aliphatic HCs, MAHs	[50]
Bagasse	PP	HZSM-5	1:1	500	Microwave oven	Aliphatic HCs	[50]
Rice straw	PS	HZSM-5	1:1	500	Microwave oven	MAHs	[50]
Bagasse	PS	HZSM-5	1:1	500	Microwave oven	MAHs, PAHs	[50]
Cellulose	PP	HZSM-5	1:1	500	Microwave oven	BTEXs, Light olefins	[51]

In co-pyrolysis, interactions between feedstocks are complicated, resulting in additional molecules and changes in product distribution; it is possible that thermal cracking, radical reactions, or catalysts are the factors responsible for the interactions. Diversity arises because of the effect of the feed on the processes and trends. Feedstock compatibility is essential when using co-pyrolysis [26]. Chemical composition, functional groups, and preferred thermal dissociation determine the compatibility of two materials. When suppliers interact, they streamline processes. Using incompatible materials can lead to unexpected reactions or ingredient changes [27]. The heating rate, residence time, and temperature are all critical variables for co-pyrolysis processes. These variables influence reaction rate, end-product distribution, and breakdown temperature. Optimum operating conditions are necessary to obtain products and properties [24]. Product yield or quality is typically improved due to the efficiency gains offered by co-pyrolysis processes. These synergistic effects can be caused by several factors, such as the enabling effect of one feedstock on the volatility of another feedstock, the low oxygen content of compost and plastic waste, and the increased energy content of the waste [5, 33]. As the feedstock composition and processing parameters are varied, the product distribution in co-pyrolysis also changes. Bio-oil created from a combination of biomass and plastic waste, for instance, has a higher energy density and a lower oxygen content than bio-oil produced from either feedstock separately. Co-pyrolysis of biomass and rubber waste produces a bio-oil with improved stability and heating value [32, 33].

5.1 Synergistic Effects

Synergistic effects, when discussing pyrolysis and co-pyrolysis, refer to the increased output and quality of pyrolysis products that occur when two or more feedstocks are thermally decomposed simultaneously. During co-pyrolysis, multiple feedstocks, such as biomass and plastic waste, biomass, rubber waste, or biomass and yet more biomass, are pyrolyzed all at once [5]. It may be possible to establish that a synergistic effect occurs during the co-pyrolysis of plastic and biomass mixtures by comparing the indices derived from the experimental and calculated values. Calculating the theoretical value requires averaging the individual pyrolysis measurements' weighted proportional values [5, 52]. A positive synergistic impact (Y) from co-pyrolysis would be predicted if the experimental value were greater than the weighted aggregate calculated value, as shown by Equations 8 and 9 [53]:

$$Y_{\text{Calculated}} = a \times Y_{\text{feedstock 1}} + (1 - a) \times Y_{\text{feedstock 2}} \tag{8}$$

$$\Delta Y = \frac{Y_{\text{experimental}} - Y_{\text{calculated}}}{Y_{\text{calculated}}} \times 100 \tag{9}$$

5.2 Enhanced Product Yields

Co-pyrolysis has the potential for higher product yields than pyrolysis of individual feedstocks, which is a significant benefit. Synergistic effects can be achieved by combining diverse feedstocks, leading to increased conversion rates and a more even distribution of products. To illustrate, the presence of plastic trash during co-pyrolysis can operate as a heat transporter, easing the pyrolysis of biomass and increasing the overall conversion efficiency [54]; as a result of this combination, oil production increases while char formation decreases. Similarly, the catalytic impact of rubber on biomass pyrolysis can boost oil output when the two are co-pyrolyzed. Oil extraction and biomass thermal cracking are both enhanced by rubber by-products. Biomass and rubber waste interactions can change the bio-oil's composition and quality, which increases its versatility [55].

5.3 Improved Product Quality

The use of co-pyrolysis improves the quality of the pyrolysis product. The synergistic effects of feedstock chemical composition can alter the specific properties of oil, char, and gas. One example is the production of bio-oil with high heating value and stability by co-pyrolysis of biomass and plastic wastes. Hydrogen supplied from plastic waste can increase the energy content of biooil, reducing its oxygen content [5]. The co-treatment of biomass and rubber waste can improve the bio-oil quality. Bio-oil with improved fuel characteristics can be produced using new and modified biomass and waste rubber chemicals. Rubber degradation reduces the oxygen content of the oil and facilitates the production and use of bio-oil [32, 33].

5.4 Synergistic Catalytic Effects

In co-pyrolysis, when another enhances one feed catalyst, there is a synergistic catalytic effect. The method influences the distribution and composition of the co-pyrolysis products. Chars can work as catalysts and susceptors, produced by pyrolyzing biomass and plastic waste, accelerating secondary reactions, and enhancing methane and hydrogen production. Catalytic chars enhance gas production by decomposing products and breaking them down. The combination of biomass and rubber waste is more effective in co-pyrolysis. By degrading solid biomass components, rubber waste can accelerate biomass pyrolysis and gas production. Catalysts can be formed during the interaction of biomass with rubber waste, which can enhance catalyst activity and dispersion [56].

5.5 Environmental Benefits

Co-pyrolysis is more environmentally friendly than feedstock pyrolysis. Co-incineration of biomass, plastic, and rubber waste can reduce environmental impact and help manage waste. Multi-feedstock co-pyrolysis improves resource efficiency and reduces emissions. Co-pyrolysis produces hydrogen and methane, which can further a sustainable energy system. Industrial activities that use these gasses instead of fossil fuels can lower our carbon footprint and climate impact [57].

5.6 Product Distribution in Co-pyrolysis

The term "co-pyrolysis" describes the practice of pyrolyzing multiple feedstocks at once. Collaborative pyrolysis provides synergistic advantages and new product distributions by thermally degrading several feedstocks [58]. The feedingstock's composition, the pyrolysis process's parameters, and the feedstock's interaction determine the product distribution in co-pyrolysis. Interactions with feedstock can take a cooperative or competitive aspect. Reduced feedstock pyrolysis is a competitive outcome [59]. There may be a decrease in product output as a result. Because biomass particles compete with plastic particles for chemical adhesion, the liquid product yield in biomass-plastic co-pyrolysis may be lower. Chemicals generated from rubber that compete with one another for the surface adsorption of biomass particles in biomass Bio-oil formation are hindered by rubber co-pyrolysis [60]. Cooperative effects are created when another enhances the pyrolysis of one feedstock. Potentially, this might result in higher product yields. Biomass-plastic co-pyrolysis enhances biomass thermal cracking and increases gaseous product production. Gaseous products are enhanced through improved rubber thermal cracking in biomass-rubber co-pyrolysis. The products' distribution depends on the co-pyrolysis conditions, including temperature, heating rate, and residence time. Optimizing product yields is achieved by modifying these components. Increasing the pyrolysis temperature can enhance the gaseous product output and feedstock thermal cracking. Char, however, can be produced by extremely hot substances [61]. Product distribution in co-pyrolysis is susceptible to feedstock characteristics and composition. The molecular structure and heat stability are two elements that influence how feedstock pyrolysis behaves. Biomass contains abundant cellulose, hemicellulose, and lignin, which, when hydrolyzed, can yield several compounds. Essential plastic components decompose during polymer heating, releasing a cloud of hydrocarbon fumes [5]. New chemicals and products are created when feedstocks interact in co-pyrolysis. A higher-grade bio-oil can be obtained by co-pyrolyzing biomass with plastic, provided that certain aromatic compounds are generated. Compounds of interest are produced by heating rubber and biomass. These molecules can then be transformed into valuable compounds [30, 33]. It is possible to examine the dispersion of co-pyrolysis by-products using GC-MS, FTIR, and NMR. These methods are employed to identify and measure the many products that emerge during co-pyrolysis [5, 61].

6 Advantages and Challenges of Co-pyrolysis

There are a lot of advantages to co-pyrolysis with various feedstocks over single-feedstock pyrolysis. The effect of co-pyrolysis will be discussed here.

6.1 Synergistic Effects

Interactions between pyrolysis components hasten the thermal breakdown and boost the production of valuable by-products, including bio-oil, char, and gases. Through the co-pyrolysis of feedstocks, this interaction can lead to synergistic advantages [5, 59, 61].

6.2 Product Diversification

Compared to pyrolysis using just one feedstock, co-pyrolysis enables the creation of a broader range of products. Combining feedstocks with diverse qualities can change the distribution of a product and increase its value. Many industries and products can benefit from the bio-oil and syngas that are by-products of co-pyrolysis of biomass and waste plastic [41, 62, 63].

6.3 Improved Bio-oil Quality

In conjunction with other feedstocks like plastics or rubber, bio-oil made from biomass is the way to enhance the pyrolysis process of bio-oil; one can incorporate hydrogen by reusing plastics or rubber. Decreasing bio-oil oxygen levels and boosting energy density improves thermal efficiency, adaptability, and reliability [24, 33, 64].

6.4 Waste Valorization

Through co-pyrolysis, it is possible to generate value from hard-to-recycle/unwanted waste. Acquiring the bio-oil, char, and gases from waste and biomass is feasible. In addition to reducing negative environmental impacts, this method can also generate profit from waste [5, 63].

6.5 Process Intensification

Using co-pyrolysis to enhance pyrolysis also shortens the reaction time. Meanwhile, many feedstocks can speed up thermal decomposition, improving conversion efficiency. In contrast to single-feedstock pyrolysis, this method can increase output while decreasing energy use [65, 63, 66].

6.6 Feedstock Compatibility

One of the most challenging issues for co-pyrolysis is to find feedstocks that work well together and are efficient for feedstock pyrolysis, including thermal decomposition temperature and reaction kinetics. Experiments must be conducted and the process optimized to determine which feedstock combinations produce valuable products with a synergistic effect [67].

6.7 Product Distribution Control

Co-pyrolysis can make it harder to control the product yield because of the complicated variety of products. Depending on the feedstock used, pyrolysis pathways and product selectivity can change. Understanding the mechanisms of pyrolysis is necessary so we can adjust the parameters of the process to get products appropriately distributed [68].

6.8 Process Optimization

Feedstock ratios, heating rates, reaction temperatures, and reaction times are some factors that must be optimized in the co-pyrolysis processes. Extensive experimental testing and analysis may be necessary during the optimization process, which can be time- and resource-intensive. Additionally, the ideal conditions for co-pyrolysis may differ from those performed on a single feedstock pyrolysis, adding complexity to the process development [69, 70].

6.9 Scale-up Challenges

The transition from the laboratory scale to the industrial scale of co-pyrolysis systems can be difficult. The compatibility of different feedstocks, process dynamics, and heat transport properties may vary at different scales. During the scaling-up process, important considerations include ensuring the product quality is constant, keeping the process stable, and addressing concerns regarding safety or the environment; because the microwave-assisted pyrolysis reactor with microwave absorbent bed is capable of working continuously and effectively for pyrolysis processes, it has the potential to be scaled up to a larger reactor [71, 72].

7 Conclusion

Bio-oil produced by microwave-assisted pyrolysis shows promise as a marketable result. Bio-oil's oxygen concentration can be lowered through catalytic upgrading, making it a more stable and profitable product. Sustainability, adaptability, and the opportunity to create new products are just a few benefits of using bio-oil. However, issues with its complicated composition and high oxygen content must be resolved to realize bio-oil promise entirely. Synergistic effects, product diversity, enhanced bio-oil quality, waste valorization, and process intensification are just a few of the benefits of co-pyrolysis compared to pyrolysis of a single feedstock. In order to successfully implement co-pyrolysis technologies, it is necessary to address issues such as feedstock compatibility, product distribution management, process optimization, scaling up, and environmental consequences. Co-pyrolysis plays a role in waste management and generates bio-oil, char, and gases, which allows it to overcome these limits and realize its full potential for the recovery of resources and the generation of sustainable energy. Utilizing bio-oil derived from co-pyrolysis can serve as a chemical feedstock and sustainable fuel. Char, being similar to coal, can be burned. Optimize co-pyrolysis and find novel bio-oil and char uses. Syngas production by co-pyrolysis is fascinating.

Hydrogen-rich gases are used in energy generation, chemical and fuel production, and more. Environmental benefits make co-pyrolysis a feasible waste management approach. Feedstock heterogeneity and syngas impurities must be addressed to optimize the process and ensure syngas quality. These impediments must be addressed to maximize co-pyrolysis for syngas production, necessitating more research. Advances in microwave-assisted and co-pyrolysis offer new ways to recycle biomass, plastic, and rubber. Reactor design, catalysts, hybrid processes, process optimization, integration with renewable energy sources, and feedstock conversion improve pyrolysis systems' efficiency, scalability, and environmental impact. These developments benefit pyrolysis's long-term viability and contribute to building a greener, more closed-loop economy. For their many benefits in efficiency, adaptability, and the generation of high-value end products, microwave-assisted pyrolysis and co-pyrolysis technologies are poised for rapid commercialization. Market conditions favor these technologies because eco-friendly waste management options and renewable replacements for traditional fuels are needed. Successful commercialization, however, requires solving problems of scale-up, feedstock variability, and economic viability. MW-assisted pyrolysis and co-pyrolysis can improve sustainability and the circular economy with additional study, development, and teamwork. The product distribution and yield in MW-assisted pyrolysis and co-pyrolysis processes are affected by factors such as feedstock composition, heating rate, temperature, residence duration, and reactor design. Optimizing these factors allows maximizing the intended product outputs and boosting the technology's overall efficiency. Improvements in product distribution and yield can be made by more research and development into the complex interplay between these factors in MW-assisted Pyrolysis and co-pyrolysis.

Competing Interests

The authors declare that they have no competing interests.

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