



Review Article

Recent advancements, challenges in recycling of waste plastic using microwave assisted catalytic co-pyrolysis of biomass and waste plastic for production of value added chemicals: a review

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ABSTRACT

The endeavor aim to addressed environmental issues by converting biomass and plastic waste into high-value products such as bio-oil, syngas, and biochar, consequently encouraging sustainability and energy saving. Our goal is to investigate the efficacy of an amalgamation of processing technologies and microwave irradiation, which has resulted in noticeable increases in reaction productivity as well as significant reductions in processing time, emphasizing its importance in addressing the environmental crisis caused by plastic waste accumulation. Microwave processing provides greater yields and cleaner profiles when contrasted to pyrolysis, high temperature carbonization and gasification techniques. This is indicative of its exceptional thermal and non-thermal effects, which distinguish it from other methods of heating. The use of catalysts in co-pyrolysis promotes product selectivity and quality, with different catalysts such as biochar, activated carbon, and zeolites being employed to enhance yields and product composition. The results indicate that the optimal yields of bio-oil are 72.1% from 95:5 weight percent corncob and high density polyethylene without catalyst, and 67.1% from 90:10 weight percent corncob and high density polyethylene with a catalyst. The optimization of microwave treatment settings, establishing large-scale continuous processing technology, and undertaking techno-economic assessments for commercial production are all challenging. Microwave pyrolysis is an effective process for producing fuels with high calorific value. Future recommendations, given the numerous benefits of microwave pyrolysis, should be optimized on an industrial scale.

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INTRODUCTION

Fossil fuels are widely used and steadily depleted as a result of rising population and worldwide energy demands, which exacerbate the energy crisis and worsen environmental issues [1-4]. Consequently, there is an incremented in public awareness of the need to examine innovative green options and sustainable production and utilization of renewable resources. Energy crops, forest wood, and agricultural waste can all be converted into biomass, an essential renewable energy source. It has several advantages over traditional fossil fuels, mainly because it is readily available and environmentally friendly. More biomass is created as a result of the planet's expanding population and rising waste production [5].

Therefore, biomass has the potential to work in conjunction with fossil fuel sources in the years to come. The efficient synthesis of several goods from biomass, such as biodiesel bioethanol, and, bio-hydrogen, demonstrates its dependability and cleanliness as an energy source [6, 7] Table 1 illustrated the third generation fuel production observed at lab scale due to algae growth and mostly cultivation environment created for third generation fuel. Plastics and other lignocellulosic waste are a substantial and plentiful. That can be easily converted into energy through thermochemical processes. Biomass resources have drawn interest as a renewable carbon resource in the wake of increasing energy and environmental issues [8].

Recent developments in waste plastic recycling by microwave-assisted catalytic co-pyrolysis with biomass have

driven broad enthusiasm due to their potential to produce value-added compounds. The catalytic conversion of biomass and waste plastics illustrates that both materials contain structural similarities, which may be utilized to increase conversion efficiency and yield [9]. This approach not only overcomes the environmental difficulties faced by petroleum-based plastics, but it also corresponds with the concepts of a circular economy, discussed in the context of bioplastics and sustainable production processes [10]. Furthermore, insights from global practices, such as Japan's extensive plastic waste management plans, highlight the necessity of combining technical advances and regulatory frameworks to enhance recycling processes and promote sustainability in plastic waste management [11]. Collectively, these studies emphasize the need for a unified approach in research and policy to overcome existing challenges and leverage opportunities in the recycling of waste plastics. A promising method that can transform solid biomass into useful liquid fuel, charcoal, and syngas is Microwave-assisted Pyrolysis (MAP) as illustrated in Figure 1. It is considered as one of the most attractive approaches for promoting change in the way manufacturing is now done in the thermal conversion of biomass [12]. The expansion of microwave assisted pyrolysis from lab-scale devices to large-scale operations may be made possible by the rising demand for efficient technology. Through increased yield and selectivity in rapid pyrolysis, catalysts significantly contribute to increasing the synthesis of aromatic compounds and other important products within biofuels [13]. The use of metal modified zeolite and

Table 1. First, second, and third generations of bio-fuel [8]

Primary sources of the first-generation	Virgin resources	Forest resources	Various types of wood, including pine, woody biomass, such as willow, and well-known aspen, are frequently used.
		Oil crops	Other crops that are widely used include pasture grasses, sugar-cane, corn, canola, rape seed, wheat, barley, palm oil, soybean, and oats.
Origins of the second generation	Residual	Residues of Wood	Following harvest, the following materials are left over: bark, limbs, treetops, leaves, sawdust, and shavings from sawmill and pulp operations.
		Agricultural residues & waste	Leftovers from harvesting oil-producing crops, extra oil/fat.
		Livestock residues	Animal excrement and cattle remnants.
	Municipal Solid Waste (MSW)	Residential waste	Electronics, plastics, Cardboard, tires and other types of paper, glass, various metals, and biological material.
Sources associated with the third generation	Algae	Non-residential	Sediment in wastewater.
		----	Microalgae, Macro algae

traditional zeolite catalysts in processes like CFP (Catalytic-fast Pyrolysis), MAP (Microwave-assisted Pyrolysis), and CCP (Catalytic Co-pyrolysis) is briefly examined in this article. It has been widely studied how different catalysts have an effective impact on the yield produced and selectivity of the products during the process of pyrolysis. Microwave-Assisted Pyrolysis (MAP) which quickly heats biomass between 500 and 700K, has the promise for creating bio-oils [14]. In addition, adding water to the feedstock may hasten heating and lower the peak pyrolysis temperature in procedures like MAP, reducing the influence of advanced cracking and degradation mechanisms. This article seeks to provide a comprehensive review of microwave irradiation methods while illuminating the state of microwave processing technology. It also looks into the possibility of using microwave technology to produce biodiesel more efficiently than using traditional methods. Syngas, high-valued carbon products, and biofuels' output and quality could all be considerably enhanced by integrating microwave adsorbents, catalysts, and parametric effect on microwave-assisted pyrolysis conditions.

COMPARISON OF DIFFERENT PYROLYSIS TECHNIQUE

According to estimates by the Food and Agricultural Organization, around 1.3 billion tons of garbage is created annually in the world, with 45% to 80% of that waste ending up in landfills. Even though it is thought unneeded, this trash can be properly harnessed to become a valuable resource.

In light of the expanding understanding on the contribution of organic waste, such as food waste, to global warming, certain countries have started implementing legislation to restrict the disposal of garbage in landfills. Through thermochemical processes, aromatic chars with a higher calorific value that may be utilized as solid fuel in combustion facilities can be created from municipal waste [15]. The use of thermochemical processes, pyrolysis, hydrothermal carbonization, and microwave-assisted pyrolysis to produce char from waste is examined as shown in Figure 2. Table 2 illustrated the comparison of different pyrolysis techniques. Three pyrolysis techniques were observed as shown in Figure 2, High temperature carbonization (HTC), Pyrolysis (PY), Microwave (MW). HTC showed when temperature achieves 180°C; the yield obtained is 77%, having high heating value 4200 kcal/kg. When the temperature is 180°C then most of the biochar produced, when temperature increased more than 180°C, then most of the organic compounds converted into gaseous yield. When temperature is below than 180°C, then most of the moisture contents removed and observed complete conversion not occur smoothly. Pyrolysis showed when temperature is 500°C, and then the yield of char is 30%, having high heating value 5700 kcal/kg. When the temperature is 500°C, then most of syngas is produced, when temperature increased more than 500°C, then most of the organic compounds converted into

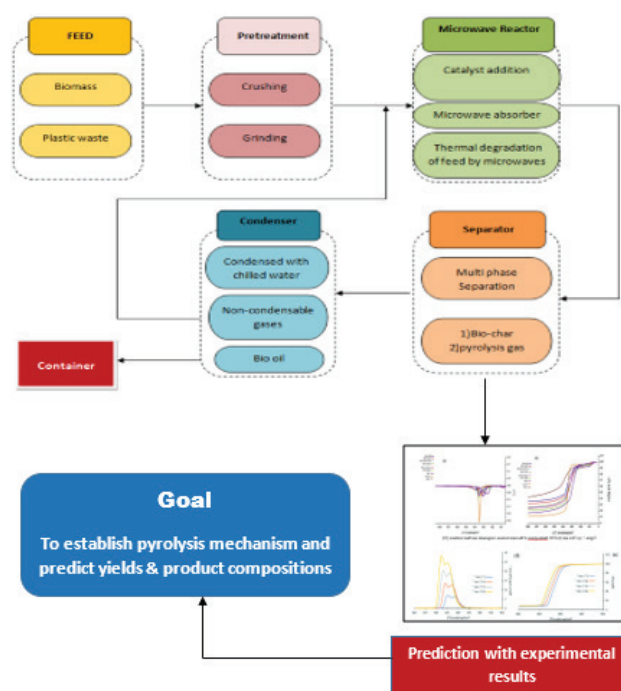


Figure 1. Pictorial representation of microwave assisted pyrolysis.

[From Masood, M. et al. [1], with permission from Taylor & Francis.]

gaseous yield. When temperature is below than 500°C, then most of the moisture contents removed and observed complete conversion not occur smoothly. Microwave pyrolysis showed when temperature is 300°C, and then the yield of char is 58%, having high heating value 500 kcal/kg. When the temperature is 300°C, then most of bio-oil is produced, when temperature is increased more than 300°C, then most of the organic compounds converted into oil. When temperature is below than 300°C, then most of the moisture contents removed and observed complete conversion not occur smoothly. These procedures entail the chemical breakdown of waste products. In pyrolysis, trash is subjected to anaerobic decomposition at temperatures between 130 and 1300°C, producing a thick and energetic char [16]. In contrast, HTC uses hydrolysis and thermal processes to turn biomass waste into char at temperatures between 180 and 260°C and pressures between 10 and 20 bars. Instead, waste microwave-assisted pyrolysis (MW) uses microwave energy, operating at pressures between 10 and 50bar, with power levels ranging from 300 to 2700W, to induce trash pyrolysis. The use of MW is beneficial since it expedites the burning process, conserves energy, and improves the quality of the resulting char [17].

It is possible to achieve the adsorptive removal of metal ions from wastewater with the help of char since it has numerous important physicochemical features. Thermal stability and oxygen group surface functioning are some

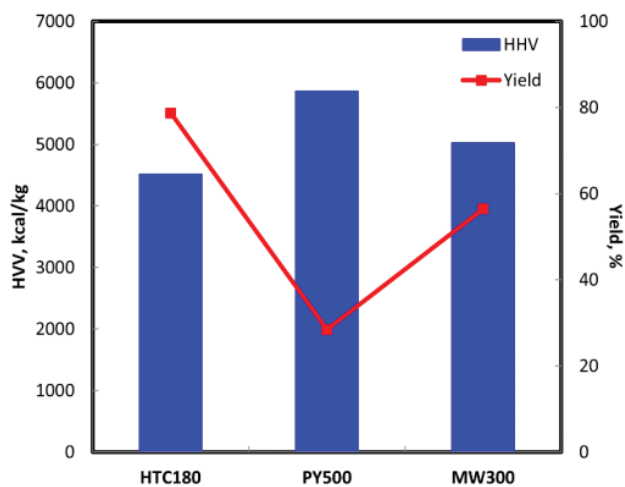


Figure 2. Comparison of pyrolysis techniques.

[From Al Qahtani et al. [21], with permission from MDPI.]

of these characteristics [18]. Furthermore, char made from trash has high carbon content (between 45% and 93%), high energy values (between 3585 and 7170 kcal/kg), and low ash content (between 2.3% and 6.4%) [19]. These characteristics make char a great replacement for solid fuel. The fuel qualities of char can change based on the precise thermochemical process used and the underlying mechanism, it is crucial to keep in mind [20, 21].

EFFECTS OF CATALYST

Catalytic Fast Pyrolysis

AlO_4 and SiO_4 , which are hydroaluminosilicate compounds, are two important aluminate and silicate species that are converted into zeolite [23]. Zeolite's structural plasticity allows it to display a variety of open holes and

crystal shapes during chemical reactions. Rocks include well-known zeolites like mordenite naturally, but synthetic zeolites like HZSM5, H-Beta, and H-Y, as well as their altered varieties, are frequently used in both academic and commercial settings. Zeolite catalysts are commonly utilized in petroleum and biofuel catalytic processing due to their ion exchange characteristics, pore structure, structural selectivity, and acidity. These catalysts can also transform biomass or pyrolysis steam into desirable compounds, particularly aromatics, through the alkylation and aromatization processes [24]. This provides a means to improve the output items' quality while using less energy. The use of conventional zeolite catalysts in catalytic fast pyrolysis (CFP) has been the subject of recent studies.

By using lodgepole pine that had been severely impacted by insects in a pyrolysis experiment, Heather used an original method. This was accomplished using a fast ablation reactor and granular HZSM-5 zeolite. The results showed a remarkable 94% selectivity toward benzene, toluene, and xylene (BTX), along with a minimum coke production of 9.4% and a maximum yield of aromatic hydrocarbons at 3.5 wt% [25]. Zhang. In a study involving the speedy pyrolysis of rice straw, cetyl trimethyl ammonium bromide (CTAB) was used as a modified catalyst, which was part of this alteration, was added in a preset amount to HZSM-5 as shown in table 3. A rigorous tuning process was used to make this change, which led to a decrease in coke yield and an increase in the production of aromatic hydrocarbons [26]. But when CTAB was added too much, the results were different. With a CTAB/ SiO_2 molar ratio of 0.01, the catalyst known as HZ-0.01 displayed the best performance among the various addition ratios that were examined.

According to Chen, adding the right amount of nickel and copper to the HZSM-5 catalyst increased its activity and boosted the generation of aromatics. However, a heavy metal loading decreased the aromatics' output. Mesopores were added to the catalyst using alkali treatment to increase the aromatics production. For a different experiment into

Table 2 Comparison between pyrolysis technologies [22]

Pyrolysis	Description	Process Parameters			
		Vapour Residence Time (min)	Temperature (°C)	Heating Rate (°C/min)	Particle Size (mm)
Slow Pyrolysis	It has a long vapour residence time, very low heating rate, for large particle size and operates at a moderate temperature range.	5–30 10–100	300–700	0.1–1	5–50
Fast Pyrolysis	It has short vapour resistance time, a smaller particle size, moderate heating rate and occurs in at high-temperatures.	>5(s)	400–800	10–200	>1
Flash Pyrolysis	It has the shortest vapour resistance time, a finer particle size, highest heating rate, and it occurs at a very high temperatures.	>5(s)	800–1000	>1000	>0.5

the catalytic fast pyrolysis (CFP) of maize cobs, Dai . added nickel as an additional ingredient to a hierarchical ZSM-5 catalyst. According to their research [27], nickel's addition improved the ZSM-5 catalyst's structural stability and decreased the activation energy needed for reaction kinetics. As seen during N_2 adsorption-desorption characterization, the introduction of nickel caused depletion in the particular surface area and microporous volume of the substitute ZSM-5 catalyst. The production of aromatic compounds, particularly monoaromatic compounds, rose as a result of this change. In a different study, Liang. found that adding transition metals including cobalt, nickel, and zinc to ZSM-5 catalysts dramatically incremented the output of bio-oil. The redesigned catalysts enhanced the selectivity of phenol and aldehyde/ketone chemicals (which make up 50% of the GC/MS area) while maintaining the topological shape of the main catalyst. The most efficient catalyst among them was determined to be Zn/ZSM-5 (with a Si/Al ratio of 46) [28].

The waste polypropylene (WPP) composite was pyrolyzed, and the compositions that were left behind were examined by Py-GC/MS. Metal oxide catalysts, such as CaO, MgO, ZnO, and Fe_2O_3 , were used as catalysts. When metal oxides were added, the peak area percentages of the end products shifted, revealing a variety of unique compounds. These recently discovered substances were divided into eight different categories, including mastics, furans, carboxylic acids, phenols, ketones, esters, alkenes, and alkadienes.

Catalyst Slow Pyrolysis

Catalysts offer a different, energy-saving route for reaching specific product yields. The thermal decomposition of solid biomass and polymers produces indiscriminate byproducts at high temperatures in the absence of catalysts. Metal catalysts like Nickel, Zinc, Aluminum, zeolites, and Potassium have been used in slow pyrolysis to increase H_2 generation. These catalysts have encountered difficulties due to problems such as chemical toxicity, metal

sintering, and poor metal dispersion [29]. The copious supplies, improved porosity, and customizable structure of biochar, a carbon-based substance, make it an attractive choice for catalytic applications [30]. Biochar catalysts have been demonstrated to exhibit good catalytic activity in the esterification/transesterification, hydrogenation, and oxygen reduction processes [31]. Studies show that adding biochar increases the percentage of phenols and acetic acid in bio-oil [32] and the generation of high-quality syngas [33]. Even though research suggested utilizing activated carbon (AC) as catalysts, employing biochar as a substitute for conventional AC, although it was investigated activated carbon (AC) economically more favorable. can be prepared That biochar with fewer energy and chemical products than AC while still having similar physiochemical qualities [34].

Pyrolysis is essential to the process of making biochar since it has a big impact on both the material's effectiveness and the cost of manufacturing as a whole. Microwave-assisted pyrolysis is gaining popularity due to its capacity for volumetric and selective heating [36]. Biochar also has distinct surface properties, including a high permeability, large surface area, more aromatic carbon, and increased mineral content [37].

Catalytic Microwave Assisted Pyrolysis

In our earlier research, reviewing the microwave heating behavior of clean biomass, clean biomass combined with different catalysts, and their combinations. Drying (25 to 110°C), heating, pyrolysis, and torrefaction (110 to 260°C, involving partial devolatilization and depolymerization) main steps of entire microwave-catalytic pyrolysis process. Heating rates, as shown in Table 4, clearly show the combined impacts of microwave and catalysts. Table 4 shows the overall heating rates for microwave-assisted catalytic pyrolysis, as well as the exact microwave heating rates for biomass when coupled with different catalysts or their mixes at different stages, such as pyrolysis and torrefaction. It is interesting that the pyrolysis stage (260 to 400°C) has

Table 3. Examine the rate of heating of switch grass by using various catalysts or activated carbon mixtures during various heating processes during microwave-assisted pyrolysis [35]

Weight of Sample	Abbreviations	Heating Rate, °C per minute (110 to 260°C, Torre faction)	Heating Rate, °C per minute (260 to 400°C, Torre faction)	Overall Heating Rate, °C per minute (110 to 440°C, Torre faction)
10 w.t % clinoptilolite	10 Clino	145	9	19
20 w.t % clinoptilolite	20 Clino	169	10	21
30 w.t % clinoptilolite	30 Clino	391	39	81
10 w.t % K_3PO_4	10 KP	173	10	20
20 w.t % K_3PO_4	20 KP	380	38	79
30 w.t % K_3PO_4	30 KP	219	9	19
10 to 30 w.t % Bentonite	Bento	Massive temp < 200°C	-	-
20 w.t % activated carbon	20AC	265	22	46

Table 4. Catalytic Fast Pyrolysis (CFP) using the use of traditional zeolite catalyst [38]

Biomass	Catalyst	Conditions of Reaction				Reactor	Major Products	Ref.
		Feedstock: catalyst (weight)	Temperature (°C)	Acidity	Mode of Operating			
Corncob	Zeolite (ZSM-5)	1 : 2	550	27	(In situ)	Double shot Pyrolyzer	Arene Hydrocarbons	17
Corncob	HZSM-5	1 : 2	550	27	(In situ)	Double shot pyrolyzer	Arene Hydrocarbons	17
Kraft Lignin	Zeolite (ZSM-5)	1 : 2	600	11.5	(Ex situ)	Fixed bed reactor	Arenes, Alkylphenols	18
Kraft Lignin	Zeolite (ZSM-5)	1 : 2	600	25ev	(Ex situ)	Fixed bed reactor	Arenes, Alkylphenols	18
Kraft Lignin	Zeolite (ZSM-5)	1 : 2	600	40	(Ex situ)	Fixed bed reactor	Alkylphenols, Arenes	18
Lignin	Zeolite (ZSM-5)	1 : 1	450	60	(In situ)	Fixed bed reactor	Phenolics, Monomeric-Arenes	19
Poultry Litter	ZSM-5/MCM-41	10 : 1	500		(Ex situ)	Microwave oven	PAHs, benzene, xylene, Toluene	20
Wood-sawdust	Zeolite (ZSM-5)	10 : 1	600	17.3	(Ex situ)	CDS Pyro probe 5200-HP Pyrolyser	Phenols, Arene hydrocarbons	21
Pinewood Sawdust	Zeolite (ZSM-5)	25 : 1	500	46		CDS Pyro probe 5200-HP pyrolyser	Arene hydrocarbons, phenols	22
Saw-dust	HZSM-5	-	400-600	25	(In situ)	Drop-tube quartz reactor	Olefins/alkene, Arenes	23
Saw-dust	HZSM-5	-	400-600	50	(In situ)	Drop-tube quartz reactor	Olefins/alkene, Arenes	23
Saw-dust	HZSM-5	-	400-600	80	(In situ)	Drop-tube quartz reactor	Olefins/alkene, Arenes	23
Maize-Straw	ZSM-5/SBA-51	1 : 2	400-700		(In situ)	Fixed bed reactor	Hydrocarbon, Phenols	24
Soda-lignin	Zeolite (ZSM-5)	1 : 2	500-900	30-40		CDS pyro probe 5200HPR	Catechol, Arenes, phenol	25
Soda-lignin	Y-Zeolite	1:2	500-900	8-9		CDS pyro probe 5200HPR	Catechol, Arenes, phenol	25
Corncob	HZSM-5	1:2	700	25			Arenes, Acetonitrile	26
Corncob	HZSM-5	1:2	700	25			Arenes, Acetonitrile, pyridines	26
Corncob	MCM-41	1:2	700				Arenes, Acetonitrile	26
Lignin	MCM-41	1:2	700	25	(Ex situ)		Pyrroles, Acetonitrile	26
Lignin	Zeolite	1:2	600		(Ex situ)		N-doped carbon, Aromatic amines	27
Lignin	HZSM-5	1:2	600	50	(Ex situ)		N-doped carbon, Aromatic amines	27
Cellulose	ZSM-5	2:1	600	25	(In situ)		Light-olefins (C ₂ H ₄ , C ₃ H ₆)	28
Jatropha-Residual	HZSM-5	1:1	500	40		Pyro probe pyrolyzer		16

the greatest influence on heating rate. In this phase, catalyst combinations reach heating rates that are higher than would generally be anticipated from a straightforward combination of the two catalysts [39]. The microwave heating rate was observed typically slower during the pyrolysis stage (260 to 400°C) than during the torrefaction stage (110 to 260°C), with sample 30 K₃PO₄ showing the lowest rate, which was probably because of endothermic biomass pyrolysis reactions. The greatest value was reported for sample 10 K₃PO₄/10 Bentonite, however the catalyst mixes show the maximum heating rate during pyrolysis process. It was noticed that increasing amount of bentonite in biomass did not dramatically speed up microwave heating as shown in Table 3; temperatures that were measured remain well below 200°C varied loading up to 30wt. %. This supports the idea that catalyst combinations work together to increase microwave heating rates.

Effect of Microwave Absorbers

Microwave absorber addition

Biomass often has weak microwave absorption characteristics. However, the addition of microwave-absorbing elements improves the treated materials' ability to absorb microwaves. Numerous studies have shown the applications of Microwave-assisted pyrolysis process using Bio-mass, whether or not inorganic materials are used as microwave absorbers. These experiments have shown that, even at very modest microwave power levels, the use of microwave absorbers may successfully raise the temperatures of pyrolysis reactions. Microwave absorbers, which subsequently raise the temperature of the nearby biomass particles, help to support this improvement. Similar to this, some studies have shown that adding microwave absorbers and particular catalysts to bio-mass could change the

way products are being distributed, improvement of certain bio-oil, bio-char, and gas constituent concentrations in various treatment environments or boost whole process's energy efficiency [40]. For instance, Menéndez, Arenillas (2010) was examined the effectiveness of adding microwave absorbers to the pyrolysis of empty fruit bunches. The samples included 5% char from a prior pyrolysis as an addition. In contrast to the meager 177°C attained without the absorber, this intervention produced a significantly greater maximum temperature of 590°C. But the operational temperature did not seem to rise any further when the char content was increased to 10% or 15%. However, increasing the char concentration led to a decrease in the yield of CO and a rise in the lower heating value (LHV), as well as a reduction in the output of hydrogen gas. Oil palm shell char produced by conventional pyrolysis was used to examine the effect of microwave absorbers on the microwave pyrolysis of oil palm biomass [41]. The absorber particles were between 100 and 300m in size. A high production of about 70% of bio-char was attained when the microwave absorber was applied with a biomass to absorber ratio of 1:0.25. This result showed that simply a small amount of microwave absorber could not properly heat the biomass. The highest biomass to absorber ratio, on the other hand, produced bio-oil and gas products, yielding about 25% and 30%, respectively. The highest operating temperature that could be obtained at this ratio was 273°C.

The generation of syngas was increased by as much as 66% when char was combined with microwave-heated sewage sludge, but only by a very modest 62% when graphite was added [42]. These increases were much greater than those made possible by conventional pyrolysis. Although lower than those obtained through traditional pyrolysis (14 MJ/m³), Gases created by microwave pyrolysis had heating values that ranged from 7 to 9.5 MJ/m³.

Table 5. Dielectric loss tangents of several materials at 2.45 GHz frequency and room temperature [43]

Material	Temperature (°C)	Frequency (GHz)	$\tan \delta = \epsilon'' / \epsilon'$
Water	25	2.45	0.12
Cellulose	25	2.45	0.035
Hemicellulose	25	2.45	0.062
Lignin	25	2.45	0.052
Polypropylene	25	2.45	0.0003–0.0004
Polystyrene	25	2.45	0.0002–0.0003
Polyethylene	25	2.45	0.0001–0.0002
Carbon foam	25	2.45	0.05–0.20
Charcoal	25	2.45	0.11–0.29
Carbon black	25	2.45	0.35–0.83
Activated carbon	25	2.45	0.62
Carbon nanotube	25	2.45	0.25–1.14
SiC	25	2.45	0.02–1.05
Carbon	25	2.45	0.28

For microwave pyrolysis, five metal oxides Fe_2O_3 , CaO , Al_2O_3 , ZnO , and TiO_2 were added to demineralized discharged sludge. Fe_2O_3 and ZnO were shown to encourage the production of solid residue, whereas Al_2O_3 , CaO , and TiO_2 had the reverse effect and inhibited the formation of residue. Therefore, the breakdown of organic molecules was thereby facilitated by the presence of Al_2O_3 , CaO , and TiO_2 , leaving a very small amount of residue behind.

Additionally, the inclusion of CaO can speed up the initial breakdown of hemicellulose and facilitate the subsequent degradation of lignin, particularly given that it increased the temperatures at which sludge is converted below 177°C and above 487°C . On the other hand, Fe_2O_3 appeared to slow down the breakdown of cellulose and lignin at temperatures higher than 237°C . The fact that Fe_2O_3 largely increased sludge conversion at lower temperatures was evidence of this.

Effect of Microwave Absorber Radiation

Microwave absorbers are materials that react with microwaves to produce heat. Absorbers can be physically represented in a variety of ways, such as stiff epoxy, flexible elastomers, foam, or plastics. The majority of carbon-based materials and some inorganic oxides make effective microwave absorbers. Dielectric heating is the term used to describe heating caused by high-frequency radiations from electromagnetic fields, often known as microwave and radio frequency waves. These waves are characterized as having wavelengths between 0.001 and 1 m and frequencies between 300 and 0.3 GHz. Dielectric ferromagnetic substances are used to fill electromagnetic interface (EMI) microwave absorbers. The wave is attenuated and loses strength as it interacts with these materials. Phase cancellation, which converts EMI energy to heat energy, is the cause of the energy loss. Electrical permittivity, or dielectric constant, and frequency both affect how much a microwave attenuates.

Dependence and co-relation

A material's dielectric loss tangent determines whether it may be heated in the presence of a microwave field:

$$\tan\delta = \epsilon'' / \epsilon' \quad [44] \quad (1)$$

The two parameters that make up the dielectric loss tangent are,

Dielectric constant (real permittivity) ϵ'

The amount of incident energy that is reflected and absorbed depends on the dielectric constant (ϵ'), and The dielectric constant (ϵ') demonstrates how adequately material polarization exhibits due to electric field whereas the efficacy with which the dielectric loss factor (ϵ'') typically used to calculate the rate at which a material emits electromagnetic radiation and emits heat as shown in Table 5. The dielectric loss tangent, or dissipation factor ($\tan \delta$), is the ratio of the dielectric loss factor to the dielectric constant. Table 5 shows the dielectric loss tangent ($\tan \delta$) values of several materials.

Dielectric loss factor (imaginary permittivity), ϵ''

Table 6. Dielectric-losses in the carbon material

Carbon material	$\tan\delta = \epsilon'' / \epsilon'$
Coal	0.02-0.08
Carbon foam	0.05-0.20
Charcoal	0.11-0.29
Carbon black	0.35-0.83
Activated carbon	0.57-0.80
Activated carbon2	0.22-2.95
Carbon nanotube	0.25-1.14
CSi nanofibers	0.58-1.00

The material's ability to dissipate electrical energy as heat is indicated by the dielectric loss factor (ϵ'').

$$\epsilon = \epsilon' - i \epsilon'' \quad [44] \quad (2)$$

Where complex permittivity is ϵ

The electromagnetic radiations reserving wavelengths on electromagnetic spectrum with a range from one meter (1 m) to one millimeter (1 mm) along with the frequencies confined to align with

300 GHz to 300 MHz are recognized as Microwave radiations where the customary usage of frequencies in modern microwave application is 2450 ± 50 MHz and subsequently 915 ± 13 MHz Since microwave possess vital role in current research and technological growth, studied have categorized solid materials into four regimes on the basis of their interaction with microwaves so as to ensure their suitable selection , (i) Perfect conductors which demonstrate complete reflection of microwaves from their surface (metals or graphite) (ii) Insulators; microwaves may travel through such materials without loss (transparent). (Ceramics or Quartz Glass)(iii) Dielectric materials (absorbers) absorb microwaves and heat up (activated carbon, silicon carbide). (iv) Magnetic loss materials in which magnetic losses occur in the microwave area, as shown in Figure 3 (metal oxides such as ferrites and other magnetic materials).

When absorber (dielectric material) confronts microwave radiations, polar molecules are compelled to rotate which in turn gives rise to friction when alignment with corresponding electromagnetic field is focused as shown in Figure 4. More polarized dielectric material generates greater internal friction which leads to the heating of material. This temperature rise in microwave absorber is due to phase lag which exists when the dipole's response time is insufficient towards the corresponding external field created due to microwaves leading to collision and heat generation [44].

Hence, microwave absorber heating undergoes three phenomena: (i) dielectric heating, (ii) magnetic heating, and (iii) conduction loss heating which consequently inhibits due to Polarization, production of induced dipoles followed by Interfacial polarization, which is accumulation of charges in contact areas and ionic conduction where

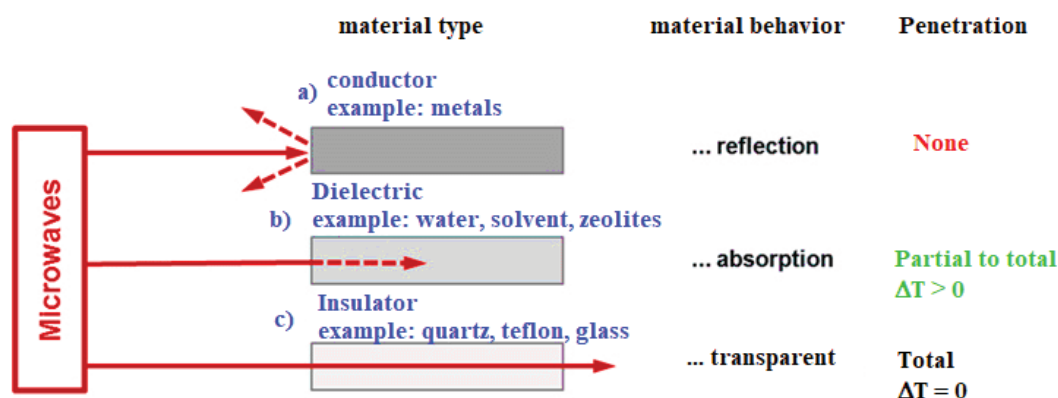


Figure 3. Microwaves and solids, (a) conductors, (b) dielectric loss materials, (c) insulators, Polarized dielectric material.

[From Palma, V. et al. [44], with permission from MDPI.]

electromagnetic radiations cause ionic transfer insinuating friction. Dielectric loss tangent ($\tan \delta$) is parameter for the determination of material's ability to absorb and transform electromagnetic energy into heat at corresponding frequency and temperature. Higher dielectric loss tangent ($\tan \delta$) values imply strong microwave absorption capacity of material. This loss factor is expressed in Table 5.

Influence of Biomass/Plastic Ratio

Pyrolysis experiments with maize cob and HDPE were performed both with and without a catalyst to perform mass balance analyses. The purpose of these tests was to learn more about the impact of the catalyst and plastic content on the synthesis of biofuels. The Table-7 data illustrated the mass equilibrium and products for different biomass to plastic ratios. The variation between the starting and final sample holder weights was used to figure out the residual or char output post-pyrolysis. Steam is frequently used in the process to speed up Water Gas Shift (WGS) and steam reforming processes that helps the generation of bio-oil. The results, as shown in the Table 7, showed that all scenarios had reasonably sound mass balance closures in the 92–95 weight percent range. The mass balance calculations

considered both the mass of the injected water and the sample's mass (a mixture of plastic and biomass). Condensed liquids were collected from condensers were primarily a mixture of water and oil with a brownish hue. Table 7 illustrated that adding HDPE to the non-catalytic process accelerates the yield of gas and hydrogen. Addition of HDPE, a polyolefin plastic, was significant since it provides a significant source of bio-oil. In catalyst-free reactions, the increment in HDPE content from 0 weight. When absorber (dielectric material) confronts microwave radiations, polar molecules are compelled to rotate which in turn gives rise to friction when alignment with corresponding electromagnetic field is focused as shown in Figure 4. More polarized dielectric material generates greater internal friction which leads to the heating of material. This temperature rise in microwave absorber is due to phase lag which exists when the dipole's response time is insufficient towards the corresponding external field created due to microwaves leading to collision and heat generation [45].

Hence, microwave absorber heating undergoes three phenomena: (i) dielectric heating, (ii) magnetic heating, and (iii) conduction loss heating which consequently

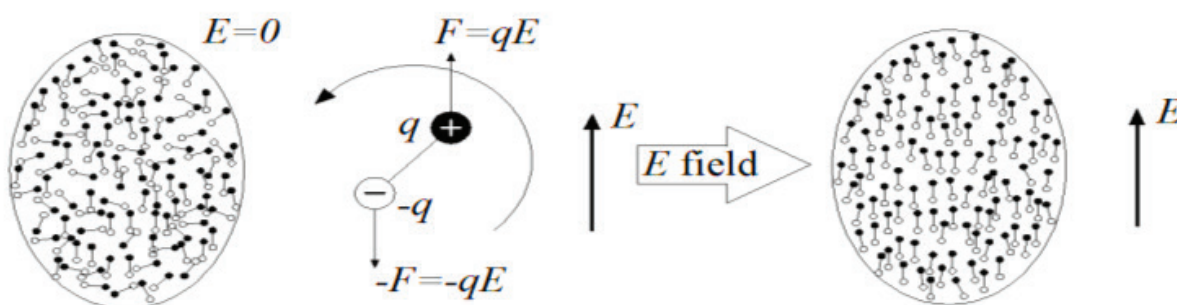


Figure 4. The effect of an electromagnetic field E on the dipoles of a polar molecule.

[From Palma, V. et al. [44], with permission from MDPI.]

inhibits due to Polarization, production of induced dipoles followed by Interfacial polarization, which is accumulation of charges in contact areas and ionic conduction where electromagnetic radiations cause ionic transfer insinuating friction. Dielectric loss tangent ($\tan \delta$) is parameter for the determination of material's ability to absorb and transform electromagnetic energy into heat at corresponding frequency and temperature. Higher dielectric loss tangent ($\tan \delta$) values imply strong microwave absorption capacity of material. This loss factor is expressed in Table-5.

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The breakdown of aromatic compounds in the biomass was then sped up as a result of the increased production and release of H and OH radicals, which served as hydrogen donors [46]. Additionally, a decrease in char and liquid formation was associated with a rise in plastic content, indicating that secondary reactions including condensation and repolymerization have slowed down [47]. During the starting steps of co-pyrolysis, hydrogen released by polyolefin polymer inhibited the recondensation events that lead to char formation [48].

THERMAL DEGRADATION OF WASTE PLASTIC AND BIOMASS

Binary Mixture of HDPE and Biomass

The TGA analysis of HDPE and walnut shells is shown in Figure 5. Three different heating rates of 25°C, 20°C, and

10°C/min were examined for thermal deterioration. By raising the temperature to 110°C, the moisture content is removed in the first stage, and the second step of weight loss involves the elimination of volatile compounds and primary cracking. A portion of the char also broke down and merged with the volatile matter curve. A largely liquid product was produced at 427°C due to the material's rapid breakdown rate at the high heating rate. During the third process, decomposition was seen because of the secondary cracking, and the major result was a gaseous form of product. No change was seen in the fourth stage, when the weight loss curve flattened down after all of the mixed material had been transformed into products. It emerged that the end product is mostly coal at a slow heating rate. Figure 6 shows the DTG results. The conversion rate was similarly high as the high heating rate of 25°C/min.

Thermogravimetric analysis (TGA) was used to evaluate the biomass samples and biomass components in order to figure out the features of the samples' thermal degradation. Figure 5 illustrates the differential weight loss (DTG) thermograms, as well as the thermograms of the individual biomass samples and the three major biomass components. Furthermore, the primary components of biomass—cellulose, hemicellulose, and lignin—were mixed and submitted to a TGA analysis to examine for any component interactions during the thermal degradation process. Figure 6 illustrates the findings.

Figure 7 and 8 illustrates the results of DTG and TGA thermograms for hemicellulose, lignin, and cellulose, respectively. A hemicellulose representative, Xylan, broke down between 200°C and 350°C, decomposition of cellulose takes place between 350°C and 400°C, and lignin showed a larger range of decomposition temperature that ranged from about 250°C to about 500°C [49], investigated the thermal breakdown of biomass components and found that, in agreement with this study, the temperature range for hemicellulose mass loss is between 200°C and 327°C, the range for cellulose is between 327°C and 450°C, and the range for lignin is between 200°C and 550°C. According to reports [50, 51], that, in comparison to cellulose and hemicellulose, lignin is Considered to be an exceptionally stable, temperature-sensitive aromatic polymer with an alkyl-benzene structure composed of three-dimensional linkages. Hemicelluloses are believed to be composed of branching polysaccharides that break down at temperatures lower than those of cellulose and lignin. They consist of a variety of biopolymers that are more sophisticated than cellulose [52]. Cellulose is a polysaccharide that breaks down from 325°C to 400°C and is made up of a linear polymer of $\beta(1/4)$ linked D-glucose units. [53].

This study's samples of agricultural waste biomass may be related to the heat degradation of the cellulose, lignin, and hemicellulose [50, 54]. All of the agricultural waste biomass samples' mass loss thermograms based within the parameters of the three types of biomasses. Figures 7 (a) and (b) illustrate that the thermal decomposition (TGA)

of the samples containing six waste biomasses began at around ambient temperature and increased to 900°C, and the DTG thermograms revealed multiple peaks for each biomass sample, indicating the presence and manifestation of these primary biomass components. Wheat straw's DTG thermogram exhibited one notable DTG peak at around 330°C, illustrating that it is mainly composed of cellulose and contains little hemicellulose. At temperatures of 240°C, 300°C, and 360°C, sugarcane bagasse had three DTG peaks, with the largest peak showing evidence of cellulose degradation, indicating that cellulose and hemicellulose make up the majority of the material [55]. The first two DTG peaks for sugarcane bagasse corresponded with hemicellulose, whereas the third peak was related to cellulose. The thermal breakdown of rice husks at 300°C and 360°C produced two DTG peaks, with the main peak corresponding to cellulose and hemicellulose and including some lignin. Other studies show that cellulose and hemicellulose are the main components of rice husks [54, 56, 57].

Thermal breakdown of palm kernel shells resulted in two DTG peaks at 280°C & 370°C, with the greater peak approximating lignin breakdown, indicating that lignin made up a larger percentage of the palm waste bio-mass than the other main elements. According to other studies [58] the principal ingredients in palm shell waste are cellulose and lignin. When cotton stalks were thermally decomposed, two DTG peaks between 300°C and 350°C, which correspond to the temperature at which hemicellulose and cellulose break down, were observed. Several studies [59, 60] In contrast to hemicellulose and lignin of heat degradation of stalks of cotton indicate a larger amount of cellulose. Additionally, two DTG thermal breakdown peaks at 280°C and 360°C were observed for coconut shell, indicating that cellulose and hemicellulose make up the majority of the material.

Effect of Feed

Biomass

Figures 8 (a) and 8(b) illustrate the TGA & DTG thermograms respectively of hemicellulose, cellulose, & lignin mixes. One DTG peak appeared between separate DTG peaks of lignin & cellulose in case of the 50:50 mixing of the two substances. Two thermal decomposition peaks for hemicellulose and lignin was observed for the 50:50 mixture of xylan & lignin. However, the thermogram DTG appears to be shifting to lower breakdown temperatures, demonstrating an association between the different components. The 50:50 xylan-cellulose combination contained three peaks that were identical to the two-hemicellulose decomposition DTG thermogram peaks (although displaced to a higher temperature) and the cellulose decomposition DTG peak. The mixture of three biomass components, which is composed equally of cellulose, xylan, and some lignin, shows two separate DTG peaks, one of which appears between 300°C and 400°C and may be attributed to xylan

mass loss. The second peak appears between 300°C and 400°C and may be attributed to cellulose and some lignin mass loss.

Plastic waste

Figures 9 (a) and (b) illustrate the first-order derivative thermogravimetric (DTG) curves (rate of mass loss vs temperature) and thermogravimetric (TG) curves (mass loss) for the examined combination at four different heating rates ranging from 5 to 200°C min⁻¹. Every peak or shoulder, as demonstrated by Vyazovkin [57, 61, 62], indicates a minimum of one reaction step. According to analysis of the curves of TG, heat degradation occurred between 350 and 510°C in at least two steps, with shifting towards higher temperatures. Depending on heating rate, the initial visible peak of DTG shoulder temperature was measured around 417°C, 428°C, 439°C, and 449°C, and the 2nd DTG shoulder temperature was shown around 445°C, 458°C, 468°C, and 476°C (Figure 8b). Pure PET deteriorated between 375°C and 490°C, according to a TG study [63], whereas PE and

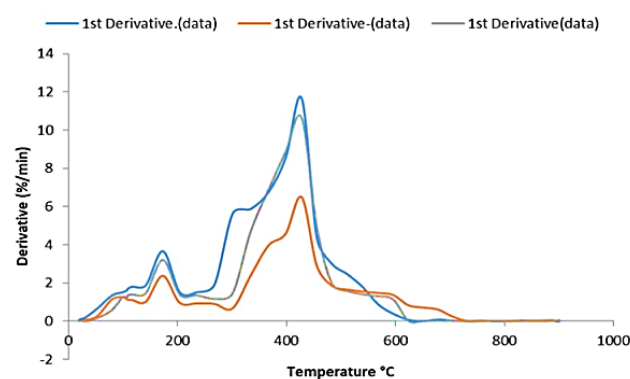


Figure 5. TGA analysis of blend of walnut shells.

[From Masood, M. et al. [1], with permission from Taylor & Francis.]

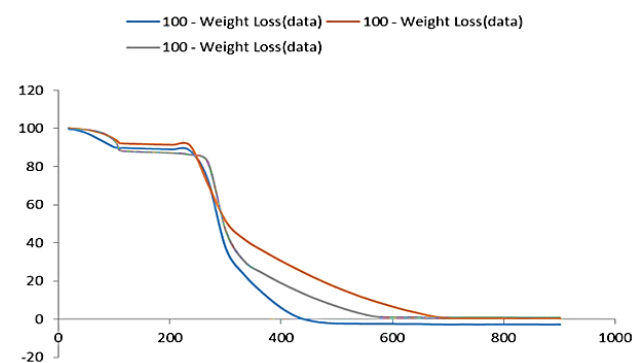


Figure 6. DTG analysis of blend of walnut shell.

[From Masood, M. et al. [1], with permission from Taylor & Francis.]

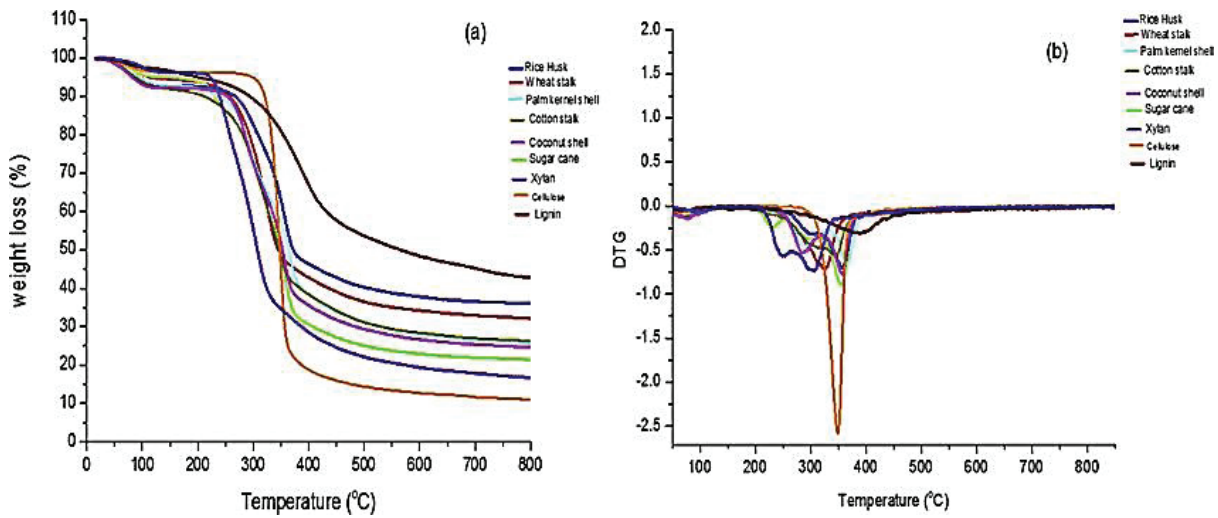


Figure 7. a) TGA b) DTG thermograms of biomass samples and main biomass components.

[From Akubo, K., M.A. Nahil, and P.T. Williams et al. [57], with permission from Elsevier.]

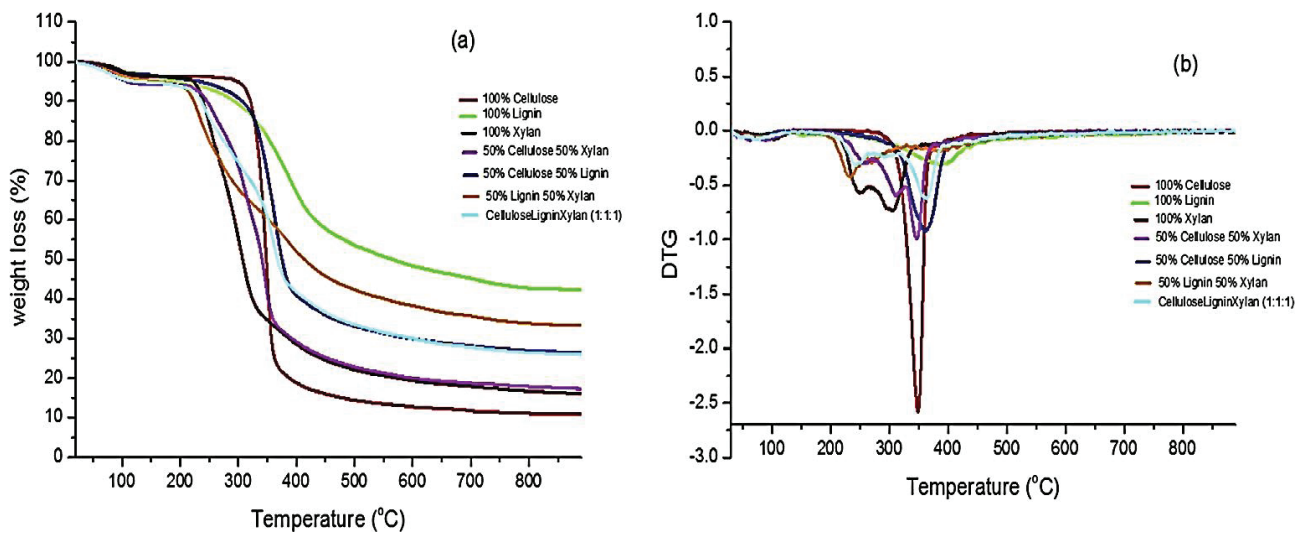


Figure 8. a) TGA b) DTG of main biomass components and their mixtures.

[From Akubo, K., M.A. Nahil, and P.T. Williams et al. [57], with permission from Elsevier.]

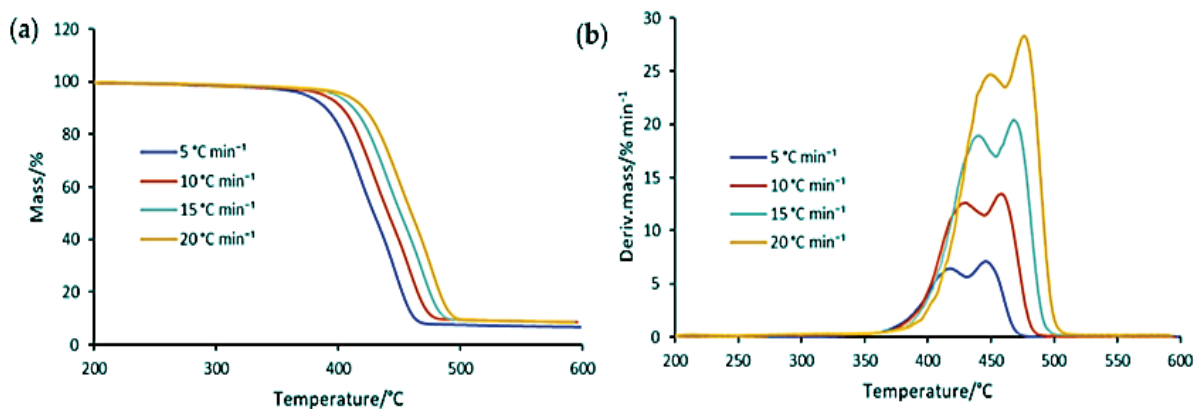


Figure 9. a) TGA b) DTG of PS, PE, PP, and PET

[From Kremer, I. et al. [62], with permission from MDPI.]

PP did so between 440°C and 510°C and 415°C to 510°C, respectively [64]. As a result, the first peak corresponds to PET, whereas the following peaks represent PE and PP. The maximum temperature at which pure PET degrades was determined to be 438°C [63]; for PE is estimated to be 473°C [63], & for PP it is 458°C [64] at 10°C min⁻¹. Possible synergistic affects are noted based on the mixed pyrolysis findings that were obtained. The temperature for degradation was lowered by 10°C and 15°C for PET and PE during procedure of pyrolysis. The temp at whom PP degrades stayed constant. The pyrolysis of the examined combination enhanced heat deterioration of both PE and the PET. Mass loss of combination was more than 90%, which showed that there was a lot of volatile material present. Typically, highly volatile materials increase the formation of liquid oil.

Non-Catalytic Pyrolysis of Biomass, Plastic Waste and Blend

Different feedstock was being pyrolyzed in the first stage; the yield and quality of product were then calculated. Creating condensable and non-condensable fractions from feedstock showed following pattern, as shown in Figure 8 Corn cob (B) (72.6%) versus HDPE (PS) (99.8%). This pattern highlights the entire conversion of the feedstock's accessible volatile matter into liquids and gases, which is reasonable given the amount of unstable matter that is present in this feedstock (Table 7). The products' dehydration processes within the carbohydrate fraction and physically

trapped moisture inside the biomass are both responsible (16–17 wt%) moisture content. Because condensable hydrocarbons were produced during the pyrolysis of HDPE, a high yield of pyrolysis of oil (82 wt%) was obtained. This HDPE pyrolysis oil output is more than that of traditional pyrolysis that was carried out in a glass reactor, according to Brebu, Ucar, and colleagues (2010). In comparison, less bio-oil (26 wt%) was produced during the pyrolysis of corn cobs. This result demonstrates the amount of biochar and non-condensable gases produced, highlighting the refractory nature of the biomass. The degree of change was larger in the case of the maize cob, and the output of bio-oil was consistent with the outcomes of conventional pyrolysis, as described in the literature at the time [65]. High biochar yields are obtained (27–30 wt%) because of the presence of fixed carbon and ash content in the biomass.

As elucidated in Table 8, the physicochemical characteristics of the oils produced by microwave pyrolysis, that includes density, flash point, viscosity, and higher heating value (HHV), were examined. The pyrolysis oils' dynamic viscosity lies between 1.5 and 208cP. Notably, bio-oils made from HDPE-biomass blends showed greater viscosity values, probably because the former had long hydrocarbon chains. It's important to note that these bio-oils have viscosities that are on par with those of styrene, which has a viscosity of 0.762 cP (at 20°C). In contrast, the viscosity of diesel made from petroleum is about 3cP [67].

Table 7. Regarding different biomass to plastic ratios, mass distribution and primary products output are discussed [66].

Without Catalyst					With Catalyst			
Corn cob (w.t%)	100	95	90	80	100	95	90	80
HDPE (w.t%)	0	5	10	20	0	5	10	20
Mass Balance on the basis of sample & water (w.t%)								
Gas	15.5	15.9	16.1	17.9	15.4	19.0	20.3	28.1
Liquid	71.0	72.0	70.6	68.6	74.0	65.0	67.1	61.6
Char	6.3	6.1	5.5	5.4	5.9	6.3	5.6	5.5
Mass Balance (w.t%)	92.8	94.1	92.2	91.9	95.2	90.3	93.0	95.7
Mass Balance on the basis of sample (w.t%)								
Gas	51.6	51.5	55.1	56.9	53.6	59.5	69.8	85.0
Char	20.9	19.9	18.0	17.3	20.6	19.8	19.3	16.9

Table 8. Oil's physical and chemical properties as a consequence of research with pyrolysis and co-pyrolysis without a catalyst [68]

Feed	Viscosity (Cp)	Density (gcm ⁻³)	HHV (MJkg ⁻¹)	Flash Point (°C)
HDPE	1.5+0.2	1.109+0.045	39.1+0.4	101.0+1.0
Corn cob	25.6+1.0	0.853+0.04	29.1+0.6	110.8+1.0
HDPE: corn cob	1.1+0.1	0.951+0.04	38.1+0.5	105.1+1.0

Recommendation

There has been a noticeable change in favor of alternative fuels consequently of the anticipated depletion of fossil fuels within the next 50 years and the related environmental concerns. In contrast to these options, biodiesel stands out as a potentially effective way to address global transportation demands, particularly for diesel engines. Its increased popularity is mostly due to its positive effects on the environment, notably in lowering carbon emissions. Being a renewable, non-toxic, and biodegradable resource, biodiesel has appeal for boosting energy security. It is noteworthy that biodiesel emits less greenhouse gas than conventional diesel fuel, including less CO₂, SO₂, CO, HC, and PM. The use of biodiesel is projected to grow thanks to its growing popularity. The creation of a sustainable biodiesel industry is the overarching objective, while increasing demand for and accessibility of locally produced biodiesel are the immediate aims [69]. However, producing biodiesel is fraught with difficulties and problems, including fierce worldwide rivalry, incompatibilities between the production of food and fuel, and problems with the availability of feedstock. Among these, the price of producing biodiesel stands out as a major barrier to large-scale manufacturing [70]. Type of feedstock, production processes, additives, and operational costs are all variables that affect biodiesel pricing. Notably, processing expenses, especially those associated with the transesterification procedure, have a considerable influence on the cost of biodiesel production overall.

CONCLUSION

The conclusion of this study highlighted the fact that, under the right carbonization conditions, the pyrolysis, microwave, and hydrothermal carbonization processes were very effective at turning waste mixtures into chars that are suitable for a variety of uses, including the production of fuel. It was discovered that hydro-char demonstrated a higher degree of complexity in contrast to pyro-char and micro-char by the thorough examination of chars produced from waste mixes employing hydrothermal carbonization, pyrolysis, and microwave across various reaction conditions [39][70]. Pyrolysis generated the chars with the largest oxygen loss (54.2%) and calorific value (5864 kcal/kg). These results matched the relevant H/C and O/C ratios. Pyrolysis has shown its capacity to create char with a thermal value similar to coal. However, pyrolysis bio-oil has a number of drawbacks, including a high oxygen concentration, acidity, a low calorific value, and insufficient stability. The zeolite catalysts demonstrated impressive abilities for aromatization and alkylation in the context of catalytic cracking pyrolysis (CCP). The quality of pyrolysis byproducts was raised as a result of these catalysts' improved product, Aromatics and other goods' selectivity. Microwave-assisted pyrolysis (MAP) is a more efficient and reliable method of converting biomass because it outperforms conventional heating

techniques in terms of energy efficiency, heating rate, and selectivity. It has been shown that the process of microwave-assisted catalytic pyrolysis results in a higher yield of bio-oil as well as a higher concentration of aromatic chemicals in the final product. For pyrolysis operations to yield the optimum results, selecting the appropriate pretreatment is essential. Syngas, high value carbon products, and biofuel's output and quality could all be considerably enhanced by integrating microwave adsorbents, catalysts, and suitable pyrolysis conditions. Despite significant breakthroughs, more work has to be done to use microwave assisted pyrolysis technology in expansive industrial environments. The evolution of production of micro-wave adsorbents that have high efficiency, with advancement of fundamental microwave pyrolysis process theories, and lowering of production cost should be the main goals of future work.

Outcomes

The following are potential results of current developments and difficulties in the recycling of waste plastic by microwave-assisted catalytic co-pyrolysis of biomass and waste plastic to produce compounds with added value:

- By improving catalyst designs and reaction conditions, it may be possible to boost production efficiency and, as a result, the yields of valuable compounds from waste plastic and biomass.
- A wide range of value-added chemicals, such as aromatics, olefins, hydrocarbons, and other specialty chemicals, can be produced through the use of sophisticated analytical techniques and process
- By lowering reliance on fossil fuels and minimizing plastic pollution, the integration of waste plastic recycling technologies and renewable biomass feedstocks can improve the pyrolysis process' sustainability and environmental benefits.

If microwave-assisted catalytic co-pyrolysis technologies are successfully scaled up and shown to be economically feasible, they may be commercialized and widely adopted in the chemical and waste management sectors

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

STATEMENT ON THE USE OF ARTIFICIAL INTELLIGENCE

Artificial intelligence was not used in the preparation of the article.

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