

Research Article

Production and Optimization of Energy Rich Biofuel through Co-Pyrolysis by Utilizing Mixed Agricultural Residues and Mixed Waste Plastics

Chirag Vibhakar,¹ R. S. Sabeenian,² S. Kaliappan ,³ Pandurang Y. Patil,⁴ Pravin P. Patil,⁵ P. Madhu ,⁶ C. Sowmya Dhanalakshmi ,⁷ and Habtewolde Ababu Birhanu ⁸

¹Electrical Engineering Department, Gujarat Power Engineering & Research Institute, Mehsana, Gujarat 382710, India

²Department of Electronics and Communication Engineering, Sona College of Technology, Salem, Tamil Nadu 636005, India

³Department of Mechanical Engineering, Velammal Institute of Technology, Chennai, Tamil Nadu 601204, India

⁴Department of Environmental Science, Ratnagiri Sub-Campus, University of Mumbai, Ratnagiri, Maharashtra 415639, India

⁵Department of Mechanical Engineering, Graphic Era Deemed to be University, Bell Road, Clement Town Dehradun, Uttarakhand 248002, India

⁶Department of Mechanical Engineering, Karpagam College of Engineering, Coimbatore, Tamil Nadu 641032, India

⁷Department of Mechanical Engineering, SNS College of Technology, Coimbatore, Tamil Nadu 641035, India

⁸Faculty of Mechanical Engineering, Arba Minch Institute of Technology, Arba Minch University, P.O. Box 21, Arba Minch, Ethiopia

Correspondence should be addressed to Habtewolde Ababu Birhanu; habtewold.ababu@amu.edu.et

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Two totally waste products, agricultural residues and mixed plastic wastes collected from domestic and industrial sectors, are used in this study for the recovery of energy rich biofuel and value-added chemicals. The copyrolysis experiments using fixed bed reactor are conducted in order to analyse the synergetic effects. The experimental works are carried out with different proportion of mixed plastics blended with agricultural residues. The reaction temperature and biomass-to-waste plastics ratio on product distributions are studied and addressed. The thermogravimetric analysis conducted at different temperatures clearly distinguished the pyrolysis behaviours of biomass and plastics. The positive synergistic effects defined as higher yield of volatiles compared to predicted yield for bio-oil were identified at particular mixing ratio. Both biomass wastes and plastic wastes show optimal performance of 60.42 wt% oil yield at 60% addition of waste plastics. The oil products obtained under favourable conditions have a higher heating value compared to the oil obtained from biomass pyrolysis. The GC-MS study confirmed that the interaction between biomass and plastics during copyrolysis resulted in decreased oxygenated contents in the oil products.

1. Introduction

The development of renewable energy by utilizing waste materials is a promising solution to fossil fuel depletion and global warming issues. It is predicted that coal stocks would be depleted by 2112 and crude oil reserves will be depleted by 2042; at the same time, the energy needed around the world is expected to increase by 56% by 2040 [1]. Utilization of

waste biomass for various purposes has been focused on by many researchers in the past three decades.

The use of agricultural biomass for fuel production is renewable and sustainable. Many literatures reported the use of various agricultural wastes for energy recovery. Lignin, cellulose, hemicelluloses, and a considerable amount of extractives are the primary components of biomass materials [2]. The wastes from agricultural fields are generally burnt in

the open air in the field itself due to their lower bulk density and low value. They are not seasonable and are abundant throughout the world. The agricultural residues generally refer to the remains of plants including pods, stems, and corn. Forest wastes, wood chips, and municipal solid waste are also the examples of biomass energy sources today [3]. The production of liquid fuels from agricultural wastes is recognized as an important renewable resource. The organic liquid from agricultural residues has better fuel properties with considerable heating value. Previously many authors have presented the use of agricultural residues for fuel production through thermochemical conversion processes including pyrolysis. The production of liquid products through pyrolysis is called pyrolysis oil. The properties and quantity of oil produced during pyrolysis depend on the feedstock composition.

With the introduction of plastics, their use extended to every corner of the world. Plastics are currently critical for sustaining a resource-efficient economy [4]. Because of their advantageous properties including lightweight and durability, the plastics are widely used around the world. However, these positive characteristics accelerated the accumulation of plastics in the environment with huge volume [5]. By 2015, around 6300 Mt of waste plastics was produced throughout the world and more than 80% was dumped in the natural environment. Plastic waste management is one of the critical challenges throughout the world due to lack of technology development. India's current waste biomass availability is estimated to reach more than 500 million metric tonnes per year. Biomass presently accounts for 32% of total primary energy consumption in the country. India produces a massive amount of waste plastics every year. However, only one-fourth of this is recycled due to lack of a functioning solid waste management system. In 2019-20, India generated an annual plastic waste of 3.46 Mt of plastic garbage, compared to 3.360 Mt in 2018-19 and 2.383 Mt in 2017-18. In terms of environmental concerns, land filling technique is not suitable and costly, as the by-products are extremely hazardous to both the environment and human health [6]. However, very poor degradability of plastics, on the other hand, generates substantial environmental issues and poses a significant challenge. In 2018, worldwide plastics output surpassed 359 Mt, with major contribution from China and European countries [7]. However, India produces 5.58 Mt of single-use plastics annually followed by Japan with 4.7 Mt. In India, only 60% of the plastic wastes are being recycled and the remaining 40% end with landfill. Improper plastic waste disposal can create structural deterioration. The chlorinated plastic can leach hazardous chemicals into the soil, which can seep into groundwater and harm both the environment and the ecosystem. Aside from landfilling, incineration is the possible alternate method to decompose plastic wastes. It is a commonly utilized and approved technique, since it can permanently degrade plastic waste with huge volumetric basis and thermal energy recovery, which may then be converted to electrical energy [8]. It also helps to regulate carbon emissions in the conventional energy industry by substituting alternative fuels [9]. Incineration of plastic wastes resulted in the release of very

dangerous toxic pollutants and dusts which are more harmful to all living organisms [10]. Aside from landfilling and incineration, utilization of these wastes for converting fuels is more popular in order to avoid resource wastage and contamination. When compared to traditional digestion, decomposition of plastic wastes thermally with controlled oxidation gives more benefits including lower emission and higher energy recovery [11]. Thermochemical conversion processes such as pyrolysis and gasification can offer effective recovery of medium-to-high grade fuels.

The intersection of environment protection, resource management, and energy recovery could be a viable research option to gain more popularity among the researchers. In recent years, combination of agricultural and plastic wastes for bio-oil production has gained much interest due to contribution of plastics towards increased heating value. Copyrolysis of biomass and plastics has grown in popularity as a viable alternative method for improving the quality of pyrolysis products. In comparison to traditional biomass and plastic pyrolysis, copyrolysis experiment has been gaining a lot of interest in the recent years. The synergistic impact of chemical interactions between diverse feedstocks plays a key part in copyrolysis process. However, the synergistic effect varies greatly depending on the nature of the raw materials. Because of their unique heating characteristics, microwave pyrolysis and solar pyrolysis have received a lot of attention in the recent years. Furthermore, the kinetics of biomass copyrolysis with plastics have recently been studied in order to gain a better understanding of the mechanism of the synergistic impact. Copyrolysis is the improved technique to produce high energy liquid products by interacting biomass and plastics. According to Johannes et al. [12], the interaction of feed materials and their product distributions are dependent on various parameters including mixing ratio, pyrolysis length, process temperature, and heating rate. Yang et al. [13] analysed the copyrolysis experiment on cedar wood and LDPE and observed a synergistic effect on oil production. The copyrolysis experiments on biomass and plastic waste have been studied extensively by many authors to analyse the process parameters on product yield and quality [4,14,15]. Oyedun et al. [16] and Hassan et al. [17] demonstrated that the type of biomass and amount of plastic during copyrolysis determine the quality of the yield products. Dewangan et al. conducted copyrolysis experiments on sugarcane bagasse combined with LDPE at the blend ratio of 1 : 1 and produced maximum oil fractions with calorific value of 40 MJ/kg. In another experiment carried out by Xue et al., the yield of oil was dependent on the reaction temperature [18]. According to Costa et al. [19], the copyrolysis of rice husk with polyethylene at a temperature range of 350–430°C enhanced the conversions of both biomass and polyethylene towards oil yield. Martinez et al. [20] investigated the effects of slow pyrolysis of biomass and polymers and discovered that the viscosity and acidity of the pyrolysis oil reduced; however, the energy content of the oil increased when compared to pyrolysis oil derived only from biomass. It has also been stated that when biomass and plastics are copyrolyzed, the production of oil is significantly larger than the total amount

of individual oil products obtained from biomass and plastics [21]. The study conducted by many researchers concluded that the copyrolysis of biomass and plastics has a stronger synergistic effect compared to individual pyrolysis [22–24].

This research is based on the pyrolysis of mixed agricultural residues combined with mixed waste plastics collected from domestic and industrial sectors, which is inspired by waste-to-energy concepts. Prior to the copyrolysis process, each of the components is pyrolyzed separately and their product distributions are found. After that, they are copyrolyzed by blending waste plastics with biomass materials at the ratios of 20%, 40%, 60%, and 80% by weight. The goal of this research is to increase the oil production while simultaneously improving the quality. The physical and chemical properties of oil produced under suitable conditions have been examined in order to find its feasibility as a source of energy and a chemical feedstock for a variety of applications.

2. Materials and Methods

2.1. Feedstock Preparation. The agricultural residues utilized for this study are a mixture of wheat straw, sugarcane bagasse, rice straw, corn stover, coconut shell, tobacco leaf, and sunflower shell collected from local field. The plastic materials utilized for this study are the collection of used food containers, beverage bottles, toys, door handles, pipes, and resilient bags made by low-density polyethylene, high-density polyethylene, polyvinyl chloride, polypropylene, and polystyrene. A ball mill is used to cut these feed materials and they are subsequently sieved to keep the size less than 1 mm. The feedstock materials are then subjected to analyses and the values are given in Table 1. Before conducting analysis, they are completely dried in an oven maintained at $\pm 100^\circ\text{C}$ for approximately 2 hours.

2.2. Pyrolysis Reactor Setup. The experiments are conducted in a lab scale fixed bed reactor. Conducting copyrolysis process in a fixed bed reactor is much better compared to

TABLE 1: Properties of feedstock materials in wt%.

Content	Biomass	Mixed plastics
Proximate analysis		
Volatile matter	73.4	90.9
Fixed carbon	15.0	0.4
Moisture content	6.4	0.5
Ash content	5.2	8.2
Ultimate analysis (ash-free basis)		
Carbon	47.1	80.1
Hydrogen	6.2	15.4
Nitrogen	2.1	2.6
Sulphur	0.8	0.4
Oxygen	43.8	1.5

% of O = $100 - (C + H + N + S)\%$.

many available types of pyrolysis reactors [25]. The literature [26] contains a schematic diagram of the reactor system as well as its design specifications and further it is explained in this section. The reactor is comprised of a reactor bed with inner diameter of 100 mm and height of 150 mm. The reactor is heated using electrical resistance heater with ammeter and voltmeter set up. The temperature given to the reactor is controlled by the autotransformer. The temperature of the reactor is kept stable once it reaches the desired value by auto cut-off unit. The reactor is well insulated by insulating material to avoid unnecessary heat loss. It also consists of a condenser, oil collection system, and gas collection system. The condenser was cooled by circulating ice water maintained at a temperature of 5°C . The reaction was continued till no vapour was identified from the condenser. For this purpose, a minimum of 30 min is given to one complete reaction. The condenser's liquid products were collected in conical flasks attached to the condenser. The char at the end of the experimental runs is collected directly from the reactor. The oil fractions are collected through the condenser. After weighing char and oil fractions, the masses of the uncondensable gases are found by material balance method. The formula used to find the desired products from thermal pyrolysis of individual feedstocks is as follows:

$$\text{product yield (wt.\%)} = \frac{\text{desired product (oil or char or gas) in grams}}{\text{amount of feedstock in grams}} \times 100. \quad (1)$$

To find the synergetic effect, the experimental yields during copyrolysis process are compared with predicted yields. The formula used by Zhao et al. [27] is employed to find the predicted yield. The yields obtained from individual pyrolysis of mixed agricultural wastes and mixed plastic wastes are used to find the predicted yields shown in the following equation:

$$\text{predicted yield} = (x_1 * Y_1 + x_2 * Y_2), \quad (2)$$

where Y_1 and Y_2 are the yields of individual pyrolysis of agricultural residues and waste plastics, respectively. X_1 and X_2 are the mass ratios in the blended samples, respectively.

2.3. Analytical Instruments. The mass loss of the feedstock materials depends on the process temperature and heating rate and is investigated using a thermogravimetric analyser (TGA). The thermogravimetric analysis is performed with 10 mg of the sample heated at $10^\circ\text{C}/\text{min}$ to explore and compare the degradation process of agricultural residues and waste plastics. Proximate analyses of the materials are done to find the volatile and semivolatile contents of the sample. Elementor Vario EL-III is employed to find the amounts of carbon, hydrogen, nitrogen, and sulphur in the feedstock samples. The oil content obtained at favourable condition is tested for its physical and chemical analysis. The

pH value of the oil is determined using a digital pH metre. The viscosity of the sample is determined using a viscometer (Brookfield Engineering Company). A Pensky-Martens closed-cup device is used to find the flash point of the sample. An electronic calorimetric thermometer (Parr-6772) is employed to determine the heating value of the oil. A GC-MS (Thermo MS DSQ II) is employed to assess the distribution of chemical compounds of the oil products. The equipment consists of a capillary column of 0.25 mm diameter, 30 m length, and 0.25 μm film thickness. For this analysis, the sample of 1 mL was injected at the temperature of 250°C. The oven temperature was set initially to 70°C for 3 minutes before being increased to 250°C at a rate of 10°C/min. The sample injection was done in split mode with the ratio of 20:1. With full scan mass spectra, the mass spectrometer was tuned to an ionising voltage of 70 eV. It was run at an interface temperature of 200°C. The analysis is carried out in the range of 50–650 m/z and the chemical components are identified by the use of mass spectrum libraries (NIST14.L).

2.4. Error Analysis. Before conducting the experiment, the Measurement System Analysis (MSA) was utilized to correct the uncertainty in the temperature measurement and electronic weighing machine. Thermocouple is used to measure the temperature of the reactor and weighing machine is used to measure the mass of the pyrolysis product yields. To ensure the repeatability, Test-Retest study was conducted under the same operating conditions. Prior to that, the thermocouple used in the reactor was calibrated in accordance with laboratory standards. The errors for thermocouple and electronic weighing machine were determined as 0.25% and 0.03%, respectively.

3. Results and Discussion

3.1. Thermogravimetric Analysis. Figures 1 and 2 depict TG and DTG curve for agricultural residues and mixed plastic wastes at various temperatures heated at 10°C/min. An increase in temperature for both materials increased the degradation rate. The tests are carried out in an inert atmospheric condition (Argon) and achieved to access the pyrolytic behaviour of the feedstock materials. According to thermogravimetric analysis of agricultural residues, the devolatilization process begins at 160°C and maximum weight loss appears between 350 and 475°C. Around 475 and 550°C, an abrupt change in the slope is recorded, resulting in lower weight loss. The major weight loss of around 70% in the biomass material happens between 250°C and 550°C. During this period, the volatile matters released from the material are maximum. The thermal overlapped degradation of the agricultural residues with major cellulose and hemicelluloses content is the primary cause of the highest mass loss at this temperature range [28]. According to TGA curve, the mixed plastics start to decompose at 330°C. This is due to the long chain polymeric structure of the plastic materials. The decomposition of plastic wastes is characterized at single stage, whereas for biomass materials it was achieved by three different stages [29]. The difference in decomposition stages for

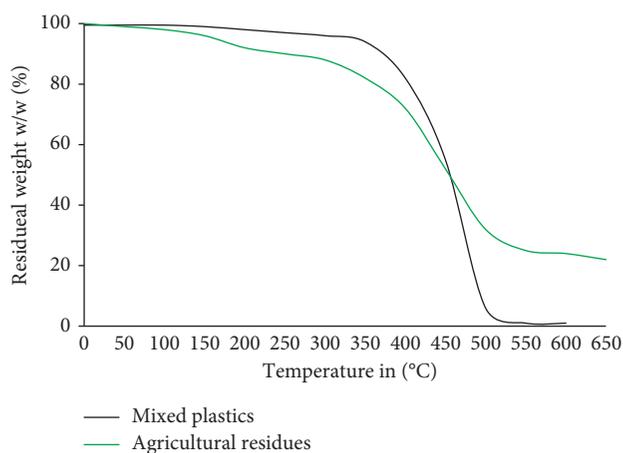


FIGURE 1: TG analysis for agricultural residues and mixed plastic waste.

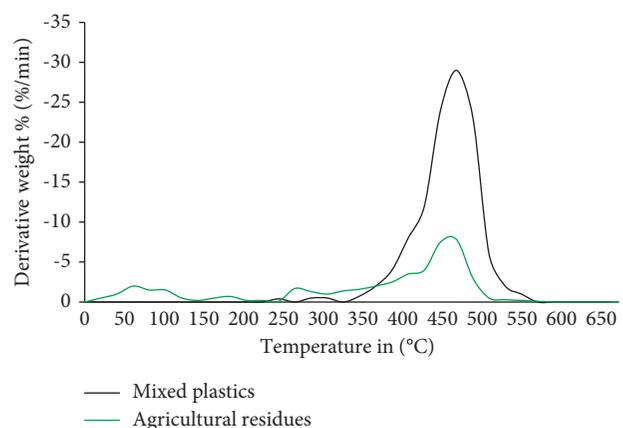


FIGURE 2: DTG agricultural residues for biomass and mixed plastics.

biomass materials is explained by their structures, since they are made up of cellulose and hemicellulose. From TGA curve, it is found that the degradation of mixed plastics took place in a single phase at higher temperature with limited temperature range. The mixed plastic loses its 97% of mass at temperatures ranging from 375 to 500°C and after that no decomposition was recorded. It can be seen from the data that both curves are overlapped at temperatures around 450°C based on maximum volatile loss, which shows these two feedstocks can be used as cofeed for this process. Compared to mixed plastics, for agricultural residues, some residues were found due to the presence of ash content [17]. The presence of ash content in feedstock is a crucial parameter for the yield of oil products. The ash in the feedstock will affect the quality of the entire pyrolysis products [30]. The amount of ash in the biomass sample has a direct impact on the production and composition of the pyrolysis products. During pyrolysis, ash particles generally extinguish the vapour conversion. In general, biomass with lower ash content is preferable for pyrolysis reactions. On the basis of the data, it can be clear that the appropriate reaction temperatures for both materials are around 450°C to 500°C.

3.2. Pyrolysis of Mixed Agricultural Residues. Based on the TGA and DTG curve of the mixed agricultural biomass, the pyrolysis experiments are performed between the temperature limits of 300°C and 550°C to find the effect on product distributions. Figure 3 illustrates the yield of oil, char, and gas fractions related to reactor temperature. By applying temperature, the primary activation processes are initiated followed by subsequent vapour phase cracking reactions. According to this study, the product distribution from pyrolysis of mixed agricultural residues is temperature-dependent; however, pretreatments raised the initial degradation process and resulted in higher yields of condensable products. As the pyrolysis temperature was changed from 350 to 450°C, it became obvious that the yield of oil products reached its maximum value at 450°C. However, by increasing the temperature to 550°C, the yield of oil was decreased to 36.5 wt%. The yield of oil fractions reached its maximum at 450°C with a value of 39.8 wt% and it reduced with increasing the temperature. The reduced heat and mass transfer limitations at 450°C resulted in higher yields of oil products. It has been found that higher pyrolysis temperatures accompanied with more secondary reactions lead to more gaseous products with reduced oil products [31]. As shown in Figure 1, the char yield reduced from 41.2 wt% to 23.7 wt% as the final pyrolysis temperature increased from 350 to 550°C. The decrement in char production was observed due to enhanced primary decomposition of biomass or the secondary decomposition of the char residue at higher temperatures [32]. The secondary reactions of the char products at higher temperatures may also result in the yield of gas fractions, which is proportional to the increased pyrolysis temperature. For the temperature of 350°C, the gas yield was observed as 27.2 wt% and maximum of 39.8 wt% at 600°C. The changes in the physical properties of the pyrolysis products are mainly affected by the secondary reactions of tar vapours and the conversion time.

3.3. Pyrolysis of Mixed Plastic Wastes. Figure 4 shows the pyrolysis behaviour of mixed plastics with respect to reactor temperature. The yield of char is nearly low for all temperatures. At the same time, the oil and gas yields are highly influenced by temperature. The pyrolysis of mixed plastics can be constructed by a narrow range of reactions due to simple monomeric structure. It has been proposed that almost all synthetic polymers disintegrate by a radical mechanism. The yield of char is varied from 18.9 wt% to 3.5 wt% when the temperature is raised from 350°C to 550°C. The lower degradation of plastic products at lower temperature yields higher char products. The yield of gas fraction is steadily increased with respect to increased temperature due to variation in stability of the polymer materials under different temperatures. For 350°C, the yield of gas is 19.9 wt% and the value is changed to 28.4 wt% for the final temperature of 550°C. Many other authors have also found similar findings [33,34]. According to the results, no volatiles were released from the reactor till it reached 300°C. These results were also predicted with TGA analysis. Beyond 300°C, the plastic waste generates condensable volatile contents. The oil products are

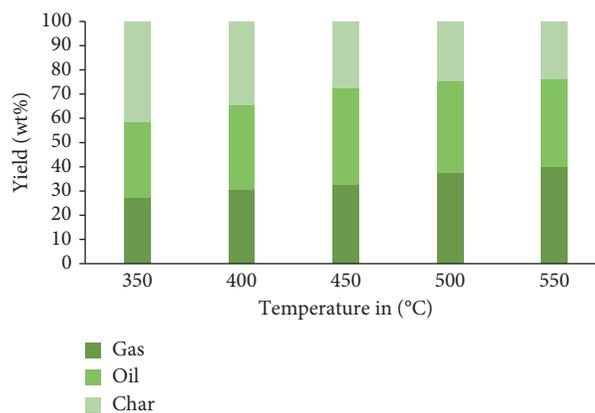


FIGURE 3: Pyrolysis of mixed agricultural residues performed at 1.0 mm particle size, at 20°C/min heating rate, and at different temperature.

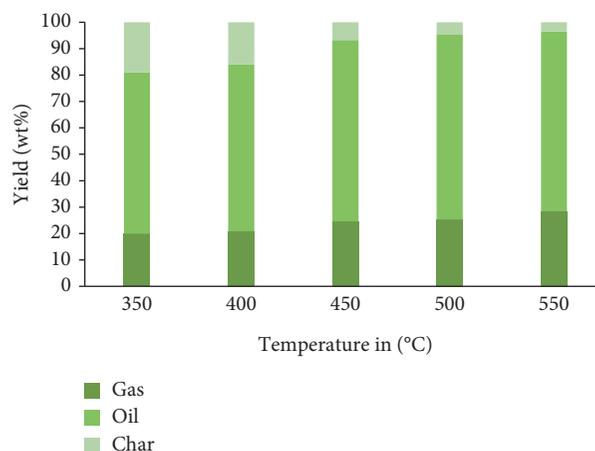


FIGURE 4: Pyrolysis of mixed plastic wastes performed at 1.0 mm particle size, at 20°C/min heating rate, and at different temperature.

gradually increased from 61.2 wt% to 68.1 wt% when the temperature is changed from 350°C to 550°C. The yield of oil attained maximum at 500°C with 70.2 wt%. The stability of hydrocarbons decreases as the temperature increases. So, at optimum temperature of 500°C, the C=C bonds are broken significantly, resulting in higher volatile product yields. Further increment up to 550°C decreased the oil production to 68.1 wt%. Generally the plastics had lower stability at higher temperature. The higher temperature breaks C=C bonds of the plastic wastes and releases more volatiles [35].

3.4. Copyrolysis Behaviour. The oil, char, and gas distributions during the copyrolysis under different blend ratio are shown in Figure 5. There was no major difference observed between theoretical and experimental yields up to 40% blend of mixed plastics with agricultural residues. In order to get complete valorization, the holding time was kept constant for all experiments. In comparison to thermal pyrolysis of agricultural residues, the oil products obtained from copyrolysis were substantially higher. For instance, the oil obtained at 60% blend shows maximum compared to the

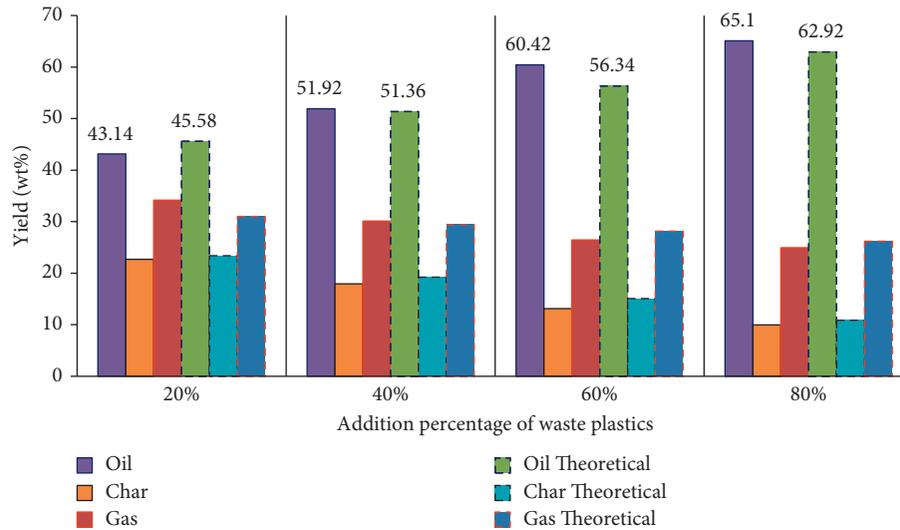


FIGURE 5: Assessment of synergistic effect.

TABLE 2: Physical properties of oil products obtained under different conditions.

Properties	Standard	Source			
		Biomass oil	Mixed plastic oil	Copyrolysis oil	Diesel [40]
Density in kg/m ³	ASTM D445	1025	930	1010	850
Viscosity in cSt	ASTM D4052	7.9	2.4	6.1	3.9
Flash point in °C	ASTM D92	140	95	105	57
Carbon in wt%	ASTM D5373	48.44	86.26	74.74	86.5
Hydrogen in wt%	ASTM D5373	9.0	10.94	9.6	13.2
Nitrogen in wt%	ASTM D5373	0.86	0.78	0.31	0.02
Sulphur in wt%	ASTM D5373	0.18	0.12	0.07	0.24
Oxygen in wt%	By difference	41.52	1.9	15.28	—
Heating value in MJ/kg	ASTM D445	20.9	43.12	35.3	43.6

% of O = 100-(C+H+N+S)%.

predicted value. The yield of oil is increased from 43.14 wt% to 65.1 wt% when the amount of plastics during reaction increases from 20% to 80%. In contrast, the char and gas yields are reduced from 22.7 wt% to 9.96 wt% and from 34.16 wt% to 24.94 wt%, respectively. At 60% addition of plastics, the result shows higher synergistic effect on oil production. At that condition, the predicted yield was only 56.34 wt% but experimentally the yield was recorded as 60.42 wt%. The result shows 7.24% increment compared to prediction. The radical secondary reactions are the main reason for the synergetic effect in this condition [36]. Furthermore, the presence of plastics on the reaction serves as a hydrogenation medium for lignocellulosic material, potentially reducing the polymerization and cross-linking activities ensuing major weight loss [37]. At 80% blend also the synergistic effects are identified for oil yield, but the increment was only 3.46%. As previously mentioned in the literature, during copyrolysis process, the plastics can act as a good hydrogen donor and will result in increased oil products. The higher hydrogen molecules present in the plastic materials will facilitate the conversion of oxygenated compounds into hydrocarbon molecules [38]. According to Onal et al., the radical interaction created by copyrolysis process favours the formation of higher oil products with no phase separation [39].

3.5. Characterization of Oil Products

3.5.1. Physical Analysis. Table 2 shows some of the basic physical characteristics of the oil fractions obtained under optimized conditions from pyrolysis and copyrolysis process. All of the analysis was measured by following ASTM protocol. The heating values of the oils are mostly determined by their hydrocarbon and oxygen content. The oxygen contents in the biomass oil, plastic oil, and copyrolysis oil are 41.52%, 1.9%, and 15.28%, respectively. The large number and concentration levels of oxygen compounds reduce the energy density to less than half those of ordinary fossil-derived fuel. The significant amount of the oxygenated species will cause instability during storage and transportation. The large decline in oxygen percent may explain the increase in heating value of the copyrolysis oil. Due to natural phase separation and radical interaction, the oxygen content of copyrolysis oil is significantly lower than that of other oils. The result shows that the copyrolysis process is an efficient approach for producing oil with higher heating value.

3.5.2. GC-MS Analysis. Gas chromatography-mass spectroscopy is a commonly used technology for the identification and quantification of compounds generated

TABLE 3: GC-MS analysis of the total pyrolysis oil.

Compound name	Molecular formula	Source		
		Biomass oil	Mixed plastic oil	Copyrolysis oil
3-Furaldehyde	C ₅ H ₄ O ₂	0.41	—	0.24
Pyrogallol 1,3-dimethyl ether	C ₈ H ₁₀ O ₃	2.04	—	—
3-Methyl-1-phenyl-1H-inden	C ₁₆ H ₁₄	1.21	0.44	1.04
2,4-Dimethyl-1-heptene	C ₉ H ₁₈	—	4.01	3.48
Phenol, 4-methyl-	C ₇ H ₈ O	0.52	—	—
9-Octadecenoic acid (z)-	C ₁₈ H ₃₄ O ₂	2.33	—	—
1,3-Pentadiene, 2,4-dimethyl	C ₇ H ₁₂	—	9.42	3.46
1-Hydroxy-2-methoxy-4-methylbenzene	C ₈ H ₁₀ O ₂	3.34	—	—
Phenol	C ₆ H ₅ OH	8.41	—	6.03
Azulene	C ₉ H ₈	—	10.42	7.44
Phenol, 2-methoxy-	C ₇ H ₈ O ₂	7.34	—	2.42
Naphthalene, 2-methyl-	C ₁₁ H ₁₀	—	1.42	—
1,2-Diphenylcyclopropane	C ₁₅ H ₁₄	5.12	2.41	4.55
Phenol, 2,6-dimethyl-	C ₈ H ₁₀ O	4.32	—	1.04
2-Furancarboxaldehyde,-5-Methyl	C ₆ H ₆ O ₂	1.10	—	—
Benzaldehyde, 4-hydroxy-3-methoxy	C ₈ H ₈ O ₃	0.68	0.12	—
Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	0.32	—	0.98
Dibenzo[a,e]cyclooctene	C ₁₆ H ₁₂	3.54	4.26	—
3-Methyl-1-phenyl-1H-indene	C ₁₆ H ₁₄	—	2.68	1.04
Pyrene, 1-methyl-	C ₁₇ H ₁₂	1.21	0.22	0.94
1,4-Dimethoxybenzene	C ₈ H ₁₀ O ₂	3.27	—	—
Stearic acid, methyl ester	C ₁₉ H ₃₈ O ₂	5.26	3.42	3.46
2-Isopropyl-2,5-dihydrofuran	C ₇ H ₁₂ O	3.46	—	0.55
Octadecanenitrile	C ₁₈ H ₃₅ N	6.44	—	0.94
1,2-benzendiol	C ₆ H ₆ O ₂	5.05	—	—
Trimethylamine	C ₃ H ₉ N	4.21	0.85	3.45
1-Ethynyl-1,2,3,4-tetrahydro-a'-carboline	C ₁₃ H ₁₂ N ₂	—	3.01	2.88
5-Hydroxymethylfurfural	C ₆ H ₆ O ₃	0.24	—	—
Acetol	C ₃ H ₆ O ₂	5.48	—	1.46
Acetic acid	C ₂ H ₄ O ₂	16.42	—	6.79
3-Undecene, (Z)-	C ₁₁ H ₂₂	—	3.49	—
Tetradecane	C ₁₄ H ₃₀	—	4.47	—
Furfural	C ₅ H ₄ O ₂	1.72	—	—
Butyrolachone	C ₄ H ₈ O ₄	3.77	0.49	2.07
2,5-Pyrrolidinedione, 1-methyl	C ₅ H ₇ NO ₂	0.44	—	—
2-Methoxy tetrahydro furane	C ₅ H ₁₀ O ₂	0.97	0.10	0.12
4-Ethyl-2-methoxy phenol	C ₉ H ₁₂ O ₂	1.92	—	—
Ethisterone	C ₂₁ H ₂₈ O ₂	—	6.42	1.46

during pyrolysis. The analysis was performed on the oil fractions acquired under optimized conditions. The NIST library and the compound probability percentage are used to trace the GC-MS compounds in the oil samples. The identified chemical components in the raw biomass pyrolysis are mostly the oxygenated contents and the plastic oil has majority of aliphatic hydrocarbons. Table 3 shows the presence of various chemical components in the pyrolysis and copyrolysis oil. The decreased oxygenated components in mixed plastic oil enhance the stability of the oil. The acid contents present in the biomass pyrolysis oil resulted from the decomposition of hemicellulose in the biomass materials. On the other side, decomposition of lignin is the primary reason for the presence of phenolic compounds in the biomass derived oil. The components of the oil contain the mixture of alkane, alkene, and alkyl group compounds with oxygenated elements.

4. Conclusion

This study found that pyrolysis of mixed agricultural residues combined with mixed plastic wastes has the potential options for the production of high-grade pyrolysis oil with a higher oil yield of 60.42 wt% at 60% blend of waste plastics. The yield of pyrolysis oil was greatly affected by the reactor temperature. It is the most significant parameter to valorize the feedstock. The physical characteristics of the oil acquired under copyrolysis process have higher heating value with reduced oxygen content. The synergistic impacts of copyrolysis process were investigated in terms of the pyrolysis process and its product yield. In comparison to theoretical data, synergistic effects occurred at 60% plastic blend showing 7.24% higher oil yield than other blend proportions. Rather than creating cross reaction products, these synergistic effects were discovered by identifying the composition of chemicals in copyrolysis oil. The copyrolysis oil obtained

from mixed agricultural residues and mixed plastics was identified as a biofuel candidate with heating value of 35.3 MJ/kg, which is higher compared to biomass pyrolysis oil. The higher heating value represents that it can be used directly as furnace oil for boiler and can be upgraded to be used as a fuel for IC engines. The report received by GC-MS confirmed the relations between biomass and plastics throughout the copyrolysis process resulting in decreased oxygenated products. Further study is possible to analyse the reaction kinetics and applications to get benefits in waste treatment and utilization.

Nomenclature

ASTM:	American Society for Testing and Materials
DTG:	Derivative thermogravimetry
GC-MS:	Gas chromatography-mass spectrometry
LDPE:	Low-density polyethylene
TGA:	Thermogravimetric analysis
X_1 :	Mass ratio of agricultural residues
X_2 :	Mass ratio of waste plastics
Y_1 :	Pyrolysis yield of agricultural residues
Y_2 :	Pyrolysis yield of waste plastics.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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