

Co-pyrolysis of Plastic Waste and Lignocellulosic Biomass for High-Recovery Fuel Oil

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Abstract. The application of bio-oil is possible by increasing quality of bio-oil and adds its durability. Pyrolysis of biomass along with some proportions of plastic waste increases the quality of bio-oil and is termed fuel-oil. On the basis of characterization of Mixed plastic wastes (HDBE; PP; LDBE) and lignocellulosic biomass (sawdust, red gram stalk, Melia dubia, and coconut husk) are arrived as 25:75; 50:50; 75:25:100:0 to recover fuel oil at a varied temperature range from 400 to 550°C with the increment of 50°C in a laboratory set up. The solid residue (char), liquid material (fuel-oil), and gas (pyro-gas) are the products of the pyrolysis process. The maximum fuel oil is recovered with a ratio of 75 % mixed plastic waste and 25 % biomass. FT-IR analysis confirms the presence of alkanes, alkanes and aromatic hydrocarbons in the obtained fuel-oil.

Keywords: Biomass; Bio-oil; Co-pyrolysis; Fuel-oil; plastic waste.

1 Introduction

As petroleum resources are degrading and non-renewable, it leads switch over to alternative renewable energy sources to meet the energy crisis. Bio-oil is an eco-friendly fuel and acquires more merits compared to fossil fuels. Bio-oil is a clean fuel and it has several ecological advantages over fossil fuels. Bio-oil production leads to the generation of carbon credits as it reduces the emissions of CO. The feasibility of substituting petroleum fuels and chemical raw materials with bio-oil directly is restricted owing to its elevated viscosity, higher moisture and ash content, reduced calorific value, immiscibility with hydrocarbon fuels, instability, and elevated corrosiveness [1]. The technical developments and fiscal progress have turned out to be conceivable an extreme usage of fossil resources. Due to its high resilience, affordability, and ease of practical application, plastics consumption has been drastically increased. As a consequence, plastics lead to significant

environmental problems even if it does not endanger the environment directly. The cost of plastic management with the current disposal methods viz., incineration and shrinking landfill capacity leads to permanent environmental issues and does not provide a guarantee for a sustainable solution. Recycling these wastes using alternative technologies to create chemicals or energy is undoubtedly a better way to use superior pyrolysis technology compared to conventional disposal methods. Since bio-oil and petroleum fuels have an invariant chemical nature, it is not considered for petroleum fuel substitution [2, 3]. Co-pyrolysis will add to the economic advantage of increasing the waste voluminous as more leftover is spent in landfills, save energy and cost in waste treatment, and solve several environmental issues and area occupancy of landfills. Co-pyrolysis will be the best alternative technology for handling these wastes in the future and to replace petroleum fuels and conventional waste treatment methods. This also paves the way to our nation's security in energy and reduction in import of fossil fuels [4, 5, 6]. Additionally, several key elements of co-pyrolysis such as its products, characteristics, quality of the fuel-oil, merits, efficiency, and efficacy pave the way for co-pyrolysis of biomass and plastics [7, 8]. This brings an end to the discussion of the function of certain operating factors, particularly the temperature of the pyrolysis process, biomass-plastic ratio, and product yield in the co-pyrolysis process [9]. Thus, co-pyrolysis is required to produce fuel oil, a liquid product that can be used as a liquid fuel in a variety of applications. Findings of the study demonstrate that co-pyrolysis technology, particularly when applied to waste plastics and biomass, is a promising technology that can be used to reduce over-dependence on fossil fuels, increase a country's energy security, and manage waste effectively. It is also simple and optional. Hence, co-pyrolysis process will facilitate the production of fuel-oil for the substitution of fossil fuels in numerous applications.

2 Methodology

On the basis of availability and research articles, screening of lignocellulosic biomass viz., red gram stalk (field level residue), coconut husk (plantation crop residues), sawdust (agro-industrial waste) and *Melia dubia* (energy crop) are enumerated and characterized to co-pyrolysis with mixed plastics. There are some mixed plastic wastes collected, such as; polypropylene (PP), low density polyethylene (LDPE), and high density polyethylene (HDPE). Based on ASTM procedure physico-chemical characterization of the sample is performed. The testing laboratory setup is a stainless-steel cylindrical container of 1 mm thickness (thermal conductivity = $10 \text{ W m}^{-1} \text{ K}^{-1}$, 550 mm diameter and 40 mm height. The reactor is provided with two holes with a diameter of 5 mm on the lid for the exit of pyrolysis gas and condensed to recover the fuel oil.

3 RESULTS AND DISCUSSION

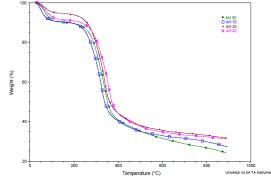
Physico-chemical characterization such as moisture content (Mc), Volatile Matter (VM), fixed carbon (FC), ash content, lignin (L), hemicellulose (HC), and cellulose (C) of selected biomass were assessed (Table 1).

The average moisture content of the selected biomass varied from 6.1 to 8.6 %, plastic wastes do not absorb the moisture, and mixed plastic waste moisture content was found to be 0.3 %. The average volatile content of the selected biomass varied from 62.5 to 81.1 % and plastic wastes were

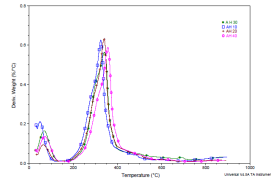
Table 1: Physicochemical characterization

Feed stock	Mc %	VM % db	FC db	Ash db	L %	HC %	C%
RGS	8.6	62.5	13.6	15.3	33.8	22.6	41.4
CH	6.1	67.4	17.6	8.9	40.8	18.3	25.9
SD	6.37	76.2	14.2	3.3	33.1	31.8	40.7
MD	7.4	81.1	9.2	2.3	27.4	26.4	47.2
MPW	0.3	94.3	1.8	3.6	-	-	-

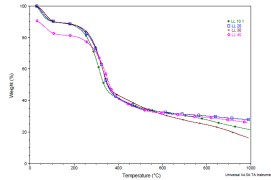
found to be high with 94.3%. The average fixed carbon content of the selected biomass varied from 9.2 to 17.6 % and plastic was found to be less at 1.8 %. The average ash content was found to be 2.3 to 15.3 %. The average lignin, hemicellulose, and cellulose content of biomass are 33.8, 24.8, and 28.8 % respectively. The results reveal that the selected samples can be utilized for pyrolytic conversion [10, 11]. According to thermogravimetric analysis, there are three phases to biomass pyrolysis like, 1. Evaporation of moisture, 2. Initial devolatilization, and 3. Complete devolatilization. The mass loss of all the biomass is a similar trend concerning an increase in temperature with varied mass loss values. Fig. 1. Depicts that the TGA graphs for various samples produced at two different temperatures. There were differences in the thermal degradability of the plastic and biomass samples, but the left over mass at the highest temperature beyond 800 °C seems to be the same contributing to ash content and devolatilization starting beyond 110°C.



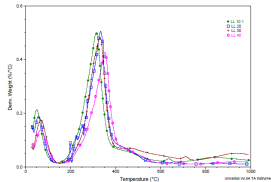
(a) TG - Redgram stalk



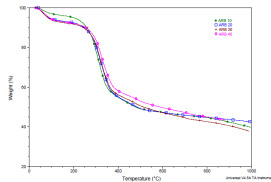
(b) DTG - Redgram stalk



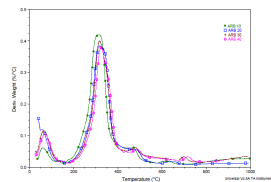
(c) TG - Coconut husk



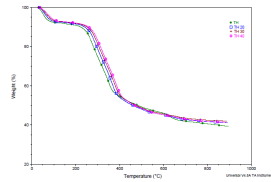
(d) DTG - Coconut husk



(e) TG -Sawdust



(f) DTG - Sawdust



(g) TG -Meliadubia



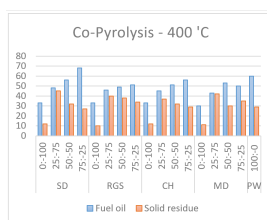
Under inert conditions, lignocellulosic biomass can decompose into three different phases such as; 1. Dehydration (up to 150 °C), 2. Active pyrolysis (150-400 °C) and 3. Passive pyrolysis (beyond 400 °C) [12]. The removal of moisture from the biomass is responsible for the first phase of the weight loss curve. Therefore, the moisture is completely vaporized at each heating rate at 150 °C. The Comparative studies confirmed that lignocellulosic materials exhibited the same phenomenon. Most changes occurred between 200 and 550 °C. Above 400 °C, the biomass showed a significant weight loss at 400 °C and 450 °C. The data also suggest that the raw material type, pyrolysis temperature, and heating rate are not the only factors responsible for the complete pyrolysis of the raw material [13]. To ensure a complete release of volatile substances, it is recommended to maintain the maximum temperature until the end of the pyrolysis process. On the basis of the characterization of Mixed plastic wastes (HDBE; PP; LDBE) and lignocellulosic biomass, combinations of Mixed plastic wastes and biomass were arrived at 25:75; 50:50; 75:25:100:0 to recover higher liquid fuels. The Laboratory studies on fuel oil production from arrived combinations of plastics and biomass at reaction temperatures 400, 450, and 550 °C are studied in the TNAU-developed pyrolytic reactor (1 kg h⁻¹). Different product yields like solid residue and fuel oil are recovered. The remaining value is accounted as non-condensable pyro-gas [14]. The fuel oil production from the feedstock quantity and quality of the final product varied from optimizing and changing the different process parameters for this experiment. In this experiment, the reaction temperature and Nitrogen gas flow rate are considered as process parameters. For all trials, the feed rate of 1 kg h⁻¹ is used. Different product yields like solid residue and fuel oil are recovered and the unaccounted yield goes as gas. There are many ways to determine the heating rate in pyrolysis studies. When plastic waste enters the pyrolysis reactor, it is quickly broken down and vaporized in a rapid pyrolysis process. The hydrocarbon gets a phase change at the temperature of approximately 500°C, which is very ahead of 110°C. Plastic cracking is the first step in the production of several hydrocarbon compounds, including (C1-C4) gases. In these situations, the temperature increase per unit time (10 °C/min) during the exposure time is called the heating rate and can vary between 400 and 500 °C. However, controlling the heating load of the pyrolysis reactor at a given feed rate is the most practical way to control the heating rate. It was found that the heating rate affects the fuel oil yield distribution and the pyrolysis reaction rate [15]. This part of the experimental study sought to find out how temperature affected the plastic and biomass sample and its cracking under experimental conditions and how it is affected in the pyrolysis process and product distribution. [16, 17]. Based on the TGA results, the reaction temperatures selected for the experiments are 400, 450, and 500 °C to study the quantity and quality of fuel-oil production along with char and pyro-gas. The optimum value of the process conditions is revealed in Table 2.

Figure 2 illustrates the fuel-oil and solid residue yield at different process conditions. The fuel oil yield in percentage from plastic waste with biomass in the different combinations is found to be in the range of 43 to 59 (25:75); 49 to 68 (50:50) and 50 to 77 (75:25). The fuel oil yield from plastic and biomass are found to be 58 to 64 and 31 to 35 % respectively. Co-pyrolysis of plastic waste with sawdust increased the fuel oil yield by 10 % whereas *Melia dubia* declined by 14 %. Co-pyrolysis offers an increase in fuel oil yield compared to pyrolysis yield [18]. Products from the co-pyrolysis process are suitable for thermal energy and energy production and can also be utilized in chemical industries [19]. The selection of biomass affected the yield. The research confirms that saw dust with

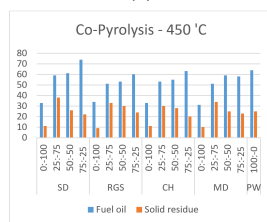
Table 2: Parameters for experiment

Sample	N ₂ flow, 1 min ⁻¹	Temp., °C	Fuel Oil yield, %
PW: SD (75:25)	15	460	
PW: RGS (75:25)	15	460	71.5
PW: CH (75:25)	25	460	72.1
PW: MD (50:50)	15	520	68.3

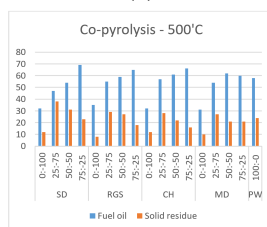
plastic waste yields a better result than other combinations [20, 21].



(a)



(b)



(c)

Fig. 2. Yield details on co-pyrolysis

The FT-IR and GC-MS analyses are carried out to study the compounds present in fuel-oils. From the FT-IR results, it is inferred that the occurrence of C=C bonds: alkenes; C-H bonds:

methyl and methylene groups, aromatics; C=O bonds: ketone and aldehyde groups; C–O bonds: Acids; O–H bonds: phenols and alcohols in fuel-oils [22, 23]. The FT-IR and GC-MS analysis of fuel oil produced with 75 % plastics and 25 % saw dust are represented in Figures 3 and 4. Thirty compounds were identified from GC-MS results [24]. The compounds are 1-Octadecane (5.00 %); 1-Heptadecane (4.94 %); 1-Pentadecene (4.86 %); 1-Tetradecene (4.73 %); 1-Nonadecene (4.71 %) and aliphatic hydrocarbons (alkanes and alkenes). It is confirmed that the quality of fuel-oil meets the conventional fossil fuel [25].

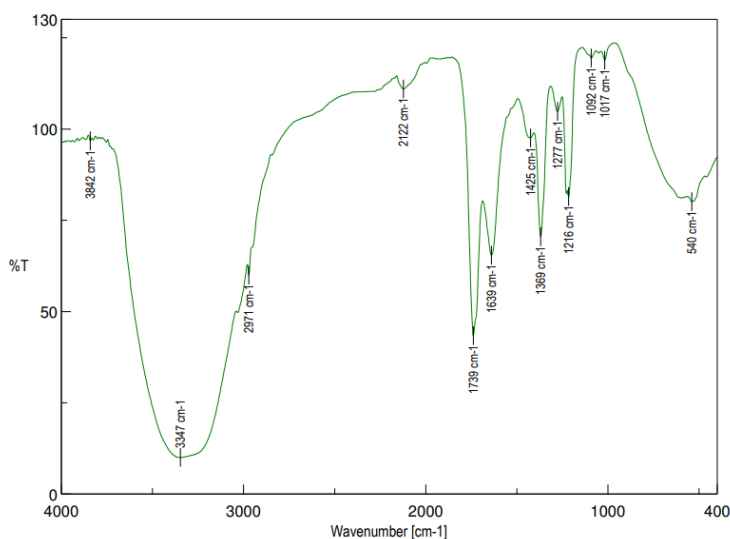


Fig. 3. FT-IR spectrum

4 CONCLUSION

Biomass and plastic as feedstock in co-pyrolysis in the production of value-added goods and alternative fuels is an energy-efficient process towards attaining sustainability of fuels and environments. It leads to a synergistic solution for waste management, mitigating climate change, and protecting the environment. This technology is an alternative and practically possible management process for the conversion of waste into fuel ensuring that fossil fuels have a circular destiny [26]. On the basis of characterization of Mixed plastic wastes (HDBE; PP; LDBE) and lignocellulosic biomass (sawdust, red gram stalk, *Melia dubia*, and coconut husk), combinations of Mixed plastic wastes and biomass arrived at 25:75; 50:50; 75:25; 100:0 for fuel-oil production. The reaction temperature is taken as 400 to 550°C with an increment of 50°C as high devolatilization happens in the range of 400 to 550°C. Different product yields like solid residue and fuel oil were recovered. The remaining value is accounted as non-condensable pyro-gas. The highest fuel oil yield obtained from

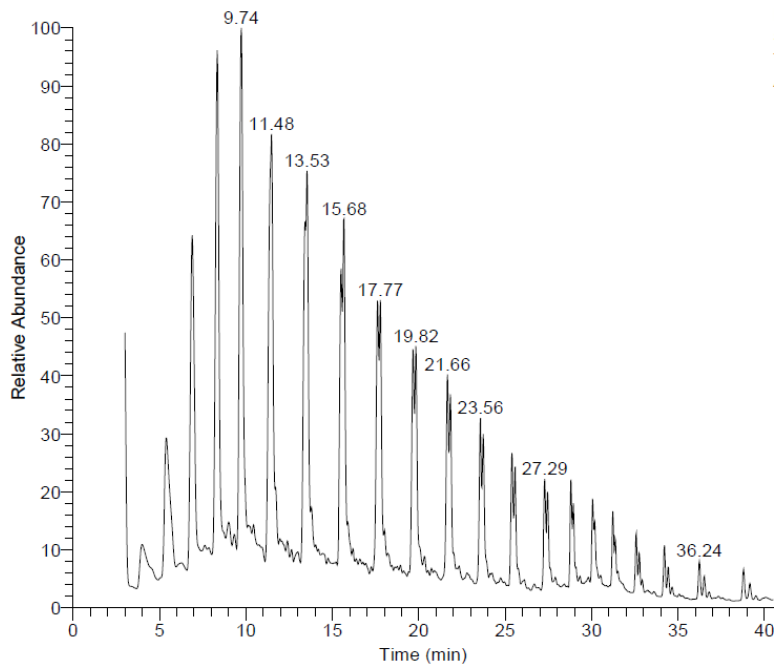


Fig. 4. GC-MS- graph

sawdust, red gram stalk, *Melia dubia*, and coconut husk was 74 (450°C), 65 (500°C), 62 (500°C), and 66 % (500°C) with mixed plastic waste. The maximum fuel oil was recovered with a ratio of 75 % mixed plastic waste and 25 % biomass. The solid residue varied from 16 to 21 %. FT-IR analysis inferred the prevalence of alkane and alkene compounds (2900–2850 cm⁻¹) and aromatic hydrocarbons (700-900 cm⁻¹) in the produced fuel-oil. The GC-MS analysis confirmed the presence of 1-Octa, hepta, penta, non-decane and aliphatic hydrocarbons in fuel-oil. To enhance the synergistic impact, lower input energy, product transformation, eliminate toxin emission, and meet waste management difficulties, co-pyrolysis is the best method to treat both biomass and plastic together. Apparently, there are still a lot of obstacles that we must concentrate on and get past in the future. There are lots of chances for engineers and researchers in these areas.

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