

Plastics/Biomass copyrolysis in an auger reactor: Physico-Chemical analysis of the products

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Abstract

This work intended to study the recovery of two types of waste by the process of pyrolysis. We demonstrated experiments with auger pyrolyser (2 kg/h) at 500°C in the presence of nitrogen under atmospheric pressure for copyrolysis of three plastics, high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS), individually with deoiled cake of jatropha (JC) in equal mass proportions to produce upgraded bio-oil. Detailed characterisation of bio-oil was analysed with a little assessment of by-products, i.e., char and non-condensable gas. GC-MS analysis of bio-oil was observed to be quite interesting, which shows significant reduction of oxygenates by addition of plastics with biomass.

Keywords: Waste-plastics, Jatropha, Co-pyrolysis, Bio-oil

1. Introduction

Biomass derived bio-oil is a promising alternative source of energy. However, bio-oil is reported to be highly oxygenated, complex and chemically unstable which contribute to high water formation and lower heating values (40–50% of diesel), high viscosity, and high specific weight of bio-oil. These limit its application as fuel [1]. Thus, the bio-oil needs to be upgraded by lowering the oxygen content [2].

As referred to this issue, we had attempted co-pyrolysis as in-situ hydrogenation tool. During co-pyrolysis of biomass with plastics, the hydrogen requirement is met by the polymer (HDPE and PP contain 14 wt. % of hydrogen, PS contains 8.0 wt. % of hydrogen) [3].

The aim of the present study was to produce upgraded bio-oil with lower oxygenates by auger copyrolysis of plastics with biomass (deoiled cake of jatropha, JC) along with little assessment of by-products, i.e., char and non-condensable gas.

2. Materials and Methods

Materials

Deoiled Jatropha cake (JC) was obtained from the biodiesel manufacturer. It was cleared of physical impurities, ground and sieved. Commercial polyolefins (HDPE, PP and PS) were stored under dry condition.

Co-pyrolysis in an auger reactor

A 2 kg/h auger-fed pyrolysis reactor used in this work comprised of a hopper, a rotary valve, an auger reactor, a cyclone separator, a vertical condenser and a product receiving tank. The auger reactor was electrically heated. The feedstock (copyrolysis mixture) was fed through rotary valve to the auger reactor, which was heated at a rate of 20°C/min.

Bio-oil characterization

Pyrolysis oil obtained from each run was determined by Perkin Elmer Clarus 600 GC-MS using BP-1(30 m, 0.32 mm) capillary column with 0.25 µm thick stationary phase (100 % methyl polysiloxane). Further, physical analysis of each bio-oil was determined, which includes viscosity, water content and calorific value.

3. Results and Discussion

Gas chromatography/mass spectrometry (GC/MS) study of the bio-oils

An analysis of liquid product by a hydrocarbon type is essential to establish their potential utilization as fuel. GC/MS analysis was used to determine the proportions of paraffins, olefins, aromatics, and oxygenates in the bio-oil generated from the pyrolysis of JC and its copyrolysis mixture with various plastics (Table 1).

Table 1. GC-MS Integration of JC and its co-pyrolysis mixture (1:1 wt %) at 500°C

Feedstock	Area%			
	Paraffin	Olefins	Aromatics	Oxygenates
JC	3.21	4.98	26.68	58.04
JC/HDPE	28.35	25.11	39.58	6.13
JC/PP	32.75	28.31	30.33	7.81
JC/PS	6.66	18.47	68.82	5.68

Pyrolysis of only plastics reported to be produced with significant amount of paraffin, olefins and free of oxygenates while substantial amount of oxygenates were observed in JC pyrolysed bio-oil [4, 5]. Degradation of

cellulose, hemicellulose and lignin may be responsible for the formation of a higher proportion of acids and oxygenates in the oil produced by pyrolysis of JC. Liquid product obtained from only HDPE and PP pyrolysis reported to be free of cyclo-alkanes and aromatics. Higher proportion of olefins was observed in the liquid products specifically in the case of PP pyrolysis [6]. Due to polycyclic nature of PS, it exhibits high proportions of aromatics in contrast to HDPE and PP [7].

In contrast to bio-oil obtain from only JC pyrolysis, co-pyrolysis offers considerable improvement in the quantity of paraffins, olefins and aromatics (Table 1). Such an improvement may be attributed to conversion of oxygenates to hydrocarbon from copyrolysis mixtures.

During co-pyrolysis of biomass with plastics, hydrogen requirement is met by the plastics (HDPE and PP contain 14 wt% of the hydrogen, PS contains 8.0 wt% of hydrogen) [3]. Addition of PS to JC causes significant increase in the content of aromatics, specifically ethyl benzene and styrene at the cost of oxygenates of the JC. Styrene (C₈) is the most abundant product along with trace amount of ethyl benzene and α -methyl styrene produced by the pyrolysis of only PS. Highest reduction in oxygenates was observed with the use of PS as a second material (about 90 %).

Physical properties

Table 2 summarizes the viscosity, water content and calorific value for each of the four pyrolysis oils. In contrast to only JC pyrolysed bio-oil, co-pyrolysis with plastics produced bio-oils of very low viscosity (maximum 56 % reduction with PS). Water content of JC derived bio-oil was 12%, resulting from the moisture content of JC itself whereas co-pyrolysis offers reduction in water content due to equal mass proportion of biomass and plastics as a feedstock. In contrast to only JC derived bio-oil, co-pyrolysis exhibited significant improvement in the calorific value of the bio-oil due to contribution of liquid fractions from plastics. Highest improvement in calorific value was observed in JC/HDPE derived bio-oil.

Table 2. Comparison of physical properties of biomass/plastic copyrolysis oil

Pyrolysate liquid	Viscosity (cSt at 50°C)	Water (wt%)	Calorific value (MJ/kg)
JC	78.00	12.00	25.27
JC/HDPE	35.12	5.10	36.63
JC/PP	34.50	5.50	34.59
JC/PS	33.56	6.50	37.11

Evolution of by-products

Non-condensable gases mixture obtained from JC pyrolysis composed by CO, CO₂, CH₄ and fractions of

C₂-C₅ in lesser proportions which exhibited calorific values about 2550 kcal/kg while Plastics/JC produced a mixture of gases with higher calorific value (about 7000 kcal/kg). Similar improvement in calorific value was observed for the char resulting from copyrolysis feedstocks.

4. Conclusion

Significant reduction of oxygenates and improvement in calorific value of copyrolysed bio-oil indicates the in-situ mild hydrogenation during the pyrolysis reaction, resulting from the degradation of plastics.

In contrast to JC derived bio-oil, copyrolysed bio-oil offers significant improvement in paraffin's, olefins and aromatics due to conversion of oxygenates to hydrocarbon under mild hydrogen medium. With the use of PS as a second material, highest reduction (90 %) of oxygenates was observed. Copyrolysis produce bio-oil exhibiting higher heating value and lower water content and viscosity. Calorific value of non-condensable gases and char increased in copyrolysis feedstocks.

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