# Fixed Bed Co-Pyrolysis of Low-Density Polyethylene and Rice Husk

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### Abstract

The co-pyrolysis of low-density polyethene (LDPE) with rice husk (RH) at different blend ratio was carried out in a fixed bed reactor with varying temperatures ranging from 350-550°C. The objective of this present work is to investigate the influence of different parameters such as blend ratio, co-pyrolysis temperature and feed size on their product yields. The feed size varied in the ranges from 0.5 to 2.36 mm for rice husk and 20×20 mm for LDPE. The experiments were conducted varying temperature between 350 to  $550^{\circ}C$  with an interval of  $50^{\circ}C$ . The maximum bio-oil obtained for LDPE/RH co-pyrolysis was 53.38% at 450°C with 3:1 blend ratio. Various properties of the bio-oils obtained under these conditions were analyzed. According to the analysis results, the produced co-pyrolysis oil had higher carbon content, lower oxygen content with a higher heating value in comparison with biomass oil. The results of FTIR analysis showed that the co-pyrolysis oil mainly comprised of the aliphatic Compound and less aromatic Compound as compared to the individual rice husk pyrolysis. The results of this study indicated that the obtained co-pyrolysis oil could be used as a potential fuel.

**Keywords** — Low-density polyethene, rice husk, copyrolysis, bio-oil

### I. INTRODUCTION

Biomass and plastic materials are the two major components of municipal solid waste. Mass consumption of plastic materials causes severe environmental pollution. Again, the massive use of fossil fuels resulted in the energy shortage, greenhouse effect and environmental pollution. Hence, researchers have paid much attention to solve these problems. Pyrolysis can play an important role in the production of alternative fuel or reuse of waste materials. Waste plastics such as low and highdensity polyethene, polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl chloride (PVC) are very suitable for bio-oil production [1-7].

Biomass composed mainly of cellulose, hemicelluloses, lignin and minor amounts of other organics, which can be the sources of energy and raw chemical feedstock. Biomass can be easily converted to energy through thermochemical conversions, such as gasification, combustion and pyrolysis. Pyrolysis of biomass has received much interest in recent decades. However, biomass bio-oil has some unstable fuel properties such as higher oxygen content and moisture content, which limited its use in automobile engines. The biomass bio-oil fuel characteristics can be improved by the addition of higher hydrogencontaining organic material. Therefore, plastics could potentially be a beneficial feedstock in the copyrolysis conversion process due to their higher hydrogen content, and lower moisture content in their pyrolysis derived oil [5].

There are many studies on thermal decomposition of plastic materials with biomass [5-20]. It is evident from these research results that the co-pyrolysis of plastic and biomass resulted in improved quality and quantity of bio-oil compared with that from single biomass pyrolysis as plastic acts as a hydrogen donor. A few investigations in the literature were found based on the co-pyrolysis of LDPE and biomass [21-25]. Dewangan et al. studied the effect of LDPE with sugarcane bagasse from biomass in a semi-batch reactor. This experiment produced a high yield of 52.75% with blend ratio 1:1, at an optimum temperature of 500°C. The copyrolysis liquid had an enhanced liquid yield, improved, calorific value, the lower amount of oxygenated compounds, water content, phenol and acidic compounds and higher amount of alkane and alkene species in comparison with SCB pyrolytic oil [22]. Yang et al. explored the co-pyrolysis of lowdensity polyethylene (LDPE) with different biomass in a dropdown tube reactor. The maximum oil relative yield in the case of the co-pyrolysis process was obtained at 600°C. The final co-pyrolysis oil showed an improved hydrocarbon content, an increase of alcohols and significant removal of aldehydes, acids, ethers, furans, ketones, phenols and sugars [25]. Fan et al. conducted fast microwaveassisted catalytic co-pyrolysis of lignin and LDPE with HZSM-5 and MgO. The maximum liquid yield was obtained when the optimal temperature, lignin to LDPE ratio, and feedstock to catalyst ratio were 500°C, 3:1 and 1:1, respectively. The addition of LDPE increased aromatic compounds and removed methoxyl group in the phenols. The use of the proper amount of catalyst increased bio-oil yield and alkylated phenols. HZSM-5 improved the production of aromatics while MgO promoted alkylation of phenols [21].

The objective of this study is to enhance the oil yield of rice husk pyrolysis with the addition of a widely used LDPE. In this study, LDPE was co-pyrolyzed with rice husk to investigate the effect of different parameters on bio-oil yield and find out the optimum conditions for bio-oil production. Moreover, the co-pyrolysis oil was characterized in detail to determine its possibility of being a potential energy source and chemical feedstock.

### II. MATERIALS AND METHODS A. Feed materials

Rice husk samples were collected from a rice mill factory in Rajshahi, Bangladesh. Low-density polyethylene (LDPE) grains were obtained from the dumped site of Rajshahi City Corporation, Bangladesh. Rice husk was sieved to different size range between 0.5 to 2.36 mm, whereas the average LDPE grain size was 20 mm  $\times$  20 mm. The rice husk samples were then oven-dried at a temperature of 110°C for 8 hours to remove moisture from the samples.

 Table. 1 Proximate and elemental analysis, heat

 value of waste LDPE and rice husk

Proximate analysis [wt%]	Rice husk	LDPE			
Moisture content	9.56	0.35			
Volatile matter	69.04	97.96			
Fixed carbon	4.4	0.26			
Ash content	17	1.43			
Ultimate analysis [wt%]					
Carbon [C]	40.41	85.12			
Hydrogen [H]	6.55	14.34			
Nitrogen [N]	1.59	0.056			
Oxygen [O] (By difference)	51.24	0.42			
Sulfur [S]	0.21	0.07			
GCV [MJ/kg]	19.64	42.50			

The compositional analyses of feed materials were done based on proximate and ultimate analysis to investigate feed materials suitability. The proximate and ultimate analyses were conducted in the Institute of Fuel Research & Development (IFRD), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh. The moisture content and ash content of the feed were determined by ASTM D1860-63 and IP 41/58 standard, respectively. The percentage of carbon, hydrogen, nitrogen, oxygen and sulphur in the feedstock was determined using Elemental Analyzer of model EA 1180. The calorific values of LDPE and RH were obtained through a bomb calorimeter of model PARR 1341. A sample of 1g was placed inside the bomb and burned in the presence of oxygen to determine higher heating value. The proximate and ultimate analyses of LDPE and rice husk are presented in Table 1.







Fig.2. DTG plot of LDPE and RH

The thermogravimetric analysis (TGA) of RH and LDPE was carried out individually using Thermo-gravimetric Analyzer (TGA) of model SETARAM-TG/DTG/DSC, according to ASTM D2887-89 standard test method. Approximately, 10-15 mg of the sample was taken in an Al<sub>2</sub>O<sub>3</sub> crucible and heated from ambient temperature up to the final temperature of 600°C with 15°C/min heating rate. The inert atmosphere was created by flowing pure nitrogen gas at a flow rate of 100 ml/min to avoid unwanted oxidation of the sample. The TG/DTG plots for LDPE and rice husk are presented in Figs. 1 and 2. From the figure, it can be seen that the decomposition is completed for both of the samples around 500°C and decomposition rate is maximum at 357°C and 469°C for rice husk and LDPE, respectively.

### B. Experimental set-up

The experimental unit consists of a fixed-bed reactor chamber, a condenser, an LPG cylinder with burner, a thermolyne sybron digital portable pyrometer of model PM-20700, and a liquid collector. Co-pyrolysis of rice husk and LDPE was carried out in a fixed bed reactor made up of stainless steel of length 300 mm, 97 mm internal diameter and 100 mm outer diameter with an outlet tube at the top. The reactor provided an apparent vapour residence time of 5 sec. The main components of the experimental set-up are presented in Fig. 3. An LPG cylinder supplied heat to the reactor. The LPG burner comprised of 4 arms of 300 mm length each having ten 5mm size holes to heat the reactor. Two asbestos laver of 50 mm thickness was used to reduce heat loss around the reactor. Coldwater circulated through the water inlet and outlet port to condense the vapour mixture. The feed materials were fed into the reactor and sealed properly. The reactor was heated to the desired temperature. Pyrolysis vapour product was passed through the condenser to quench into liquid and then collected in the liquid collector.

The uncondensed gases were flared to the atmosphere. When pyrolysis of the feed material in the reactor was completed, the vapour exit port was closed and, LPG burner was switched off. Pyrolysis char was collected after the reactor became cool. The yield of the pyrolysis product was determined by measuring the weight of pyrolysis oil and pyrolysis char; further, the weight of the gaseous product was calculated subtracting the liquid and char weight from the feedstock. A mixture of LDPE and RH with LDPE/RH ratio of 1:0, 3:1, 1:1 and 1:3 was pyrolyzed in the temperature range of 350–550°C. Afterwards, the system was made ready for the next run. The pyrolysis experiments were repeated three times to ensure the reproducibility.



Fig.3. Main components of the fixed-bed LPG heating pyrolysis system

### **III. RESULTS AND DISCUSSION**

### A. Pyrolysis products yield

### a). Effect of temperature on pyrolysis products yield

The reactor temperature is an important operating parameter which influences the copyrolysis process. To find out the optimum operating temperature, several runs on co-pyrolysis of 3:1 blends of LDPE/RH were performed in the temperature range of 350-550°C, without any sweep gas. The effect of temperature on products yield of co-pyrolysis of rice husk and LDPE is shown in Fig. 4. From this figure, it is evident that the bio-oil yield was 42.25% at the pyrolysis temperature of 350°C; it appeared to go through a maximum of 53.38% at 450°C temperature. Then as the temperature increased from 450 to 550°C, the yield of liquid product decreased and reached a value of 45% at 550°C. At 450°C temperature strong cracking reaction takes place, and secondary decomposition of char residue occurs which maximizes the liquid yield.



Fig.4. Effect of temperature on product yield for particle size 0.2 mm

## b). Effect of different blends of RH/LDPE mixture on pyrolysis products yield

Co-pyrolysis of LDPE: RH mixture was carried out at 500°C with different blends of 1:0, 3:1, 1:1 and 1:3. The effect of different blend ratio of co-pyrolysis of LDPE: RH is shown in Fig. 5. From Fig. 5, it is observed that maximum co-pyrolysis liquid product (53.38%) was obtained using 75% LDPE and 25% RH feed. The liquid product yield increase with the increase of LDPE in the RH and LDPE mixture, while the liquid yield decreases with the addition of rice husk in the blend. Consequently, the maximum char and gas yield was found with co-pyrolysis of 1:3 blends of LDPE/RH. At optimum blend ratio, the char and gas yields were 13.2% and 33.42%, respectively. Many researchers have reported that a significant increase in the pyrolysis liquid yield during co-pyrolysis of biomass and plastic wastes can be indicated as the occurrence of synergistic effect [22].



### C. Effect of particle size on pyrolysis products yield

Several runs were performed to investigate the effect of particle size on the pyrolysis product yields. The effect of particle size on product yields at 450°C is presented in Fig. 6. It is evident from the figure that the liquid yield first slightly increases up to 53.38 wt% for the particle size of 0.2 mm and then decreases for larger particle size, while the char yield increased and gas yield decreased through all the particle sizes from 0.5 to 2.36 mm. Due to too quick decomposition, the smaller particle size produces lower liquid yield. The larger particle size cannot decompose completely resulting increase in char yields and a decrease in liquid and gas yields.



Fig.6. Effect of particle size on product yield at temperature 450°C

### B. Characterization of bio-oil

## a). Physical and chemical properties of the pyrolysis oil

The typical properties of bio-oil derived from co-pyrolysis were given in Table 2. It can be seen

from Table 2, the bio-oil derived from co-pyrolysis is less viscous than the bio-oil derived from LDPE and RH individually. The density of the bio-oil at 20°C was 870 kg/m<sup>3</sup>, which is much lower than rice husk derived bio-oil. The moisture content is lower than biomass bio-oil. The presence of water content in bio-oil is mainly due to lignin-derived materials. The pH at room temperature is 3.9. Bio-oils with low pH are generally corrosive. The flashpoint of the bio-oil was very close to those of diesel. The calorific value of bio-oil was 39.5 MJ/kg. The bio-oil was characterized by lower oxygen content than that of rice husk derived pyrolysis oil. High oxygen content is not attractive for the production of transport fuels. The nitrogen content is very lower than that of diesel. The sulphur content in the derived liquids is very close to that of gasoline.

 
 Table. 2 Physico-chemical characteristics of the copyrolysis oil and its comparison

Properties	Prosont	P	Pyrolysis		Casalina
Elemental (wt%)	study	RH [26]	LDPE [27]	l [28]	[29]
С	73.01	41.7	-	86.58	85.4
Н	12.23	7.7	-	13.29	14.1
C/H	5.97	5.42	-	6.51	-
Ν	0.20	0.3	-	39.01	0.02
S	0.03	0.2	-	0.11	0.028
0	14.53	50.3	-	0.01	-
Moisture content (wt%)	9.9	25.2	-	9.75	-
Viscosity at 20°C (cSt)	4.96	128	5.56*	2.61	-
Density at 20°C (kg/m <sup>3</sup> )	870	119 0	780 <sup>©</sup>	827.1 *	780
pH value	3.9	2.8	-	-	-
Pour point (°C)	<-7.7	-	-	-	-
Flash point (°C)	54	-	41	53	-43
HHV (MJ/kg)	39.5	24.8	39.5	45.18	43.9

<sup>#</sup> @ 50°C; \* @ 25°C; <sup>©</sup> @ 15°C

### b). Functional group analysis of the pyrolysis oil

Functional group analysis of the liquid obtained from co-pyrolysis of low-density polyethylene and rice husk at the pyrolysis temperature of 450°C and particle size of 2 mm. The Fourier transform infrared spectroscopy (FTIR) analysis was performed by IRAffinity-1S FTIR. The FTIR spectra of the investigated co-pyrolysis oil have been presented in Table 3. The FTIR spectrum of the co-pyrolysis oil is quite similar to that of LDPE pyrolysis oil rather than that of RH pyrolysis oil. The O-H stretching vibrations between 3200 and 3400 cm<sup>-1</sup> of the bio-oil indicate the presence of phenols and alcohols. The C-H stretching vibrations between 2800 and 3000 cm<sup>-1</sup>; C-H deformation vibrations between 1350 and 1460 cm-1 and 1000 and 1150 cm<sup>-1</sup> indicate the presence of alkanes. The absorbance peaks between 1580 and 1670 cm<sup>-1</sup>; and 875 and 950 cm<sup>-1</sup> represent C=C stretching vibrations indicative of alkenes. The absorbance peaks between 1400 and 1500 cm<sup>-1</sup> indicate nitrogenous compounds. Absorptions between 1175 and 1300 cm<sup>-1</sup> indicate the carbonyl components. The absorbance peaks between 900 and 650 cm<sup>-1</sup> represent O-H stretching vibrations indicative of aromatic groups. The liquid product obtained from co-pyrolysis oil mainly consists of a significant amount of aliphatic hydrocarbons with smaller amounts of aromatics.

Frequency range (cm <sup>-1</sup> )	Present studies	LDPE [22]	RH [30]	Functional groups	Class of compounds
3400-3200	$\checkmark$	×	$\checkmark$	O–H stretching	Alcohols, phenols or carboxylic acids
3000-2800	$\checkmark$	$\checkmark$	$\checkmark$	C–H stretching	Alkanes
1750-1660	×	×	$\checkmark$	C=O stretching	Aldehydes or ketones
1670-1580	$\checkmark$	$\checkmark$	×	C=C stretching	Alkenes
1500-1400	$\checkmark$	$\checkmark$	$\checkmark$	-NO <sub>2</sub> stretching	Nitrogenous compounds
1460-1350	$\checkmark$	$\checkmark$	×	C–H bending	Alkanes
1300-1175	V	$\checkmark$	$\checkmark$	C–O stretching O-H bending	Primary, secondary and tertiary alcohols, phenols, esters and ethers
1150-1000	$\checkmark$	×	$\checkmark$	C–H bending	Alkanes
950-875	$\checkmark$	$\checkmark$	×	C=C stretching	Alkenes
900–650	$\checkmark$	$\checkmark$	$\checkmark$	C–H out- of-plane bending	Aromatic compounds

Table.3. FTIR analysis of co-pyrolysis oil

 $\sqrt{\text{Compound present}}$ ,  $\times$  Compound not present

### **IV. CONCLUSION**

The co-pyrolysis experiments of the low-density polyethylene and rice husk were carried out in a fixed bed reactor with different blend ratio, pyrolysis temperature and particle size. The maximum bio-oil liquid yield (53.38 wt%) was obtained at a temperature of 450°C with a particle size of 2 mm and a blend ratio of 3:1 (LDPE: RH). It was noted that the bio-oil obtained at optimum condition contains lower moisture, the higher calorific value of 39.5 MJ/kg and lower oxygen than that of biomass bio-oils. FTIR analysis showed that the co-pyrolysis liquid compositions were dominated by alkane and alkene species than the liquid obtained by the pyrolysis of rice husk alone. The decreasing amounts of phenolic and acid compounds could be beneficial for improving the stability of the obtained copyrolysis oil, which can be used as a potential fuel.

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