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Co-pyrolysis of rice straw and Polyethylene Terephthalate (PET) using a fixed bed drop type pyrolyzer

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Abstract. In this work, co-pyrolysis of rice straw and polyethylene terephthalate (PET) was carried out at different temperatures (450, 500, 550, and 600°C) at ratio 1:1 by using fixed bed drop-type pyrolyzer. The purpose of this work is to determine the effect of pyrolysis temperature on the product yield. As the temperature increased, the pyrolysis oil increased until it reaches certain high temperature (600°C), the pyrolysis oil decreased as more NCG were produced. The temperature 550°C is considered as the optimum pyrolysis temperature since it produced the highest amount of pyrolysis oil with 36 wt.%. In pyrolysis oil, the calorific value (13.98 kJ/g) was low because of the presence of high water content (52.46 wt.%). Main chemicals group from pyrolysis oil were an aldehyde, ketones, acids, aromatics, and phenol and all compound have abundant of hydrogen and carbon were identified. Co-pyrolysis of rice straw and PET produced a higher amount of carbon oxides and recycling back the NCG could increase liquid and char yields.

1. Introduction

The depletion of fossil fuels such as petroleum, coal and natural gas inspire researchers to find solutions by utilizing alternative energy. Biomass can be a sustainable and renewable source of fuel not affiliated with fossil fuels. Thermochemical conversion of biomass to liquid products has the advantage to displace petroleum fuels since it has similar characteristics to petroleum-derived. Biomass is very abundant worldwide and can be easily found in various forms such as dedicated energy crops, municipal solid waste, wood residues and agriculture residues.

After wheat, rice is the second most important crop in the world with Asia being the largest producer and consumer. The production of the rice straw in Malaysia field at 2011 was 1,933,889.3 tons [1]. Regrettably, the burning of the rice wastes such as rice straw and rice husk remains the cultural practice in Malaysia [2] and it reduced the air quality and will worsen the greenhouse effect. Thermal decomposition of biomass also known as pyrolysis is the constitutional chemical reaction that is the forerunner of both combustion and gasification processes naturally occurs in short time with the absence of oxygen. The products of biomass pyrolysis include pyrolysis oil, biochar and non-condensable gases (NCG) which consist of carbon dioxide, hydrogen, carbon monoxide, and methane. Pyrolysis is an endothermic process that required sufficient heat transfer surface to complete the process. The pyrolysis products can be applied in the production of heat, chemical, and power generation.



However, instead of using biomass as a single feedstock, the researcher has also experimented adding plastics in the pyrolysis process to enhance the quality and quantity of products. Polyethylene terephthalate (PET), polypropylene (PP), and polystyrene (PS) are non-biodegradable plastics. The disposal of these plastics became a problem as landfills are filled with these non-biodegradable wastes. One of the promising ways to manage these wastes, as well as taking a valuable profit of the energy value of these wastes is by co-pyrolysis. Co-pyrolysis of plastics polymers with biomass could balance the carbon, oxygen, and hydrogen in the feedstock with the strong effect of the dissipation products since plastic has higher thermal stability compared to plastics. Pyrolysis oil could yield up to 50 wt.% at a higher heating rate with shorter residence time [3][4].

Pyrolysis of rice straw has been studied by Tsai and Lee [5]. They found that at a higher heating rate, the larger solid yield can be obtained. Besides, the pyrolysis liquid products still contained a large amount of water (70-86 wt.%). However, the data for the study of co-pyrolysis between rice straw and plastics is not widely available. The objective of work is to study the co-pyrolysis of rice straw and polyethylene terephthalate (PET). The effect of temperature was analyzed at 450,500,550 and 600°C and constant ratio 1:1. Co-pyrolysis process was performed using a drop-type pyrolyzer and products yields of co-pyrolysis were pyrolysis oil, biochar, and non-condensable gases will be characterized.

2. Feedstocks and materials.

The rice straw that is used in work is collected from a rice field in Kangar, Perlis Malaysia. The rice straw was ground to size 0.15-0.50mm and dried in an oven at 105°C for 24 h to reduce the moisture content so it is less than 10wt% [6]. PET plastic was collected and cut into smaller size 0.30 mm x 0.30 mm and both of the feedstocks is stored in the air-tight container. Characteristics of the feedstock as shown in Table 1.

Table 1. Feedstocks properties.

	Rice straw	Polyethylene terephthalate (PET)
Proximate analysis, wt.%		
Moisture	5.93	0.23
Ash	9.56	0.10
Volatile	76.85	99.20
Elemental analysis, wt.%		
C	36.02	58.93
H	6.63	3.98
N	1.12	0.13
O	56.25	36.96
Calorific value (kJ/g)	15.63	36.72

3. Experimental setup

Figure 1 shows the fixed bed drop type pyrolyzer schematic diagram used to carry out the co-pyrolysis experiment. To create an inert condition, the pyrolyzer was linked with nitrogen gas lines. The reactor is the first purged three times to ensure inert conditions. The biomass was put on the holder zone and two ball valves in closing mode. The reactor is heated with an electric furnace and insulated to avoid heat loss during an experiment. A K-type thermocouple was attached to the reactor to record the actual temperature. After the desired reaction temperature is achieved, the biomass will be dropped down by gravity and the pyrolysis process will begin. Two condensers were connected to the reactor to increase the condensation efficiency and immersed in an ice cooled water bath to condense the pyrolysis vapors

into pyrolysis oil. A gas bag was connected to the outlet of vapor trap to collocate non-condensable gases (NCG). Meanwhile, the biochar was loaded in the reactor and collected after the experiment finished.

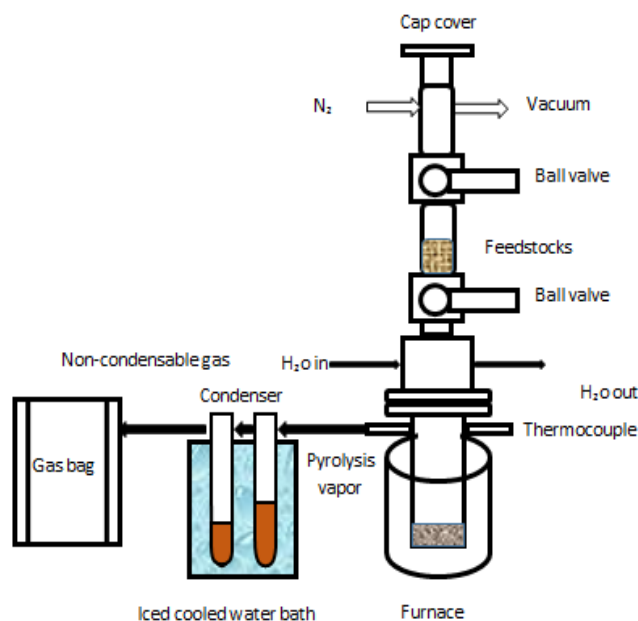


Figure 1. Fixed-bed drop type pyrolyzer schematic diagram.

4. Pyrolysis procedure

15 g of rice straw and PET feedstocks with mass ratio 1:1 was loaded into the biomass holder zone for all experiments. The feedstocks are dropped down to the reactor when the desired temperature achieved. The duration of the experiment was held at the desired temperature for 20 minutes until no significant brownish gas vapor was observed. In this study, the experiment was done and temperatures were considered at 450,500,550 and 600°C and constant ratio 1:1.

Three products yields produced from the co-pyrolysis process were pyrolysis oil, biochar, and non-condensable gases. The pyrolysis oil and biochar we determined by calculated the weight changes at before and after of the reactor and condensers respectively. The yield of non-condensable gases was calculated using an equation [7]:

$$\text{Pyrolysis oil (wt.\%)} + \text{biochar (wt.\%)} + \text{non-condensable gases (wt.\%)} = 100 \quad (1)$$

5. Products analysis

To determines the quality of co-pyrolysis products, the product analysis is done on the pyrolysis oil in which temperature yield is on the maximum liquid product. pyrolysis oil yields collected. The elemental analysis of elements of C, H, N, O, and S was carried out on pyrolysis oil and biochar using Perkin Elmer 2400 CHN Analyzer.

The water content of the pyrolysis oil was measured by a volumetric Karl Fisher titrator (Mettler Toledo, V30) with combritant 5 Keto (Merck) as a titrant and Combisolvent Keto (Merck) as a solvent. The calorific values of the pyrolysis oil and biochar were also verified by using a bomb calorimeter IKA-WERKE (2000). Thermogravimetric analysis (TGA) was performed using a TA Instruments Model QA50 at heating rate 10°C/ min with 60 mL/min of N₂.

The organic compound of pyrolysis oil was identified by using a Gas Chromatography /Mass (GC-MS). The GC-MS analysis was carried out with an Agilent Technology model 7890A series. A

BPX-5 capillary column was selected with 30mm of diameter, 0.25 μm of its film thickness. The oven temperature was held at 35°C for 2 min before and raised to 250°C with a heating rate 20°C/min and held for 20 min. Helium with 99.99% purity used as a carrier gas with 1.5 mL/min of flowrate. The injector and detector temperatures were set constantly at 280°C.

The composition of non-condensable gas formed from pyrolysis process was collected in the gas bag and tested using a Shimadzu GC-8A Gas Chromatography /Thermal Conductivity Detector (GC-TCD), with a Davidson Grade 12 Silica gel packed column for CO₂ detection and a Molecular Sieve 5A packed column to detect the presence of CH₄, O₂, CO, and H gases.

6. Results and discussions

6.1 Products yields

Figure 2 shows the co-pyrolysis effect of temperatures (450,500,550 and 600°C) on products yields. With the increase of temperature from 450°C to 550°C, the yield of pyrolysis oil and NCG increased while the yield of biochar decreased. However, the yield of pyrolysis oil dropped at temperature 600°C with 26.67 wt.%). The secondary cracking reaction was taking place by the conversion of pyrolysis vapors and char into NCG at elevated temperatures. Maximum pyrolysis oil is produced at temperature 550°C with 36wt.%, 19.33 wt.% and 44.67 wt.% of pyrolysis oil, biochar, and NCG respectively. This temperature considered as the maximum temperature for co-pyrolysis of rice straw and PET.

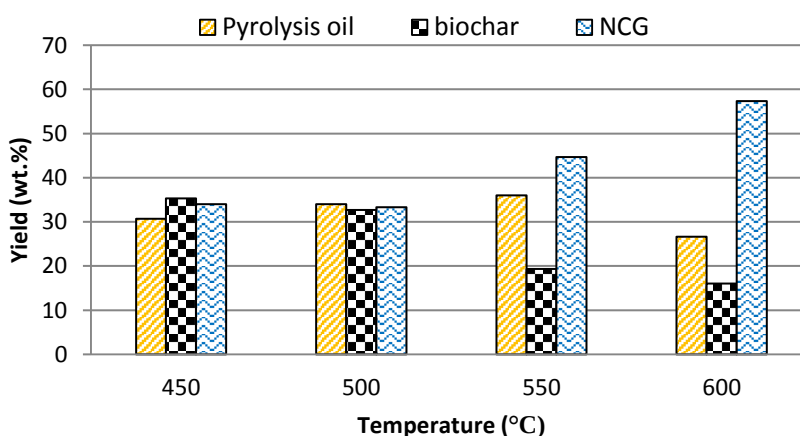


Figure 2. Co-pyrolysis products yield by different temperatures at ratio 1:1.

6.2 Proximate and elemental analysis

Table 2 shows the proximate and ultimate analysis of co-pyrolysis products for pyrolysis oil and biochar. There was some reduction of moisture content in the biochar yield compared to feedstocks (Table 1) due to dehydration during the heating process. The amount of volatile matter decomposed into vapors and reduced the amount of volatile matter in biochar. It is also noted that by mixing with PET resulted in an increase in calorific value for products yield. Carbon and hydrogen content in co-pyrolysis oil and biochar from rice straw and PET is higher because plastics contained high C and H [8] compared from feedstocks only. Higher carbon content and calorific values in biochar benefits to agriculture session as soil improver [9]

Table 2. Proximate and elemental analysis of co-pyrolysis products.

Proximate analysis, wt. %	RS: PET		RS only	
	Biochar	Pyrolysis oil	Biochar	Pyrolysis oil
Moisture	2.8	-	-	-
Ash	12.9	-	-	-
Volatile	48.70	-	-	-
Elemental analysis, wt. %				
C	73.69	46.19	57.50	9.47
H	1.71	13.71	2.61	11.43
N	0.74	0.14	1.09	0.45
O	23.86	39.96	38.80	78.65
Calorific value (kJ/g)	27.64	13.98	10.84	8.75
Water content (wt. %)	-	52.46	-	66.87

6.3 GC-MS analysis

Pyrolysis oil is a complex mixture of abundant chemical compounds [10]. Table 3 shows the GC-MS chromatograms of pyrolysis oil composition from co-pyrolysis of rice straw and PET at 550°C. More than 100 peaks were detected and only high degree of probability and peaks area greater than 0.1% were listed. Referring to Table 3, the main chemical group in the pyrolysis oil produced from the co-pyrolysis of rice straw and PET included aldehyde, ketones, acids, aromatic and phenol. Compounds consisting abundant of hydrogen and carbon were identified in the pyrolysis oil.

Table 3. Composition of pyrolysis oil

Compounds	Group	Rt (min)	% Area
Acetaldehyde (C ₂ H ₄ O)	Aldehyde	1.487	5.20
Ethanol (C ₂ H ₆ O)	Alcohol	1.535	3.36
Acetone (C ₃ H ₆ O)	Ketone	1.579	4.98
Formic acid (CH ₂ O ₂)	Acid	1.670	1.83
2-propanone (C ₃ H ₆ O)	Ketone	2.086	13.37
Propanoic acid (C ₃ H ₆ O ₂)	Acid	2.184	3.15
Acetoin (C ₄ H ₈ O ₂)	Ketone/hydroxyl	2.329	1.43
1-Hydroxy-2-butanone (C ₄ H ₈ O ₂)	Ketone	2.751	2.70
Cyclopentanone (C ₅ H ₈ O)	Ketone	2.967	0.50
Pyridine (C ₅ H ₅ N)	Aromatic	3.253	0.23
Butanone (C ₄ H ₈ O)	Ketone	3.642	0.40
2-cyclopentanone (C ₅ H ₆ O)	Ketone	3.718	0.44
Butyrolactone (C ₄ H ₆ O ₂)	Ketone	4.334	0.62
Benzaldehyde (C ₇ H ₆ O)	Aldehyde	5.090	0.20
Phenol (C ₆ H ₆ O)	Phenol	5.252	0.11
Acetophenone (C ₈ H ₈ O)	Ketone	6.608	0.39
<u>Benzoic acid (C₇H₆O)</u>	<u>Acid</u>	8.174	16.14
<u>Ethanone (C₈H₁₄O)</u>	<u>Ketone</u>	12.021	0.28

6.4 Non-condensable analysis

Figure 3 shows the composition analysis of non-condensable gases which comprises of nitrogen (N_2), hydrogen (H), methane (CH_4), carbon dioxide (CO_2), and carbon monoxide (CO). Decarboxylation formation from CO_2 , and CO mainly from the reaction between CO_2 and steam which porous char surface of the biomass [11]. Co-pyrolysis process produces a high amount of carbon oxides with 35 vol.% of carbon monoxide and 27 vol.% of carbon dioxide. Some of the researchers suggested the utilization of NCG could be recycled back as heat source into pyrolysis reaction [8][9]. Advantages of recycling the NCG was it has potential to increase the liquid and char yields. Besides, it can also increase the high heating value and pH of pyrolysis oil as well as decreased the density and viscosity [14]

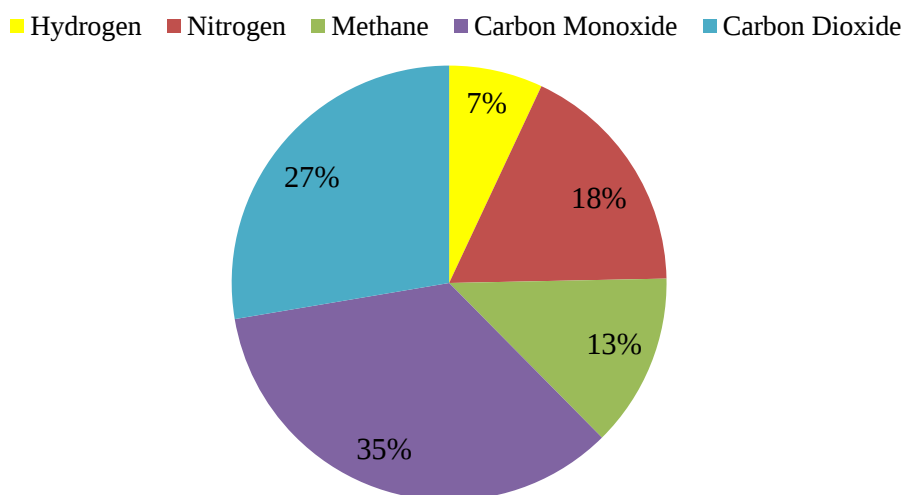


Figure 3. Composition analysis of non-condensable gases.

7. Conclusions

In this work, co-pyrolysis of rice straw and PET experiments were performed using fixed bed drop type pyrolyzer in order to assess the effect of different temperatures (450,500,550 and 600°C) on products yields. As the reaction temperature rises, the pyrolysis oil yield increases, until it reaches 550°C, where it obtained the highest yield of pyrolysis oil with 36 wt.%. The relatively low calorific value was recorded for pyrolysis oil with 13.98 kJ/ g due to high water content with 52.46 wt.%. However, comparing the calorific value of the co-pyrolysis with the pyrolysis of rice straw alone, a calorific value significantly increased at 60 wt.%. The GC-MS analysis detected aldehyde, ketone, acid, aromatic and phenol groups in pyrolysis oil. NCG from co-pyrolysis of rice straw and PET which comprises (7 vol.%)H, (18 vol.%) N_2 , (13 vol.%) CH_4 , (35 vol.%) CO and (27 vol.%) CO_2 .

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