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Fast Pyrolysis of Rice Husk in a Drop Type Pyrolyzer for Bio-oil and Bio-char production

[1]Salman Raza Naqvi, [1]Yoshimitsu Uemura and [2]Suzana Yusup

[1]*Centre for Biofuel and Biochemical Research, Chemical Engineering Department Biomass Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Tronoh, Perak, Malaysia.*
[2]*Biomass Processing Lab, Green Technology, Mission Oriented Research, Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Tronoh, Perak, Malaysia.*

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ABSTRACT

Rice husk is abundant lignocellulosic biomass which could be a potential alternative renewable and sustainable resource for production of bio-fuel and power generation. In this paper, experiments have been carried out in a drop type fixed-bed reactor by using rice husk as a feedstock in a fast pyrolysis process. The impact of the reaction temperature (350, 400, 450, 500, 550 and 600°C) on products yield and characteristics was studied. The pyrolysis temperature has a vital role on bio-oil and bio-char production. The amount of rice husk used for each experiment was 19 g. The physical and chemical properties of bio-oil and bio-char were characterized. The highest bio-oil yield of 35.5 wt.% was obtained at the pyrolysis temperature of 450°C. Bio-char yield showed decreasing trend (56.63-33.35 wt.%) with increasing the pyrolysis temperature while the gas yield increased (18.52-39.35) with the increment of pyrolysis temperature. These observations were attributed to the secondary cracking of the pyrolyzed vapor and decomposition of the solid. The Carbon content increased with increasing pyrolysis temperature, from 48.18 wt.% at 350°C to 68.09 wt.% at 600°C. The finding showed that the bio-char samples produced at higher temperature are more stable. The energy density of bio-char was observed to be higher than raw rice husk and the produced bio-oil. The highest energy density of the bio-char was 20.25 (MJ/kg) as compared to raw rice husk (15.75 MJ/kg) and the bio-oil (12.34 MJ/kg). Bio-oil properties including properties (water content, acidity, density and calorific value) were analysed and reported. Bio-oil produced at the pyrolysis temperature of 450°C has high energy density and less oxygen content which results low acidity. GC-MS peak area percentage showed that the bio-oil exhibited variety of chemical groups such as acids, carbonyls, furans, phenols, sugars and aromatic hydrocarbons. FT-IR of bio-char at higher temperature indicated that the formation of aromatic functional group.

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INTRODUCTION

Lignocellulosic biomass residues have recognized as suitable species capable of high energy outputs to replace conventional fossil fuels. Rice husk has identified as one of the most viable renewable energy sources from agricultural biomass residues, because it is abundant, cheap and does not require significant effort to collect (Ji-lu 2007, Tsai 2007, abu-bakar 2013). Malaysia has abundant lignocellulosic biomass generated from agricultural sector (Aljuboori 2013). Annually 330,000 ton of rice husks (dry basis) are generated currently in Malaysia (Shafie 2012).

Fast pyrolysis is one of the most promising thermochemical processes of lignocellulosic biomass utilization which converts the biomass into bio-oil, bio-char and non-condensable gases (Bridgwater 1999). Thefast pyrolysis is a thermal degradation of material in the absence of oxygen. Bio-oil is the liquid product of the fast pyrolysis process and regarded as a green chemical source for production of bio-fuel. Bio-char is a carbon rich and porous material which contains mineral nutrients, which is a good adsorbent of nutrients for soil amendment. The chemical composition of rice husk consists of cellulose 42.4 wt.%, hemi-cellulose 22.6 wt.%, and lignin 26.4 wt.%, respectively. In literature few studies regarding fast pyrolysis of rice husk using fixed-bed and fluidized-bed reactor were discussed (Natarajan 2009, Tsai 2007).(Lu 2008) showed that the rice husk bio-

Corresponding Author: Salman Raza Naqvi, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Malaysia.
E-mail: saloo.naqvi@gmail.com

oil is a potential liquid fuel but is thermally unstable which may cause an increase in the viscosity and water content, thus leading to phase separation.

The objective of this study is to investigate the production of bio-oil and bio-char in a drop type pyrolyzer from rice husk fast pyrolysis. The products were characterized to study their properties.

MATERIALS AND METHODS

The biomass tested for this experimental study was rice husk obtained from a rice mill in Perak, Malaysia. The biomass was dried in an electrical oven for 24 h at 105 °C to ensure reduction of moisture. Before pyrolysis, the biomass was passed through in a high speed rotary cutting mill and then sieved to give the particle size range (355 to 500 µm). Table 1 presents the proximate and ultimate analysis of rice husk. The proximate analysis was performed to measure the moisture content, ash content, and volatile matter of solid biomass using the ASTM standards mentioned by (Abu-Bakar 2013).

A drop type fixed-bed pyrolyzer was used to conduct the fast pyrolysis experiments. The experimental setup consisted of a cylindrical reactor made of stainless steel with 53 mm internal diameter and 166 mm height. The pyrolyzer was installed inside an electrical heater and was insulated to enable the heating of the reactor up to 600 °C. The reactor was equipped with a biomass holder and both vacuum and nitrogen lines used to replace the air inside the pyrolyzer with nitrogen. To record the pyrolysis temperature, a K-type thermocouple was inserted inside the pyrolyzer in the reaction zone. The pyrolyzer was connected to ice-trap immersed in ice-water bath to condense the pyrolysis vapors. The outlet of the ice-trap was connected with the gas sampling bag to collect the non-condensable gases. Experiments were carried out to evaluate the impact of the pyrolysis temperature on products yield. The amount of rice husk used for each run was 19 g. The rice husk samples were pyrolyzed in the pyrolyzer between 350 to 600 °C pyrolysis temperatures with 50 °C intervals. The total experimental time was 10 min. The pyrolysis process resulted in solid, liquid and gas products. The solid product (bio-char) remained in the reactor was collected and weighed. The liquid product (bio-oil) was collected in a trap maintained at the temperature of 0 - 5°C and weighed. The mass of gas product was estimated from the overall material balance.

RESULTS AND DISCUSSION

The analysis showed in Table 1 that rice husk comprises of high volatiles and high ash content. This large ash content could negatively affect the high quality bio-oil production.The impact of pyrolysis temperature on products yield is depicted in Fig. 1. The result indicated that the yield of bio-char decreased with the increasing temperature. This trend can be described by the pyrolysis rate increases with temperature. From the pyrolysis temperature 350 to 450 °C, the bio-oil yield increased and then decreased up to 600 °C.The highest bio-oil yield of 35.5 wt.% was achieved at the pyrolysis temperature of 450 °C. The gas yield increased with the incremental of pyrolysis temperature. These observations might be attributed to the secondary cracking of the pyrolyzed vapor and decomposition of the solid, which became significant at higher temperatures than 450 °C.

Table 1: Characteristics of Rice husk

Proximate analysis (dry basis)	wt.%
Moisture	1.37
Ash	11.98
Volatile matter	74.53
Fixed carbon	12.11
Ultimate analysis (dry and ash-free)	wt.%
Carbon	42.78
Hydrogen	5.77
Nitrogen	0.34
Oxygen	51.18
HHV (MJ/kg)	15.75
O/C (molar ratio)	0.89
H/C (molar ratio)	1.59
Empirical Formula	$CH_{1.59}N_{0.006}O_{0.89}$

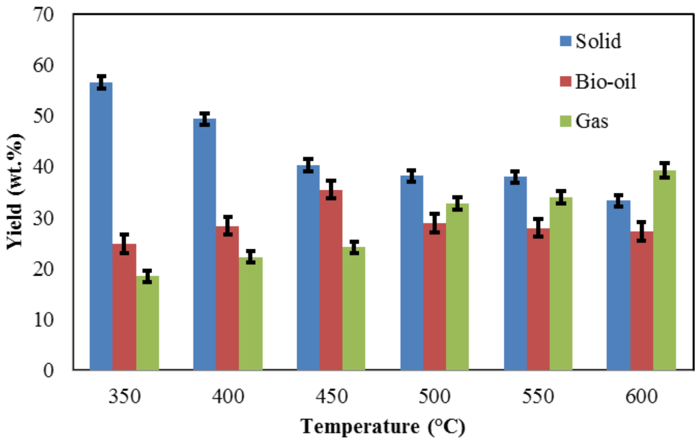

Fig. 1: Effect of temperature on pyrolysis products yield

A similar pattern has been found in fixed-bed pyrolyzer of rice husk biomass (Tsai 2007, Heo 2010, Ji-lu 2007).The ultimate analysis and properties of bio-oil at various pyrolysis temperatures were presented in Table 2. In all experiments, the bio-oils consisted of varying quantities of water which forms a stable single-phase mixture ranging from 60-68 wt.% water. It can be seen that the oxygen content decreased with the pyrolysis temperatures increasing from 350 to 450 °C, and at 450 °C the bio-oil has minimum oxygen content. The water formation increased with the increasing pyrolysis temperature.

Table 2: Ultimate analysis and Properties of Bio-oil at Various Temperatures

Ultimate analysis (wt.%)	Pyrolysis temperatures (°C)					
	350	400	450	500	550	600
Carbon	12.5	13.4	18.8	16.1	14.2	13.9
Hydrogen	7.85	9.9	10.5	9.85	8.75	6.5
Nitrogen	0.24	0.25	0.21	0.23	0.19	0.24
Oxygen [a]	16.1	14.6	9.99	10.4	11.1	13.4
Properties						
Water content (wt.%)	62.5	62.5	60.5	63.8	65.5	65.2
HHV [b] (MJ/kg)	8.24	8.76	10.5	9.14	8.56	8.05
Acidity (pH)	2.14	2.2	2.65	2.45	2.34	2.22
Density (kg/m^3) at 25 °C	1031	1034	1045	1031	1029	1028
Kinematic viscosity (cSt)	1.38	1.42	1.52	1.41	1.36	1.35

a O = 100- (C+H+N+H_2O)
b Measured through Bomb Calorimeter

The bio-char elemental analysis shows that carbon content increased while hydrogen and oxygen contents decreased with increasing pyrolysis temperature (Table 3).Losses in hydrogen and oxygen can be understood by breaking of weaker bonds within bio-char’s structure and the bio-char becoming highly carbonaceous at higher pyrolysis temperatures (Onay 2008). According to results, the high heating values of bio-char increased slightly with an increase in pyrolysis temperature. This could be due to increase in carbon content in bi-char with increased with pyrolysis temperature. The surface area of bio-char increased with increasing temperature. Higher temperature causes more devolatilization, resulting more pore volume and greater surface area. The GC-MS peak areas of identified chemical compounds are depicted in Fig. 2. The chemical groups identified in the bio-oils were classified as acids, carbonyls, furans, phenols, sugars and hydrocarbons. These chemicals generate from the degradation of cellulose, hemi-cellulose and lignin present in the biomass. After fractioning, such compounds may be used as a feedstock for the production of useful chemicals. FTIR spectra of raw rice husk and the bio-char produced at 600 °C are shown in Fig. 3. The raw rice husk spectrum is found to be characteristics of generic oxygenated hydrocarbon as the biomass is dominated by cellulosic fraction. The major bands have disappeared in the bio-char sample at 600 °C and replaced by small well-defined peaks. The strong peak at 1044 cm-1 and sharp peak around 866 cm-1 providing good evidence for the presence of aromatic structures.

Table 3: Ultimate analysis, HHV and surface area of Raw RH & Bio-char produced at various temperatures.

Material	Carbon	Hydrogen	Nitrogen	Oxygen	HHV	Surface area (m^2/g)
Raw RH	42.78	5.77	0.34	51.11	16.24	2.1
RHC- 350	46.18	3.81	0.52	49.49	17.18	11.2
RHC- 400	53.33	2.06	0.59	44.02	18.32	21.2
RHC- 450	54.54	1.38	0.49	43.59	20.05	41.4
RHC- 500	56.93	1.31	0.43	41.33	21.52	78.5
RHC- 550	61.83	1.17	0.44	36.56	22.10	115.4
RHC- 600	68.09	0.28	0.36	31.27	24.71	198.5

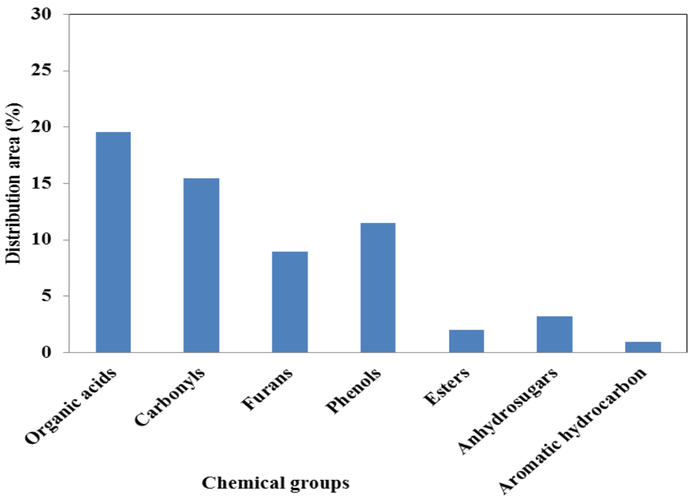

Fig. 2: Compounds identified in the bio-oil at 450 °C through GC-MS.

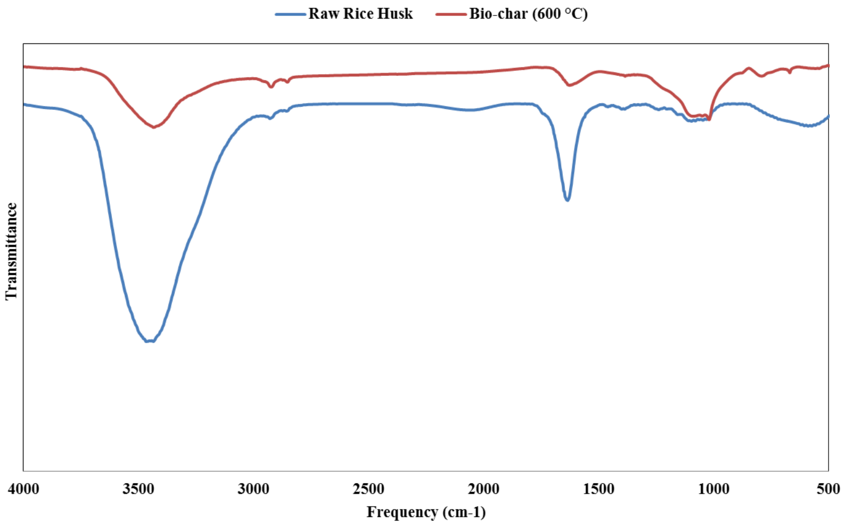

Fig. 3: FTIR spectra of raw rice husk and bio-char.

Conclusion:

Fast pyrolysis experiments were performed in a drop type fixed-bed pyrolyzer for the production of bio-oil and bio-char. The impact of temperature on yield and characteristic of bio-oil and bio-char is studied and discussed. The solid yield decreased while the liquid and gas yield increased. This might be due to the further decomposition of solid and secondary cracking of pyrolysis vapors in the pyrolyzer. The carbon content of bio-char increased with the increasing temperature showed that the char produced at higher temperature is more stable.

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