Applied Mechanics and Materials Vol. 625 (2014) pp 604-607
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doi:10.4028/www.scientific.net/AMM.625.604

Physiochemical properties of pyrolysis oil derived from fast pyrolysis of wet and dried rice husk in a free fall reactor

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Keywords: paddy husk, moisture content, fast pyrolysis, yield, quality

Abstract. Rice husk is considered as a massive agricultural lignocellulosic biomass residue for the production of bio-based fuels and chemicals products. The purpose of this study is to investigate the physiochemical properties of the pyrolysis-oil derived from wet and dried rice husk fast pyrolysis process. The experiments were performed in a drop type fixed-bed pyrolyzer at the pyrolysis temperature of 350 to 600 °C. The products, char, pyrolysis-oil and gas, yield are investigated. The pyrolysis-oil derived from dried rice husk contained higher Carbon and Hydrogen and less oxygen contents than the pyrolysis-oil obtained from wet rice husk. FT-IR results showed the oxygenated compounds present in both pyrolysis-oil. The pyrolysis oil from dried rice husk has higher concentration of hydrocarbons as compared to wet rice husk pyrolysis-oil. The dried rice husk pyrolysis-oil produced more phenols and less carboxylic acid as compared to wet rice husk pyrolysis-oil at 500 °C. More volatile released in dried rice husk conversion produced more volatile compounds. These findings suggest that the original moisture present in biomass samples is the major influencing parameter on the thermal degradation of biomass during fast pyrolysis process.

Introduction

Lignocellulosic biomass residues have the potential for conversion to many valuable energy products via thermal, mechanical and biological processes. Its utilization may be able to mitigate the CO_2 emission and fossil fuel depletion problems. Biomass residues can be converted to chemicals as well as solid, liquid or gas fuels by applying relevant technologies, some of which are still under development. One of the technologies attracting attention is fast pyrolysis of lignocellulosic biomass, which forms solid, liquid and gas products. Fast pyrolysis of lignocellulosic biomass is carried out at 400 to 600 °C under inert atmosphere using a few types of reactor including fixed bed [1,4,10,11], fluidized bed [5-7], free fall [8]. Malaysia has abundant lignocellulosic biomass generated from agricultural sector [2,10]. Annually 330,000 ton of rice husks (dry basis) are generated currently in Malaysia [10]. The amount is expected to increase to 770,000 ton of rice husks (dry basis) by the year of 2020. This objective of this study is to investigate the effect of moisture content of rice husk on the yield and quality of pyrolysis products.

Materials and Methods

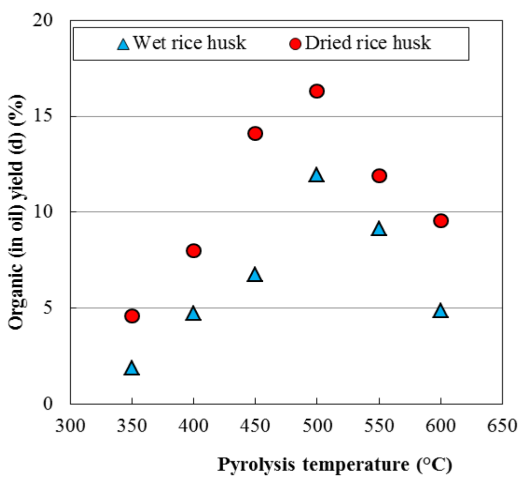
Feedstock and pyrolysis process

The rice husk was 8-10 mm long, 2-2.4 mm wide and 0.1-0.14 mm thick in size, obtained from local rice mill, Perak Malaysia. For oven-dried sample, the rice husk was dried in an oven for 24 h at 105 °C to ensure reduction of moisture. Table 1 shows the main characteristics of the wet and dried feedstocks. The analysis showed that the non-dried rice husk comprises high moisture and low volatile matter while the oven-dried sample has less moisture and high volatiles matter. The ultimate analysis was carried out with an Elemental CHNS/O 2400 analyzer. Higher heating value of biomass and bio-oil was measured by oxygen bomb calorimeter. The water content of the bio-oil was determined through Karl-Fischer titration. The pyrolysis experiments were carried in a drop type fixed-bed pyrolyzer. The reactor was equipped with a biomass holder, 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 to condense the pyrolysis vapors. The outlet of the ice-trap was connected with the gas sampling bag to collect the non-condensable gases. Both rice husk samples (dried and non-dried) were pyrolyzed at various pyrolysis temperature of 350 to 600 °C with 50 °C intervals. A 10 g sample was used pyrolyzed for each run. The pyrolysis process resulted in solid residue, pyrolysis oil and gas products. Yields of bio-char and bio-oil were determined based on the change in the mass of the rector and the condenser, respectively, before and after the pyrolysis experiment.

Table 1: Characterization of feedstocks

Rice Husk	Proximate analysis (dry basis, wt%)				HHV	Ultimate analysis (dry and ash-free basis, wt%)				
	Moisture	Ash	Volatiles	Fixed Carbon		Carbon	Hydrogen	Oxygen[a]	O/C (molar ratio)	H/C (molar ratio)
Wet	9.74	9.84	73.86	6.62	15.42	41.41	5.77	52.51	0.95	1.67
Dried	1.90	11.98	80.00	6.12	16.85	44.44	5.50	49.73	0.83	1.48

a By difference



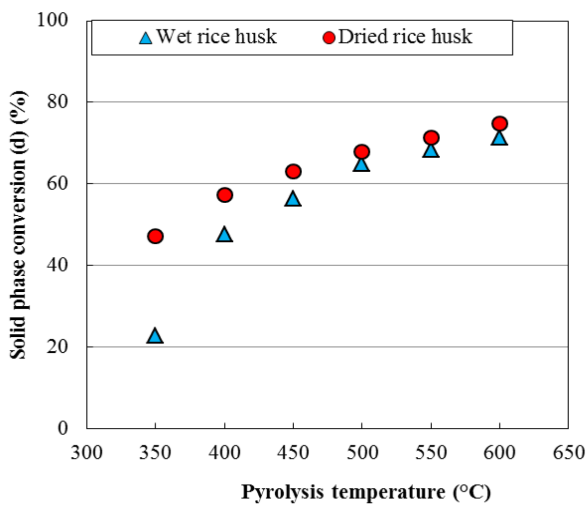


Fig. 1: (a) Organic liquid yield, (b) solid phase conversion yield, of wet and dried rice husk at various temperatures.

Results and Discussion

Yield and Physiochemical properties

It can be seen from the results presented in Fig. 1 that the wet rice husk showed high bio-char and less organics (in oil) yield than dried rice husk sample. On the other hand, dried rice husk has higher organic and less char yield. The possible reasons due to secondary reactions between organic vapor from pyrolysis and water vapor evolved from the biomass moisture. Similar observations have been described in fast pyrolysis by using agricultural wastes and wood derived material [4,8].

Table 2 shows the properties of wet and dried rice husk pyrolysis-oil. The dried rice husk oil has higher Carbon and Hydrogen contents than wet rice husk oils. At pyrolysis temperature of 500 °C, the dried rice husk oil has HHV of 11.98 MJ/kg and 50.24% water content as compared to 9.45 MJ/kg and 60.89% water content of wet rice husk oil. Dried rice husk released more volatile and produced better quality oil as compared to wet rice husk.

Table 2: Properties of wet and dried rice husk oils

Ultimate analysis (wt%)	350 ºC		400 ºC		450 ºC		500 ºC		550 ºC		600 ºC	
	dried	non-dried	dried	non-dried	dried	non-dried	dried	non-dried	dried	non-dried	dried	non-dried
C	12.35	9.90	13.88	9.98	15.35	10.54	17.85	12.00	16.85	12.10	15.76	11.45
H	8.90	7.45	9.75	9.45	10.21	10.13	10.50	10.00	10.05	8.90	9.65	8.65
N	0.42	0.35	0.38	0.4	0.36	0.42	0.42	0.45	0.39	0.37	0.31	0.35
O	78.33	82.30	75.99	80.17	74.08	78.91	71.23	77.55	72.71	78.63	74.28	79.55
Water content (wt%)	78.12	84.11	69.26	79.09	54.76	73.28	50.24	60.89	61.35	69.11	66.6	82.15
HHV (MJ/kg)	8.24	6.41	8.85	7.05	9.11	7.35	11.98	9.45	11.15	9.05	10.48	7.35
pH	2.32	2.11	2.48	2.14	2.61	2.15	2.71	2.21	2.65	2.19	2.49	2.16

The functional group composition of wet and dried rice husk oil are presented in Table 3. It indicated that both the oils have oxygenated compounds. Both oils contain moderate concentration of aromatic hydrocarbons but their quantities in dried rice husk oil are higher. Even though, both oils have similar functional groups but the water content in the wet rice husk oil is definitely high.

Table 3: FT-IR functional group compositions of wet and dried pyrolysis oil

Wave number range (cm^{-1})	Wave number (cm^{-1}) Wet rice husk oil	Wave number (cm^{-1}) Dried rice husk oil	Group	Class of compounds
3300-3900	3912, 3852 3758	3427	O-H stretching	Polymeric O-H, water impurities
3050-2000	2792	2619, 2067	C-H stretching	Alkanes
1750-1650	1714, 1634	1715	C=O stretching	Ketones, aldehydes, carboxylic acids
1650-1580	1597	1596, 1530	C=C stretching	Alkenes
1150-1490	1375	1474.7	NO2 stretching	Nitrogenous compounds
1470-1350	1420	1440, 1384	C-H bending	Alkanes
1300-950	1081, 1050	1240, 1169, 1072, 1050	O-H stretching O-H bending	Primary, secondary and tertiary alcohol, phenols, esters, ethers
950-650	924, 620	887, 812, 757, 693, 666		Aromatic compounds

Table 4 shows the peak area% of acetic acid and phenol of dried and wet rice husk oils. Phenol production is higher due to more volatile compounds produced. The effect of moisture strongly effect on phenol and aromatic hydrocarbon production. Acetic acid is one of compound formed due to degradation of hemi-cellulose.

Table 4: GC-MS area % of Acetic acid and phenol of wet and dried pyrolysis oil at 500 °C

	GC-MS area (%)	
Pyrolysis oil	**Acetic Acid**	**Phenol**
dried rice husk	11.99	18.54
wet rice husk	13.59	14.47

Conclusion

Experimental results of dried and wet rice husk fast pyrolysis using a drop type fixed-bed pyrolyzer were presented. The properties including (proximate and ultimate analysis of both biomass and their oil) and chemical characterization is shown and discussed. The organic liquid, bio-char and gas yields and quality of the produced bio-oil were determined. FT-IR and GC-MS results showed that the moisture affects strongly on the properties of oil. To produce better quality oil, the biomass should proceed through drying.

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