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Liquid Oil from Fluidized Bed Pyrolysis of Rice Husk Waste and Its Characterization

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ABSTRACT

Paddy is grown in most part of the world. About 20% by weight (wt%) of this paddy generates waste known as rice husk. The conversion of solid rice husk into liquid oil by fluidized bed pyrolysis is taken into consideration in this study. The pyrolytic products are oil, char and gas. In the fluidized bed pyrolysis system, rice husk is fed into the pyrolysis reactor in particle form. Silica sand is used as the fluidization medium and gas nitrogen as the carrier gas. The reactor and the preheater are heated by means of electrical ring heaters. The char is collected in cyclone and the vapors are condensed in condenser and collected in liquid collectors while the gas is flared. At a reactor bed temperature of 450°C for a feed size of up to 1 mm at a fluidization gas flow rate of 21 l/min, an oil yield of 40% by weight (wt%) of dry feed is obtained. The pyrolysis process conditions are found to have influence on the product yields. The oil is characterized by Fourier transform infra-red (FT-ir) spectroscopy and gas chromatography-mass spectrometry (GC-MS) techniques along with some physical properties determination.

1. INTRODUCTION

It is a fact that the conventional source of energy has been depleting at an alarming rate and hence the focus on alternative renewable source of energy is increasing. As a result biomass as a renewable energy source has continued to attract increased attention [1]. A lot of work in this area is in progress using different solid biomass as the feed material [1, 2]. Needless to say, paddy is one of the most produced crops in the world. About 20 wt% of paddy generates rice husk. It is estimated that over 100 million tons of rice husk are generated annually from which 90% is accounted for in the developing countries [3]. Mostly this is either under-utilized or unutilized as a source of heat energy. The disposal of this waste is also an environmental problem. According to a recent study of Yatim [4], Malaysia generates 3.41 million cubic meter of rice husk every year. It is creating waste management problem, especially in the rice milling sites. Thus an endeavor from the point of view of energy recovery from this rice husk waste by the thermochemical process of pyrolysis may be worthwhile. The characteristics of rice husk is presented in Table 1 [5, 6]. Besides, from a recent thermogravimetric analyser (TGA) study of rice husk [7], it appears that this husk may be used for energy recovery as a fuel. The thermogram from the thermogravimetric (TG) analysis at a heating rate of 40°C/min over nitrogen atmosphere indicates that devolatilization starts at around 250°C and completes at around 500°C. The maximum rate of devolatilization takes place at around 400°C at a rate of 0.3% weight loss/°C. Thus, the conversion

Table 1. Composition of solid rice husk.

Elemental composition % wt (dry ash free)		Proximate analysis [5] % wt (air dry)		Gross calorific value[6] MJ/kg	Average bulk density[6] kg/m^3
Carbon as (C)	64.582	Volatile matter	53.6	13.2	100
Hydrogen as (H)	3.149	Fixed carbon	15.8		
Nitrogen as (N)	0.939	Moisture	10.0		
Oxygen as (O)	22.787	Ash	20.6		
Sulphur as (S)	0.031				
Other elements	8.512				

of rice husk into liquid product by fluidized bed pyrolysis method may be considered as a promising option. The pyrolysis oil may be used as a fuel in boiler, dedicated diesel engines and industrial gas turbines for the purpose of power generation [8]. In addition to this, there are scopes to upgrade the oil to obtain high grade fuel and valuable chemicals [9]. The solid char can be used for making activated carbon, rice husk ash cement, reinforcing fillers in plastic and rubber goods [10] and as fertilizer and soil conditioner. Most recently some work has been carried out with rice husk as the feed material to produce liquid oil by using the fluidized bed pyrolytic thermochemical conversion process at the Thermodynamics Laboratory of Universiti Teknologi Malaysia.

2. MATERIALS AND METHODS

2.1 Biomass

The biomass used was rice husk particles milled and sieved up to 1 mm size. It was then oven-dried and stored in the laboratory under dry conditions.

2.2 Pyrolysis System

The rice husk was pyrolysed in an externally heated 50 mm diameter and 30 mm high stainless steel fluidized bed pyrolysis reactor system in an inert atmosphere of nitrogen as the fluidizing gas and dry silica sand as the bed material. The fluidization gas flow rate was maintained at 21 l/min. The sand particle suitable for fluidization was found to be 212 to 300 micrometer (μm) and this is the size used in the study. The system consisted of fluidized bed reactor, gas preheater, feed container with a screw feeder, solid-gas cyclone separator, liquid condenser and liquid collectors. The flow sheet of the process is given in Fig. 1. The liquid oil and the solid char were collected separately and the gas with the non-condensable vapors was flared. In order to feed the particles into the reactor a motor driven screw feeder was used. The

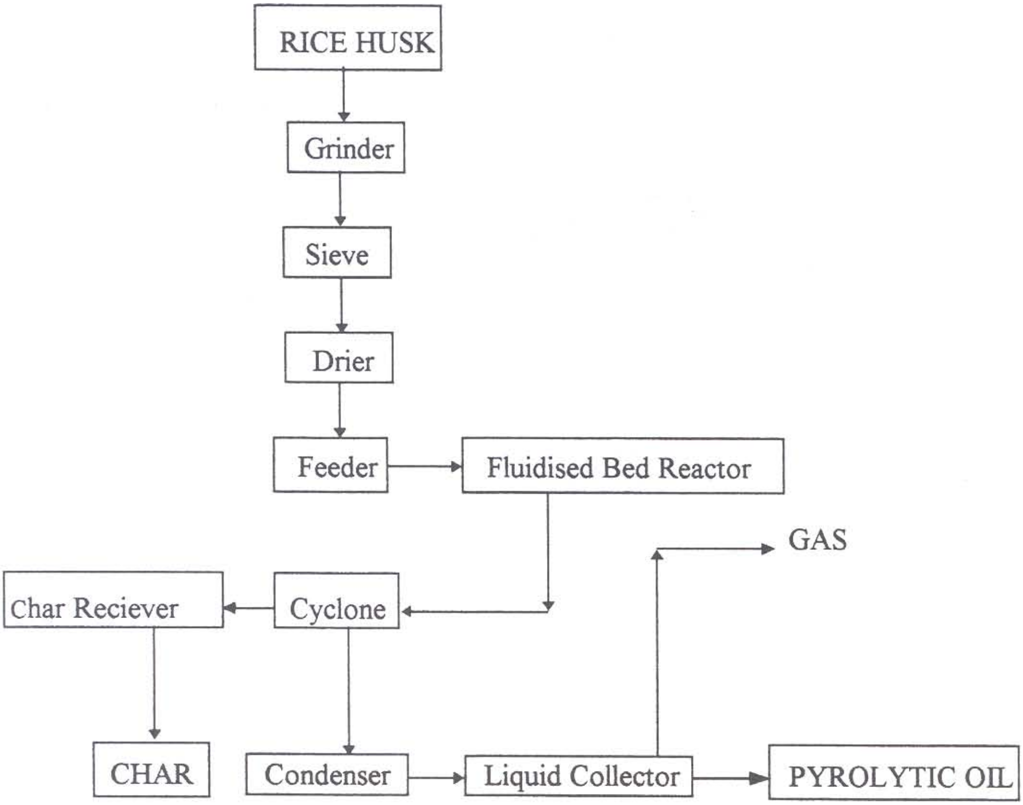

Fig. 1. Flow sheet of rice husk pyrolysis process.

feed rate was maintained at around 0.3 kg/hr. The reactor bed was heated by means of an electrical heater of 1 kilowatt (kW) power. The heating was such that fast fluidization had been maintained. Before entering the fluidized bed reactor the fluidization gas was preheated by another electrical preheater of 1 kW power. The temperature of the reactor was controlled by means of a temperature controller and was measured by a thermocouple within the bed. The temperature of the reactor was maintained in the range of 400°C to 500°C. The system was maintained at a pressure slightly above atmosphere. The fluidization gas flow rate was measured and controlled by gas flow meters. The separation of the char was done by a method known as 'blow-through' mode where the char was entrained and blown from the bed while retaining the sand in the bed [1]. The vapors and the gases were then passed through a water-cooled condenser. The liquid was collected in two ice-cooled collectors in series. In this experimental study the influence of reactor bed temperature and fluidization gas flow rate on the liquid and the solid products yield was studied. The reactor bed temperature was varied between 400°C and 500°C while the fluidization gas flow rate was maintained between 15.34 l/min and 23.64 l/min.

2.3 Oil Product Analysis

Fourier Transform Infra-red (FT-ir) Analysis

The pyrolytic oil was analyzed for its compositional group identification by Fourier transform infra-red spectroscopy. The FT-ir instrument of type Perkin Elmer 1650 model-Series 1600 and an on-line plotter were used to produce the ir-spectra of the derived liquid. A thin uniform layer of the liquid was placed between two salt cells and was exposed to infra-red beam. The absorption frequency spectra were recorded and plotted. It had provided the absorption spectrum in percentage incident intensity, along the wave numbers 4000 to 500 per unit centimetre (cm^{-1}). The standard ir-spectra of hydrocarbons were used to identify the functional group of the components of the derived liquid.

Gas Chromatography-mass Spectrometry (GC-MS) Analysis

In order to identify the individual compounds in the pyrolytic oil, it was analyzed by GC-MS technique. The system was a GC-17A + QP5000 Shimadzu unit with J & W scientific capillary column of DB-1. The temperature program was 50°C for 2 min followed by a 3°C/min heating rate to 250°C. The detector used was flame ionization detector (FID).

Physical Properties Analysis

The pyrolytic oil product at the maximum liquid yield condition was then characterized for its physical properties determination following the standard test procedures. The properties determined were: heating value, pH value, kinematic viscosity, moisture content and ash content.

2.4 Solid Char Analysis

The char obtained was further analysed for its elemental composition following standard testing procedures. This was subjected to carbon, hydrogen, nitrogen, oxygen and sulphur (CHNOS) elemental analysis by standard testing method.

3. RESULTS AND DISCUSSION

3.1 Product Yields

The products obtained from the pyrolysis process are liquid oil, solid char and gas. The liquid was found to be a single-phase dark color product. From the study it was observed that the yields of liquid product and solid char vary with process conditions. The maximum liquid yield was obtained at a temperature of 450°C for a fluidization gas flow rate of 21 l/min. This was found to be 40 wt% of dry feed while the solid char yield was 53 wt% of dry feed. At temperature lower than 450°C the liquid yield was lower and the char yield was higher. The char yield was 57 wt% of dry feed at 400°C with a liquid yield of 29 wt% only. On the other hand at temperature higher than 450°C the char yield was found to be less along with a reduction in liquid yield; however the gas yield was observed to be higher. The char yield was only 41 wt% of dry feed at 500°C with a liquid yield of 28 wt%. The reason for lower liquid yield at lower temperature may be due to the fact that the temperature rise was not enough for complete pyrolysis to take place yielding less liquid and more solid char. On the other hand at higher temperature there is a possibility of secondary decomposition reaction to take place in the free board section of the reactor rendering lower liquid and char yield. The variation of liquid yield with reactor bed temperature is presented in Fig. 2.

The influence of fluidization gas flow rate on the liquid and solid yields at 450°C is presented in Fig. 3. It was observed that the liquid yield was increasing with the flow rate up to 21 l/min. The bed sand was found to be elutriated with char disturbing the fluidization process when the flow rate was increased to 23.64 l/min. This may be due to the fact that at lower fluidization gas flow rate the fluidization was not achieved completely and hence the fast pyrolysis reaction could not take place completely. Besides there is a possibility of secondary reaction to take place because of lower gas flow rate. At higher fluidization gas flow rate particles may not get sufficient time to be heated up adequately to complete the reaction causing lower liquid yield. Besides the solid char with the fine particles may be blown away very quickly from the reactor bed yielding higher amount of char. A similar trend is observed for char yield as well as presented in Fig. 3.

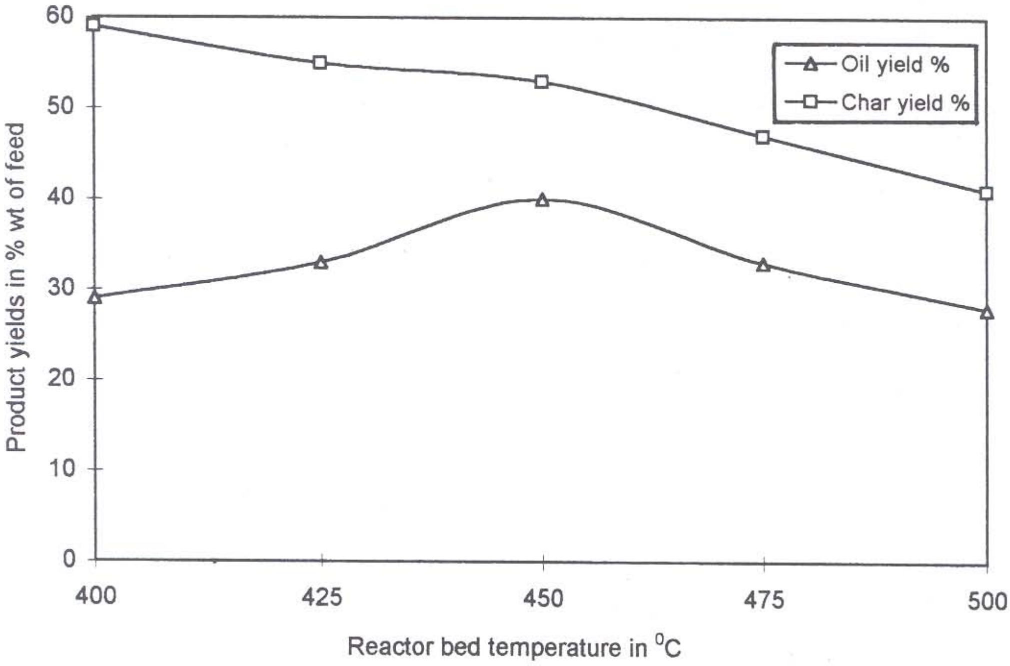

Fig. 2. Effect of reactor bed temperature at a fluidization gas flow rate of 21 l/min on product yields.

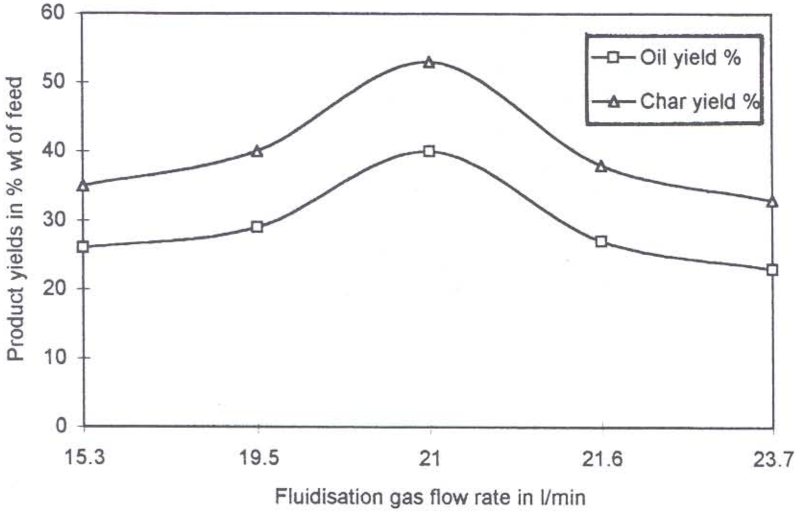

Fig. 3. Effect of fluidization gas flow rate at a reactor bed temperature of 450°C on product yield.

3.2 Oil Product Analysis

Fourier Transform infra-red (FT-ir) Analysis

From the Fourier transform infra-red spectroscopy of the derived pyrolytic oil, the FT-ir functional groups and the indicated compositions of the liquid product are presented in Table 2. The presence of water impurities and other polymeric hydroxyl group (O-H) in the oil are indicated by the broad absorbance peak of O-H stretching vibration between 3600 cm^{-1} and 3200 cm^{-1}. The presence of alkanes is indicated by a weak absorbance peak of carbon hydrogen (C-H) stretching between 3000 cm^{-1} and 2800 cm^{-1} and the C-H bending deformation vibrations between 1465 cm^{-1} and 1350 cm^{-1}. The absorbance peaks between 1780 cm^{-1} and 1640 cm^{-1} present the carbonyl group (C=O) stretching vibration indicating the presence of ketones and aldehydes. The presence of both O-H and C=O stretching vibrations also indicate the presence of carboxylic acids and their derivatives. The possible presence of alkenes are indicated by the absorbance peaks between 1680 cm^{-1} and 1580 cm^{-1}. The overlapping peaks between 1300 cm^{-1} and 950 cm^{-1} are due to the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters showing the carbon oxygen (C-O) stretching and O-H deformation vibrations.

Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

The identification and quantification of the individual compound present in the pyrolytic liquid oil are carried out with GC-MS techniques. This is presented in Table 3. The chromatograph is presented elsewhere [12]. From this it appears that the compounds are highly oxygenerated and therefore the oil is very acidic and hence, very much corrosive in nature. This is the underlying reason for the pyrolytic oil to possess lower heating value since carbon oxygen (C-O) bonds do not release energy during combustion. The proportion of phenol and its derivatives is also quite high indicating the suitability of liquid oil to be condsidered for value-added chemicals. It is interesting

Table 2. The FT-ir functional groups and the indicated compositions of rice husk pyrolitic oil.

Frequency range cm^{-1}	Group	Class of compound
3200 - 3600	O-H stretching	Polymeric hydroxyl (O-H), water impurities
3000 - 2800	C-H stretching	Alkanes
1780 - 1640	C=O stretching	Ketones, aldehydes, carboxylic acids
1680 - 1580	C=C stretching	Alkenes
1550 - 1490	$-NO_2$ stretching	Nitrogenous compounds
1465 - 1350	C-H bending	Alkanes
950 - 1300	C-O stretching	Primary, secondary and tertiary alcohols
	O-H bending	Phenol, esters, ethers

Table 3. Identification and quantification of the chemical compounds in rice husk pyrolytic oil.

Chemical compounds	Quantity in wt% of pyrolitic oil produced
2-Methyl propane	3.5
Acetic acid	13.2
3-Hydroxy 2-propanone	22.4
2-Methyl pentyl ether	1.01
Butandial	9.87
Allyl acetate-2-ene	6.96
Cyclopentenone	1.61
2-Furanaldehyde	4.55
2-Butanone	1.63
Methyl crotonate	2.50
4-Methyl butaroyate-1-ene	2.13
Cyclopentanone	2.83
5-Methyl furanaldehyde	1.96
Phenol	1.28
3-Methyl cyclopentanedione	2.70
2-Methoxy phenol	5.05
4-Ethyl phenol	1.25
4-Methyl 2-methoxy phenol	2.03
Ortho-hydroxy phenol (Pyrocatechol)	2.13
4-Ethyl 2-methoxy phenol	0.908
4-Propene 2-methoxy phenol (Eugenol)	1.53

to note the fact that unlike other biomass-derived pyrolytic oil, the polycyclic aromatic hydrocarbon (PAH) compounds are not found to be present in the oil palm shell pyrolytic oil which is very much carcinogenic in nature [13]. The chemical compounds present in the pyrolytic oil are grouped according to their carbon numbers and are presented in Table 4. The oil is found to be in betweeen C_2 to C_{10} groups.

Physical Properties Analysis

The pyrolytic oil physical properties determined by standard test procedures are presented and compared with pyrolytic oils from other sources as shown in Table 5 [5, 14]. The properties were found to be in the comparable range. Although the feed was oven-dried to less than 2% of moisture content, the water content in the oil is found to be higher which may be due to the formation of pyrolysis reaction water. However, this range of water in pyrolytic oil is usual. The oil is found to be viscous as well. This is, however within the typical pyrolytic oil viscosity range. Although the heating value of the oil is found to be less than conventional petroleum derived fuel, nevertheless this is more than that of the solid rice husk. The oil is acidic as well as corrosive in nature. The ash content in the oil is very much negligible.

3.3 Solid Char Analysis

The solid char was found to be dark in color. This was subjected to elemental analysis by standard testing method UOP 868-88. The carbon, hydrogen, nitrogen, oxygen and sulphur (CHNOS) values from its elemental analysis are presented in Table 6. The char is found to be highly oxygenated with a trace of nitrogen and no sulphur at all.

Table 4. Composition of rice husk pyrolytic oil.

Compounds having carbons of	Quantity in wt% of pyrolitic oil produced
2	13.2
3	22.4
4	17.5
5	18.08
6	9.08
7	5.05
8	3.28
9	0.91
10	1.53

Table 5. Physical properties of rice husk pyrolytic oil and its composition.

Physical properties	Method of testing	Rice husk pyro-oil	Palm shell pyro-oil	Typical pyro-oil
Heating value (MJ/kg)	DIN 51900	19.9	22.1	18
pH (-)	In house	2.25	2.7	2.5
Moisture content (%)	Karl Fischer titration	32.2	10	20
Kinematic viscosity (CST) @ 40°C	ASTM D445	86.8	14.6#	134
Ash content (%)	ASTM D482	0.06	0.10	0.10

Measured @ 50°C

Table 6. Elemental analysis of char from rice husk pyrolysis.

Elemental composition	wt%
Carbon as (C)	39.159
Hydrogen as (H)	4.899
Nitrogen as (N)	0.364
Oxygen as (O)	39.549
Sulphur as (S)	0
Other elements	16. 029

4. CONCLUSIONS

- The maximum liquid yield is found to be 40 wt% of feed with a char yield of 53 wt% at a reactor bed temperature of 450°C for a fluidization gas flow rate of 21 l/min. The liquid product yield is found to be increasing with pyrolysis reactor bed temperature up to a certain temperature after which it is decreasing with temperature. The char yield is found to be decreasing with the rise of pyrolysis reactor bed temperature for a certain fluidization gas flow rate.
- The liquid yield is found to be increasing with fluidization gas flow rate up to 21 l/min at a reactor bed temperature of 450°C. The solid char yield is also found to follow a similar trend.
- The moisture content is found to be a bit higher. The liquid is acidic in nature with a very negligible amount of ash. The heating value of the fuel is quite low, however, the value is similar to other biomass derived pyrolytic oil. The liquid is viscous in nature.
- The liquid contains a very large number of oxygenated compounds. Hence, it is important to deoxygenate the liquid by some upgrading technology.
- The liquid contains a very good percentage of monocyclic aromatic phenolic compounds. Hence, its prospect to be used as high-value chemicals need to be investigated. The liquid oil does not contain PAH compounds.
- The char is found to be oxygenated with a trace of nitrogen and no sulphur.

5. ACKNOWLEDGEMENT

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6. NOMENCLATURE

FT-ir = Fourier transform infra-red
GC-MS = gas chromatography-mass spectrometry
TGA = thermogravimetric analyser
TG = thermogravimetric
DB-1 = durabond-1
FID = flame ionization detector
pH = negative logarithm of hydrogen ion concentration
O-H = hydroxyl stretching
C-H = carbon hydrogen stretching and bending
C=O = carbonyl stretching
C=C = carbon carbon double bond stretching
$-NO_2$ = nitrogen dioxide stretching
C-O = carbon oxygen stretching
PAH = polycyclic aromatic hydrocarbon
C_2 = compound having a carbon number of 2
C_{10} = compound having a carbon number of 10
CHNOS = carbon, hydrogen, nitrogen, oxygen and sulphur analysis
ASTM = American society of testing materials

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