Journal of Energy & Environment 1 (1999) 9-16

A Comparative Study on the Pyrolytic Conversion of Rice Husk and Oil Palm Shell Solid Wastes

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Abstract

Biomass in the forms of rice husk and oil palm shell wastes is converted into value-added materials and energy by a fluidised bed pyrolysis process. The products are oil, char and gas. The product yields are compared; the optimum liquid yield condition identified and the liquid products characterized by FTIR, GC and GC/MS techniques. A comparison of the characteristics of the oils is carried out. In case of oil palm shell the maximum liquid product yield of 58 wt% of biomass fed is obtained while for rice husk this was found to be 40 wt%. The oils were found to be highly oxygenate containing acids, alcohol and phenols. The char was oxygenated with a reduced content of sulphur and nitrogen.

Nomenclature

FTIR	Fourier Transform infra-red
GC	Gas chromatography
GC/MS	Gas chromatography and mass spectrometry
GC/FID	Gas chromatography and flame ionization detector
O-H	Hydroxyl group
C_2	Compound containing a carbon number of 2
C_{10}	Compound containing a carbon number of 10
PAH	Polycyclic aromatic hydrocarbon
pH	Negative logarithm of hydrogen ion concentration
UOP	Universal Oil Company Product
C=O	Carbonyl stretching
C=C	Carbon-carbon double bond
C-H	Carbon hydrogen
C-O	Carbon oxygen
NO_2	Nitrogen dioxide
ASTM	American society of testing materials
DB-1	Dura bond-1
h^{-1}	Per unit hour
wt%	Weight percent
cm^{-1}	Per unit centimeter
d.a.f.	dry ash free
MJ kg^{-1}	Megajoule per kg
kg m^{-3}	Kilogram per cubic meter
cSt	Centistoke

Introduction

The conventional sources of fossil fuels have been depleting very fast as the demand for energy continues to outstrip supply and so necessitate the development of the renewable energy option. As a result biomass has been getting continued and increased attention. A lot of work in this area is in progress using different solid biomass as the feed material [1]. In this study two widely available waste materials, rice husk and oil palm shell have been taken into consideration. Rice is the staple food in many countries of the world and therefore, is widely grown all over the world. The world produces a significant amount of paddy rice from which about 20 wt% is generated as a waste known as rice husk. It is estimated that over 100 million tons per year are generated with 90 % accounted for by developing countries. Mostly this is an under-utilised source of heat energy. The disposal of this waste is also an environmental problem. According to Ngan and Ang [2], Malaysia generated more than 0.434 million tons of rice husk in 1994, the potential energy available from which is more than about 0.136 million tons of oil equivalent. It is creating waste management problem, especially in the rice milling sites. In the context of Bangladesh, a developing country, it has been generating more than 3.5 million tons of rice husk every year [3]. Apart from this it is a fact that Malaysia is the largest producer of palm oil in the world. It generates a significant amount of oil palm shell as solid wastes. This is true in case of some other ASEAN countries as well. According to a study of Yatim [4], Malaysia generates 7.7 million tons of empty fruit bunch, 6.0 million tons of fibre and 2.4 million tons of palm shell every year as wastes. Thus an endeavour from the point of view of energy recovery from rice husk and oil palm shell wastes by the most promising thermo-chemical conversion process of pyrolysis may be worthwhile. The elemental compositions of rice husk [5] and oil palm shell [6] are presented in Table 1. Besides from a recent TGA study of rice husk and oil palm shell it appears that these wastes may be used for energy recovery as fuel [7]. Thus, the conversion of rice husk and oil palm shell into liquid product by fluidised bed fast pyrolysis method may be considered as a promising option. The pyrolysis oil may be used as fuel in boilers, in dedicated diesel engines and in industrial gas turbines for power generation. Besides there are scopes to upgrade the oil to obtain high-grade fuel and valuable chemicals. The solid char can be used for making activated carbon, rice husk ash cement, reinforcing fillers in plastic and rubber goods [8] and as fertilizer and soil conditioner. The char has potential as solid fuel. Most recently some work has been carried out with rice husk and oil palm shell as feed materials to produce liquid oil by using the pyrolysis thermo-chemical conversion process at the Thermodynamics Laboratory of Universiti Teknologi Malaysia. This is highlighted in this paper in a comparative manner.

Table 1 Composition of solid rice husk and oil palm shell

Elemental composition wt % d.a.f.			Proximate analysis air dry wt %			Gross calorific value MJ kg^{-1}		Average bulk density kg m^{-3}	
	Husk	Shell		Husk	Shell	Husk	Shell	Husk	Shell
Carbon	44.22	55.35	Volatile matter	53.6	68.8	13.2	19.56	100	440
Hydrogen	5.06	6.43	Fixed carbon	15.8	20.3				
Nitrogen	0.50	0.37	Moisture	10.0	8.4				
Oxygen	41.81	38.01	Ash	20.6	2.3				

Experimental setup

Fig.1 presents the schematic of the fluidised bed fast pyrolysis system set-up. The system comprised of a gas preheating chamber, screw feeder, pyrolysis reactor, cyclone, char collector, condenser and liquid collectors. Nitrogen was used as the fluidising gas and silica sand of mean particle 256 μm as the bed material. The depth of the sand bed was maintained to 6 cm amounting a mass of 200 g. This was found to be the optimum depth of the bed resulting in good fluidisation behaviour from the previous hydrodynamic studies based on cold model studies with different bed depths, such as 4, 6 and 8 cm. Feed particle of oil palm shell of different sizes up to 1 mm obtained from Federal Land Development Authority (FELDA) Palm Oil Mills at Kulai (Johore), Malaysia was used as one of the feed materials. The size distribution of the particles were as follows:

i. less than 150 μm (mean particle size 75 μm)
ii. 200-300 μm (mean particle size 250 μm)
iii. 212-425 μm (mean particle size 318 μm)
iv. 300-500 μm (mean particle size 318 μm)
v. 500-1000 μm (mean particle size 750 μm)

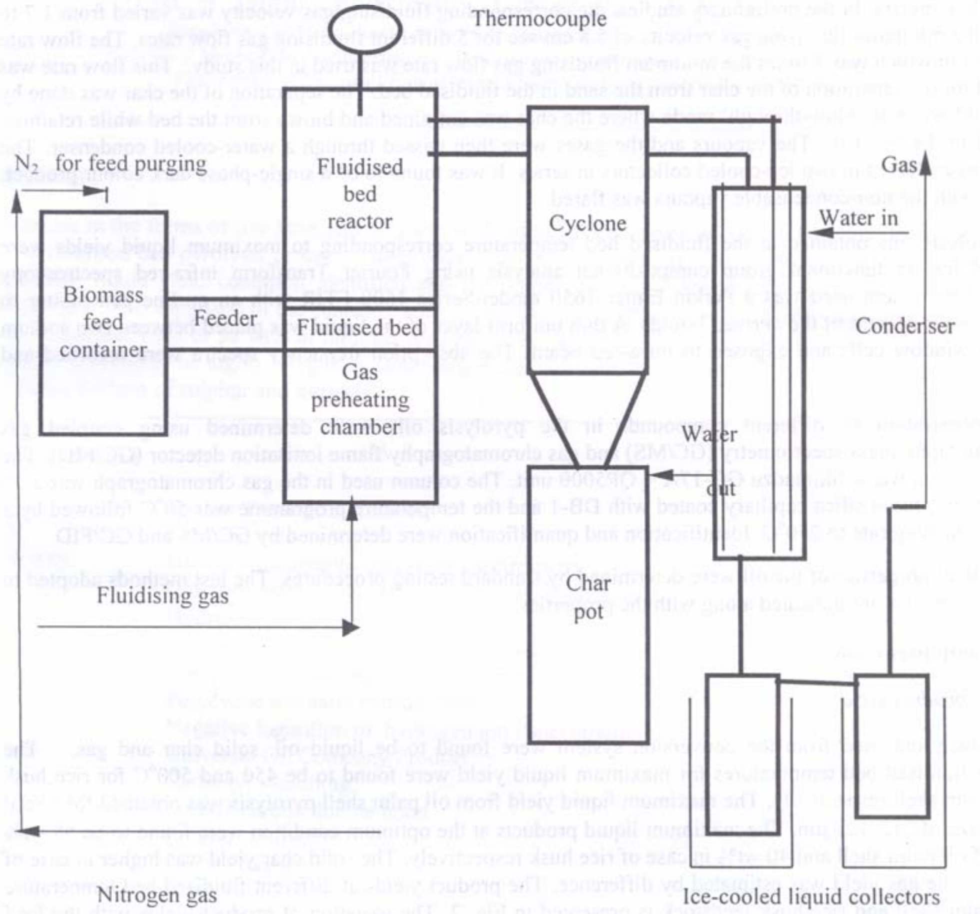

Fig. 1. Schematic of the fluidised bed fast pyrolysis system set-up.

The other feed material was rice husk particle of size less than 1000 μm. The fluidised bed reactor was made from stainless steel of dimension 300 mm x 50 mm. The feed was milled into different particle sizes, sieved and oven-dried up to less than 2 wt% moisture content. In order to feed the particle into the fluidised bed a motor driven screw feeder was used. The feed rate was maintained at around 0.4 kg h^{-1}. An electrical cylindrical heater externally heated the fluidising bed. Before entering the fluidised bed reactor the fluidisation gas was preheated. The temperature of the fluidised bed was controlled by means of a PID temperature controller and measured by a thermocouple within the bed. The temperature of the fluidised bed pyrolysis system with oil palm shell as the feed was varied from 400 to 600°C at an interval of 50°C. For rice husk fluidised bed pyrolysis system this was varied from 400 to 500°C. The 0.65 mm diameter thermocouple probe was constructed using double capillaries ceramic rods, placed inside a stainless steel thermowell of 5 mm outer diameter and 25 cm high. The tube was welded to the fluidised bed reactor top plate to provide a rigid support. The length was dimensioned in such a way that the probe could measure the fluidised bed temperature holding the feed materials. The system was maintained at a pressure slightly above atmosphere. The fluidizing gas flow rate was measured and controlled by gas flow meters. In the preliminary studies, the corresponding fluidising gas velocity was varied from 1.7 to 3 times the minimum fluidising gas velocity of 5.8 cm/sec for 5 different fluidising gas flow rates. The flow rate of 1.26 m^3/h which was 3 times the minimum fluidising gas flow rate was used in this study. This flow rate was required for the separation of the char from the sand in the fluidised bed. 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 [9]. The vapours and the gases were then passed through a water-cooled condenser. The liquid was collected in two ice-cooled collectors in series. It was found to be a single-phase dark colour product. The gas with the non-condensable vapours was flared.

The pyrolysis oils obtained at the fluidised bed temperature corresponding to maximum liquid yields were analysed for its functional group compositional analysis using Fourier Transform infra-red spectroscopy (FTIR). The system used was a Perkin Elmer 1650 model-Series 1600 FTIR with an on-line pen plotter to produce the ir-spectra of the derived liquids. A thin uniform layer of the liquid was placed between two sodium chloride window cells and exposed to infra-red beam. The absorption frequency spectra were recorded and plotted.

The concentration of different compounds in the pyrolysis oils were determined using coupled gas chromatography/mass spectrometry (GC/MS) and gas chromatography/flame ionisation detector (GC/FID). The GC/MS system was a Shimadzu GC-17A + QP5000 unit. The column used in the gas chromatograph was a 30 m x 0.25 mm fused silica capillary coated with DB-1 and the temperature programme was 50°C followed by a 3°C min^{-1} heating rate to 250°C. Identification and quantification were determined by GC/MS and GC/FID.

The physical properties of the oil were determined by standard testing procedures. The test methods adopted to find the properties are indicated along with the properties.

Results and discussion

Pyrolysis product yield

The products obtained from the conversion system were found to be liquid oil, solid char and gas. The optimum fluidised bed temperatures for maximum liquid yield were found to be 450 and 500°C for rice husk and oil palm shell respectively. The maximum liquid yield from oil palm shell pyrolysis was obtained for a feed particle size of 212-425 μm. The maximum liquid products at the optimum condition were found to be 58 wt% in case of oil palm shell and 40 wt% in case of rice husk respectively. The solid char yield was higher in case of rice husk. The gas yield was estimated by difference. The product yields at different fluidised bed temperature for oil palm shell and rice husk feedstock is presented in Fig. 2. The variation of product yields with the feed particle size at a fluidization gas flow rate of 1.26 m^3/h. is shown in Fig. 3.

Pyrolysis oil characterization

FTIR analysis

The pyrolysis oils obtained from both solid rice husk and oil palm shell at the maximum liquid yield condition were characterized for compositional group identification by Fourier Transform infra-red spectroscopy (FTIR). The maximum liquid yield for oil palm shell pyrolysis was at a fluidised bed temperature of 500°C with a feed particle size of 212-425 μm with a fluidisation gas flow rate of 1.26 m^3/h. For rice husk the maximum liquid yield was obtained at a fluidised bed temperature of 450°C for a feed particle size of less than 1000 μm with a fluidisation gas flow rate of 1.26 m^3/h.

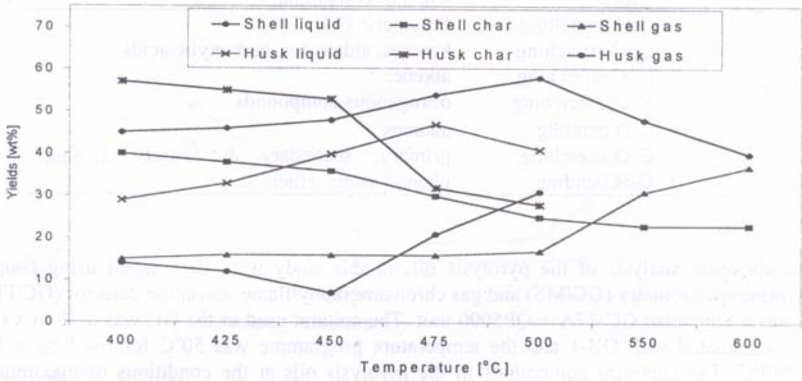

Fig. 2. Effect of Fluidised bed temperature on the pyrolysis product yields of oil palm shell of particle size 212-425 μm and rice husk of <1000 μm at fluidisation gas flow rate of 1.26 m^3/h.

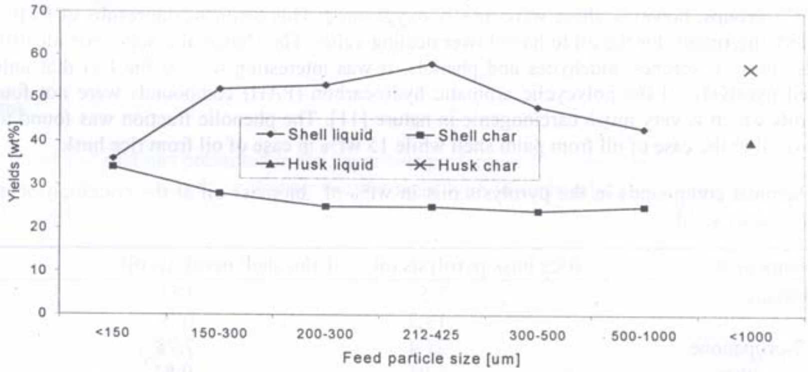

Fig. 3. Effect of feed particle size on the pyrolysis product yields of oil palm shell at fluidised bed temperature of 500°C and of rice husk at fluidised bed temperature of 450°C at fluidisation gas flow rate of 1.26 m^3/h.

From the FTIR spectroscopy of the pyrolysis oil [6] the functional groups and the indicated class of compounds of the derived oil are presented in Table 2. The presence of polymeric O-H in the oils are indicated by group in the frequency range between 3200 and 3600 cm^{-1}. The presence of alkanes and alkenes are indicated by the frequency ranges 1465-1350 cm^{-1} and 1680-1580 cm^{-1} respectively. The presence of primary, secondary and tertiary alcohol, phenols, esters and ethers are represented by the frequency of 950-1300 cm^{-1}. From the analysis it appeared that the oil was highly oxygenated.

Table 2 The FTIR functional groups and the indicated compositions of pyrolysis oils at the condition of optimum liquid product yield

Frequency range cm^{-1}	Group	Class of compound
3200-3600	O-H stretching	Polymeric O-H
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 O-H bending	primary, secondary & tertiary alcohol, phenol, esters, ethers

GC and GC/MS analysis

The chemical composition analysis of the pyrolysis oils in this study were determined using coupled gas chromatography/mass spectrometry (GC/MS) and gas chromatography/flame ionisation detector (GC/FID). The GC/MS system was a Shimadzu GC-17A + QP5000 unit. The column used in the GC was a 30 m x 0.25 mm fused silica capillary coated with DB-1 and the temperature programme was 50°C followed by a 4° C/min heating rate to 250°C. The chemical compounds in the pyrolysis oils at the conditions of maximum liquid product yield have been presented in Table 3. The maximum liquid yield for oil palm shell pyrolysis was at a fluidised bed temperature of 500°C with a feed particle size of 212-425 μm with a fluidisation gas flow rate of 1.26 m^3/h. For rice husk the maximum liquid yield was obtained at a fluidised bed temperature of 450°C for a feed particle size less than 1000 μm with a fluidisation gas flow rate of 1.26 m^3/h. The oils were found to be in between C_2 to C_{10} groups; however, these were mostly oxygenated. This confirms the results of FTIR analysis. This is the underlying reason for the oil to have lower heating value. The chemical compounds identified in the oils were acids, alcohol, ketones, aldehydes and phenols. It was interesting to note the fact that unlike other biomass-derived pyrolysis oil the polycyclic aromatic hydrocarbon (PAH) compounds were not found to be present in the oils which is very much carcinogenic in nature [11]. The phenolic fraction was found to be 43.3 wt% of biomass oil in the case of oil from palm shell while 15 wt% in case of oil from rice husk.

Table 3 The chemical compounds in the pyrolysis oils in wt% of biomass oil at the condition of maximum liquid product yield

Chemical compounds	Rice husk pyrolysis oil	Palm shell pyrolysis oil
2-Methyl propane	3.5	0.53
Acetic acid	13.2	16.9
3-Hydroxy 2-propanone	22.4	7.78
2 Methyl pertly ether	1.01	0.84
Butandial	9.87	2.13
Allyl acetate-2- ene	6.96	4.73
2-Furanaldehyde	4.55	4.41
2-Butanone	1.63	0.84
Methyl crotonate	2.50	2.69
4-Methyl butaroyate-1-ene	2.13	-
Cyclopentanone	2.83	1.34
5-Methyl furanaldehyde	1.96	-
Phenol	1.28	28.3
O-cresol (2-Methyl phenol)	-	0.79
3-Methyl cyclopentanedione	2.70	1.38

Guaiacol (2-Methoxy phenol)	5.05	4.82
4-Methyl guaiacol (4-Methyl 2-methoxy phenol)	2.03	2.02
Catechol (1,2 Hydroxy benzene)	2.13	2.16
4-Ethyl guaiacol (4-Ethyl 2-methoxy phenol)	0.908	1.09
Syringol (2,6-Dimethoxy phenol)	-	2.75
Eugenol (4-Propene 2-methoxy phenol)	1.53	1.36

Physical properties of pyrolysis oil

The physical properties of the pyrolysis oils at the conditions of maximum liquid product yield were analysed for kinematic viscosity, heating value, moisture content, ash content and pH value. This is presented in Table 4. These properties are compared with those of typical wood derived pyrolysis oil [11] and scrap tyre pyrolysis oil [6] at the condition of their maximum liquid product yield. These properties are compared with that of conventional fuels, such as diesel and gasoline [12]. The values of the pyrolysis oils from different sources are found to be in the comparable range. However, in comparison to conventional fuels like diesel and gasoline, the pyrolysis oils need to be upgraded for their heating value, viscosity, moisture content and high acidity. This can be done by some upgrading method like zeolitic catalytic cracking in order to obtain high quality gasoline range liquid product.

Table 4 Comparison of the physical properties of pyrolysis oils at the condition of maximum liquid product yield with typical biomass pyrolysis oil and conventional fuels

Physical Properties	Husk oil	Shell oil	Tyre oil	Wood pyro oil	Fast diesel	Gasoline
Heating value MJ kg^{-1} (DIN 51900)	19.90	22.10	43.40	18.00	45.80	47.70
pH	2.25	2.35	-	2.50	-	-
Moisture content % (ASTM D 4928)	32.00	10.00	0.10	20.00	-	-
Kinematic viscosity CST @ 40°C (ASTM D445)	86.80	14.40	6.63	134.00	2.60	0.73
Ash content % (ASTM D 482)	0.06	0.10	0.05	0.10	0.01	-

Solid char analysis

The char obtained from 212-425 μm oil palm shell particle at 500°C and from up to 1000 μm rice husk particle at 450°C were analysed for their elemental composition in order to determine carbon, hydrogen, oxygen and nitrogen. The percentage of oxygen was found by difference. The standard UOP 868-88 method was used for the analysis. The results are presented in Table 5. The char was found to be oxygenated. The oil palm shell char could also be converted to activated carbon [13]. The char from rice husk can be used as a starting material for the production of silicon nitride powder- an extensively investigated structural ceramic material, which can be applied in engine and turbine construction [14]. Besides it may be used as solid fuel.

Table 5 Elemental analysis of char obtained from the pyrolysis process in wt%

Elemental composition	Rice husk char	Palm shell char
Carbon	39.16	62.91
Hydrogen	4.90	3.03
Nitrogen	0.36	0.83
Oxygen	39.55	19.25
Others	16.00	14.00

Conclusions

- Both rice husk and oil palm shell produce pyrolysis oil by fluidised bed pyrolysis process. However, the liquid yield is found to be more from oil palm shell waste than from rice husk waste. The process conditions for maximum liquid product yield are found to be different in cases of different feed materials. The major chemical compounds obtained are phenols, acids, alcohol and ketones. Both the oils contain oxygenated compounds rendering low heating value and high viscosity.
- The solid char yield is more from rice husk waste than that from oil palm shell. The solid char from both the sources contains a high percentage of oxygen with a little nitrogen and no sulphur.
- The liquid oil needs to be upgraded to improve its quality. The phenol and its derivatives would be separated by some chemical methods to obtain high-value chemicals.
- Apart from its usage as a fuel the solid char may be used for making activated carbon and rice husk ash cement.

Acknowledgements

The authors wish to thank the Ministry of Science, Technology and Environment under the IRPA Research Programme for the research grant awarded (Vote no. 72107) and Universiti Teknologi Malaysia for the support to carry out the research work.

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