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FAST PYROLYSIS of RICE HUSK IN A FIXED BED PYROLYZER FOR BIO OIL PRODUCTION

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Abstract

Fast pyrolysis of rice husk was carried out in a fixed-bed reactor for bio oil production. In this work, Rice husk was characterized for proximate and ultimate analysis and the result shows volatile matter of rice husk to be 70.66% with elemental compositions of carbon and oxygen as 42.68% and 42.41% respectively. Design expert software was used in planning and optimized experimental results. The experimental runs were conducted using a retention time of 60min and the optimum conditions for fast pyrolysis of rice husk with maximum bio-oil yield of 62.8% were at the temperature of 600^{o}C, N_2 gas flow rate of 5 L/min and particle size of 1.7mm. Particle size, temperature and N_2 gas flow rate all have significant effect on bio oil yield. A retention time of 70 min at a temperature of 600 °C, N_2 gas flow rate at 5 L/min and feed particle size of 1.7 mm gave the highest [redacted] *bio oil yield of 64.7 %. The bio oil obtained at optimal conditions was analyzed using GC-MS to identify its compounds. GC-MS peak area percentage showed that the bio oil exhibited a variety of chemical groups and it was determined that the dominant chemical group was phenol.*

KEYWORDS: *fast pyrolysis, operational variables, rice husk, bio oil, design of experiment.*

Introduction

Energy security and environmental sustainability are two major challenges encountered by the world that can only be addressed through the diversification in the energy resources and clean fuels (Yin, Liu, Mei, Fei, and Sun 2013; Mukherjee and Lal, 2013). The increase in these major issues have led to a move towards alternative, renewable, sustainable, efficient and cost

INTERNATIONAL JOURNAL – ERT
VOL. 10 NO.5 DEC-2019 ISSN: 1074-4741

effective energy sources with lesser gaseous emissions (Nigam and Singh, 2011). Biomass is well thought-out one of the most important renewable energy sources with the utmost potential to contribute to the energy needs of present society for both the developed and increasing economies worldwide. It is recognized that biomass surpasses many other renewable energy sources, because of its abundance, high energy value and versatility. (European Commission, 1997; IEA, 2000). There are two fundamental processes of conversion of biomass to biofuel: thermochemical (combustion, gasification, liquefaction and pyrolysis), or biochemical (fermentation and anaerobic digestion) (Liew, Hassim and Ng, 2014). Thermochemical conversion requires much more extreme temperatures and pressures than those applied in bio-chemical conversion method ((Nigam and Singh, 2011). Fast pyrolysis is a thermochemical process, in which bio oil is a main product having a great prospective as a fuel oil. Fast pyrolysis is conducted on fine particle (< 2mm) at high temperature of 400 to 650°C (Dickerson and Soria, 2013), with very high heating rate 9>10 – 200°C/min) and short vapour residence time (<2s) in inert atmosphere.
Rice husk are a form of biomass waste generated in large quantities, it is estimated that over 100million tons per year are generated with 90% accounted for by developing countries. Apart from limited uses as a source of heat in a few mills the majority is burned in open heaps to dispose of the waste. (Paethanom and Yoshikawa, 2012). Thus, it is remarkably vital to conduct comprehensive study of conversion of waste to potential energy. The objective of this present work is to find the optimum parameters for maximum bio oil yield in a fixed bed reactor using fast pyrolysis process. The study also aims at determining the chemical compounds present in the bio oil at optimum parameters.

MATERIALS AND METHOD

Raw Material -Rice husk

The sample of rice husk used in this experiment is a by-product of rice milling industry. It was collected from Onyx Rice Mill, Badeggi, in Niger state. Immediately after getting the rice husk, it was sundried for 24hrs after which it was milled in a high speed rotary cutting mill. It was thereafter screened using Endecott test sieves mounted on an automatic sieve shaker which gave fractions of 0.15mm, 0.30mm, 0.60mm, 1.18mm, 1.70mm and 2.36mm. Table 2.1 presents the proximate and ultimate analysis of rice husk. The proximate, ultimate and component

INTERNATIONAL JOURNAL – ERT
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analysis were done by ASTM standards. The components and elements present in the rice husk are given in Table 3.1.

Experimental Apparatus and Procedure

The fast pyrolysis of Rice Husk was carried out in a fixed bed reactor. The experimental setup consisted of a cylindrical reactor made of stainless steel with 60mm internal diameter and 1010 mm height. The reactor tube has a gas inlet for inert gas (nitrogen) which also has an exit outlet. The pyrolyzer was installed inside an electrical heater and was insulated to enable the heating of the reactor. The reactor was equipped with a biomass holder and connected to nitrogen sources. The schematic diagram of the pyrolyzer setup is shown in Fig. 1. The liquid product condensed in the condenser is weighed. To record the pyrolysis temperature, a K-type thermocouple was inserted inside the pyrolyzer in the reaction zone. The outlet pipe is linked to a condenser and a bio-oil collecting flask. Experiments were carried out to evaluate the effect of the pyrolysis temperature, particle size and nitrogen gas flow rate on products yield. The amount of rice husk used for each run was 50 g. when the desired pyrolysis

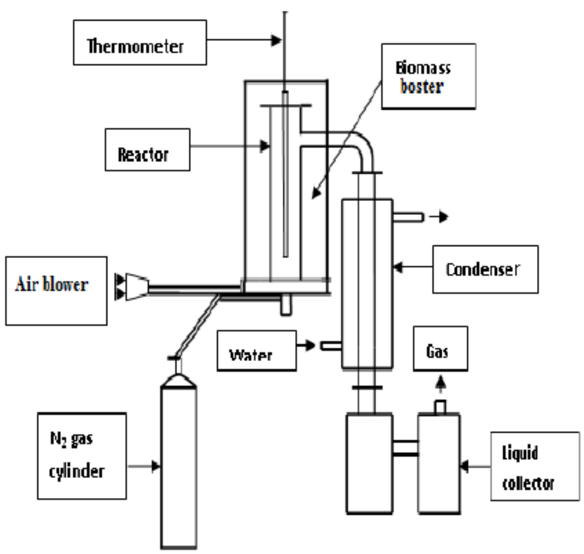

Figure 1: Schematic diagram of a fast pyrolysis setup

Temperature in the reactor is reached, a 60min retention time was allowed for all the runs. The condensable liquid product (bio-oil + water) were collected in a trap maintained at the temperature of 25°C by means of circulating the water in the condenser. The bio-oil was then collected from the condenser after the volatiles generated from the reactor were run through. When the reactor was cooled down

INTERNATIONAL JOURNAL – ERT
VOL. 10 NO.5 DEC-2019 ISSN: 1074-4741

to room temperature, the remaining bio char was taken out, weighed, and recorded. The gas yield was calculated by difference from mass balance for liquid bio-oil and solid bio char medium.

Pyrolysis experiments were conducted according to optimized results obtained from using design of experiment statistical software tool (design expert). Three operational variables (temperature, particle size and nitrogen gas flow rate) were considered and 20 experimental runs were expected. However, not all runs was conducted, as some of the runs that appeared repeated themselves and some, the particle size range were not amongst the ones obtained, so at the end of the day only 12 experimental runs as listed in Table 3.2 were conducted. The chemicals present with the bio oil obtained at optimum parameters was analyzed by Gas Chromatography/Mass Spectroscopy (GC/MS).

RESULTS AND DISCUSSION

General characterization of rice husk

The analysis showed in Table 3.1 that rice husk comprises of high volatiles and high ash content. The ash content in biomass is directly proportional to the composition of silica content. Fu, Hu, Xiang, Yi, Bai, Sun and Su (2012) investigated on the chemical analysis of ash in rice husk and found that silica forms the main component of about 87.83wt % of the rice husk. The high volatile matter is an indication of high amount of cellulose and hemicellulose content in the rice husk which makes it a potentially useful energy resource. The fixed carbon amount is low (5.77wt%) and this confirms the presence of lower amount of lignin in the material, and also have potential to produce low yield of char. Rice husk has a low calorific value of 14020 kJ/kg, could be due to high ash content. This result is in agreement with Bardalai and and Mahanta (2018). The ultimate analysis of rice husk shows that the elemental ratios of carbon, oxygen, hydrogen, nitrogen and sulphur also have an important effect on pyrolysis product yields. Rice husk is oxygenated (42.41 wt %) due to the presence of carbohydrate structure and influenced to have low HHV. Nitrogen and sulfur were found to be in small amount and thus favourable for pyrolysis oil and syngas production as reported by Friedl, Padouvas, Rotter and Varmuza (2005).

Table 3.1: General Characterization of Rice Husk

Proximate analysis	Wt.%	Ultimate analysis	Wt.%
Moisture content	8.80	Carbon	42.68
Volatile matter	70.66	Hydrogen	7.76
Fixed carbon	5.77	Oxygen	42.41
Ash	14.77	Nitrogen	2.30
Calorific value (kJ/kg)	14020	Sulphur	0.92

INTERNATIONAL JOURNAL – ERT
VOL. 10 NO.5 DEC-2019 ISSN: 1074-4741

Product Yield of Fast Pyrolysis of Rice Husk

Table 3.2: Product Yields of fast Pyrolysis at Optimized Operating Conditions

run	Particle size mm	Temperature °C	N_2 gas flowrate L/min	Bio oil %	Char %	Gas %
1	1.7	600	5	62.8	16.8	20.4
2	1.7	400	5	48.24	24.48	27.28
3	1.7	400	25	45.20	20.80	34.00
4	1.7	600	25	34.44	34.2	31.36
5	1.0	500	31.8179	35.62	31.5	32.88
6	1.0	331.821	15	23.9	42.2	33.9
7	1.0	500	15	34.62	32.6	32.64
8	1.0	668.179	15	41.27	28.1	30.63.
9	0.3	600	25	40.60	23.2	36.20
10	0.3	400	25	44.9	26.0	29.10
11	0.3	400	5	49.28	18.40	32.32
12	0.3	600	5	39.04	28.64	32.32

Table 3.2 shows clearly the optimized result as generated by the design expert conducted at residence time of 60min per run. The highest bio oil yield of 62.8wt% was obtained using 1.7mm particle size of rice husk at the temperature of 600°C with N_2 sweeping gas flowrate of 5L/min. The least amount of bio oil but high amount of char was obtained at 1.0mm particle size of rice husk at the temperature of 331.82°C with N_2 sweeping gas flowrate of 15L/min. Similarly, the highest gas yield of 36.20wt% was achieved using 0.3mm particle size of rice husk at the temperature of 600°C with N_2 sweeping gas flowrate of 25L/min.

Effect of Retention Time on Pyrolysis Yields

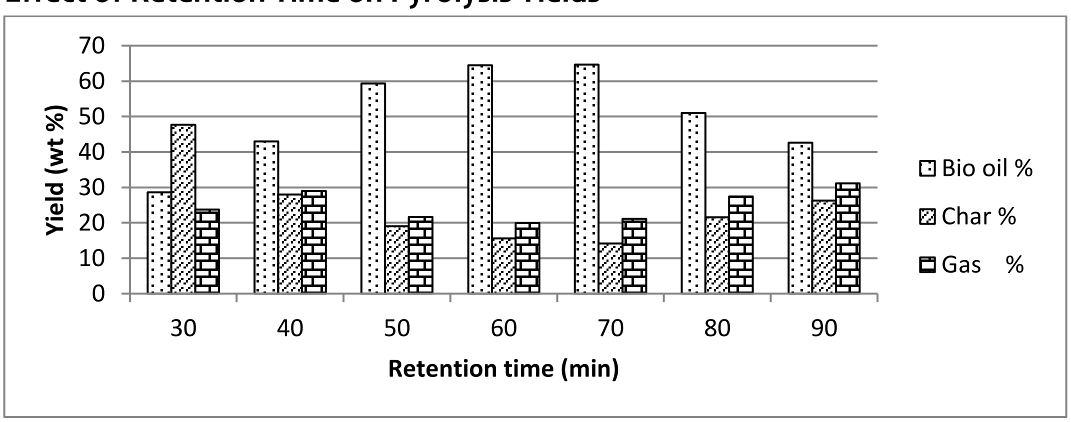

Chart 1- Products distribution as a function of retention time at a temperature of 600 °C, N_2 gas flow rate at 5L/min and feed particle size of 1.7 mm.

The effect of retention time of rice husk in pyrolysis reactor is presented in figure 3.3. The chart represents Products distribution as a function of retention time at a temperature of 600 °C, N_2 gas flow rate at 5 L/min and feed particle size of 1.7 mm. All rice husk sample completely pyrolyzed when retention time was 70 min. This is indicated by high yield of bio oil. Below this time, some fractions of rice husk was still not completely pyrolyzed, while above, the curve starts sloping down indicating that, unstable bio-oil underwent secondary reaction Wei (2006) and lead to releasing more gases and char.

Effect of Temperature, Particle size and Nitrogen gas flow rate on product yields

The Product distributions as a function of particle size of 1.7mm, 1.0mm and 0.3mm shows its effects on the yield of pyrolysis products as shown in chart 2. The 1.7mm particle size gives a better yield of bio-oil, followed by gas and the least is char produced across the particle sizes used. Although larger particle requires more time to heat by intra-particle conduction (Uzun, Pütün, and Pütün, 2007), but with high temperature of 600°C and short residence time of N_2 a high yield of bio-oil was obtained.

With respect to the effect of temperatures on the yield of the products, 600°C produced the highest bio-oil. At this temperature, the char formation decreased and bio-oil yield increased. The pattern of results indicated that rice husk was increasingly pyrolyzed and releasing more vapour containing more condensable compound (Heidari, Stahl, Younesi, Rashidi, Troeger and Ghoreyshi, 2014). At the temperature of 600 °C, bio-oil production achieved maximum yield temperature at which large fraction of rice husk components has been pyrolyzed and converted to vapour, and finally condensed as bio-oil.

A brief vapour residence time is obtained by flowing inert gas into the reactor. As shown in chart 2, when N_2 gas flow rate was set to 5 L/min, it can be observed that the amount of bio-oil yield was relatively high, while char formation and gas released were low. At this flow rate, N_2 was very fast enough to sweep out the vapour from the reactor. This condition led to shorter vapour residence time in the furnace which finally prevents repolymerisation, and secondary char formation in char pores and reduces the amount of gas released (Heo, 2010).

INTERNATIONAL JOURNAL – ERT
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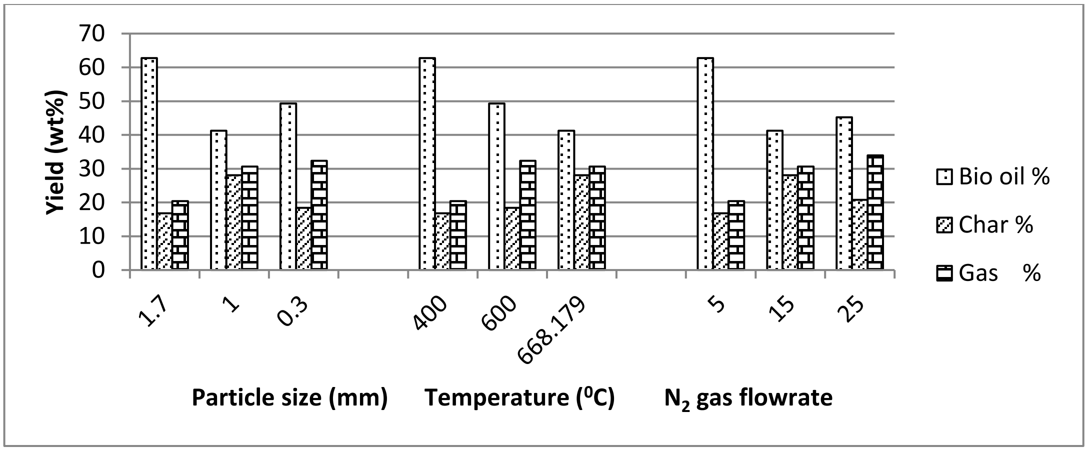

Chart 2: Effect of Particle size, Temperature and N_2 gas flowrate on pyrolytic products Yield

FTIR Spectra

The IR spectrum of the liquid obtained from fast pyrolysis of rice husk at the pyrolysis temperature of 600°C, particle size of 1.7mm, and gas flow rate of 5 L/min is shown in Figure 3.3. In the IR Spectra, absorbance vs wavenumber peaks obtained are analyzed to identify the functional groups or bonds present in the pyrolysis liquid and are shown in the table 4.5. From the FTIR analysis of bio oil, it was observed that there was no much increase in the number of functional groups present which may be due to high pressure. The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wave numbers as reported in literature.

Table 3.3: FTIR Functional Groups and Bonds of Bio Oil

Wavenumber (cm^{-1}) experimental	Wavenumber (cm^{-1}) Range	Functional Group	Bond
2874	3300-2500	Carboxylic acids	O-H
2396	3300-2500	Carboxylic acids	O-H
1008	1300-1000	Alcohols, carboxylic acids, ethers, esters	C-O
1784	1750-1625	Ketones, Aldehydes	C=O
868	680-860	Aromatics	C-H
638	680-860	Aromatics	C-H

The carboxylic acids in the pyrolysis liquid are found in the medium absorbance peak of OH of 2874 cm^{-1} wavenumber in the range of 3300- 2500 cm^{-1}. The presence of ketones and aldehydes is characterized by the strong and medium narrow absorbance peaks of C=O between the frequency range of 1625-1750 cm^{-1}. The possible absorbance peak of C-O of wave number 1021cm^{-1} in the range of 1000-1300 cm^{-1} represents alcohols, carboxylic acids, ethers and esters. The aromatic compounds are categorized by presence of the absorbance peak of 868 cm^{-1} wavenumber in 680-860 cm^{-1} range. The pronounced oxygenated functional groups of O–H; C=O; C–O and aromatic compounds showed that the oil were highly oxygenated and therefore, very acidic. The high fraction of oxygenated compounds reduces the calorific value of the oil since C=O bonds do not release energy during combustion. The presence of hydrocarbon groups C–H; C=C; and alcohols indicate that the liquids have a potential to be used as fuel

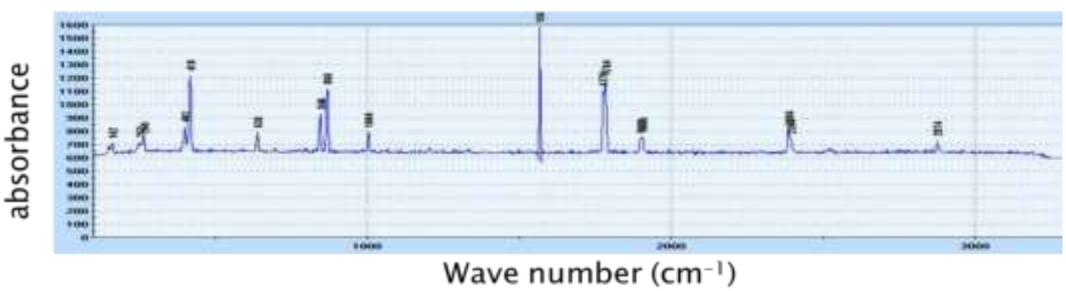

Figure 2: FTIR Spectra of fast pyrolysis bio oil

GC-MS Analysis

The chemicals present in the bio oil obtained at optimum conditions was analyzed by Gas Chromatography- Mass Spectroscopy (GC-MS) analysis. In the GC spectrum, about 34 peaks were observed. Figure 2 indicates the GC analysis of bio oil, the peaks with different retention Time (RT) indicates the presence of different chemicals in it. The chemicals with different retention time peaks were identified by the mass spectroscopy. The mass spectroscopy analysis indicates the presence of acid derivatives (relative area were 7.84%, 0.76%), phenol derivatives (relative area at 5.61%, 1.61%,4.24%, 3.31%,17.52%,1.31%,3.57%,), furan derivatives (relative area were 1.02%, 0.73%, 0.58%) and alcohol derivatives (relative area were 2.71%, 2.94%, 0.55%), Benzene derivatives with relative area at 0.97%, 1.74% and 1.92% in the bio oil. The major compounds identified in bio-oil were phenolic compounds having the highest peak area.

INTERNATIONAL JOURNAL – ERT
VOL. 10 NO.5 DEC-2019 ISSN: 1074-4741

CONCLUSION

The present study, pyrolysis experiments of the rice husk was carried out in a fixed bed reactor with different pyrolysis operating conditions. There are many factors that influence the pyrolysis process. The main factors discussed in this research are the effect of particle size, temperature, retention time and N_2 gas flow rate. The optimum conditions for fast pyrolysis process of rice husk with maximum bio-oil yield of 62.8wt % were at the temperature of 600 °C, N_2 gas flow rate of 5 L/min, retention time of 60 min and particle size of 1.7 mm.

According to the relationship between IR and the functional groups from the FTIR analysis and also the GC-MS analysis, it could be inferred that bio oil is a multicomponent mixture containing all kinds of organic compounds. Thus, it was found that the pyrolysis of rice husk may well be a future potential alternative source of liquid hydrocarbon fuels. Song *et al*. (2009) and Wang *et al.* (2008) had used GC/MS to investigate the compositions of the bio-oil from fast pyrolysis of rice husk. They also found that benzene derivatives, phenol derivatives, alkanes, cycloalkanes and aromatic hydrocarbons were the main compounds in the bio-oils. The study findings have suggested that it is possible to produce liquid fuels with better properties using the biomass sources. Further characterization studies on pyrolysis liquid products from the solid wastes should be conducted to provide ways of utilizing the liquid as fuels in boiler or as value added chemicals.

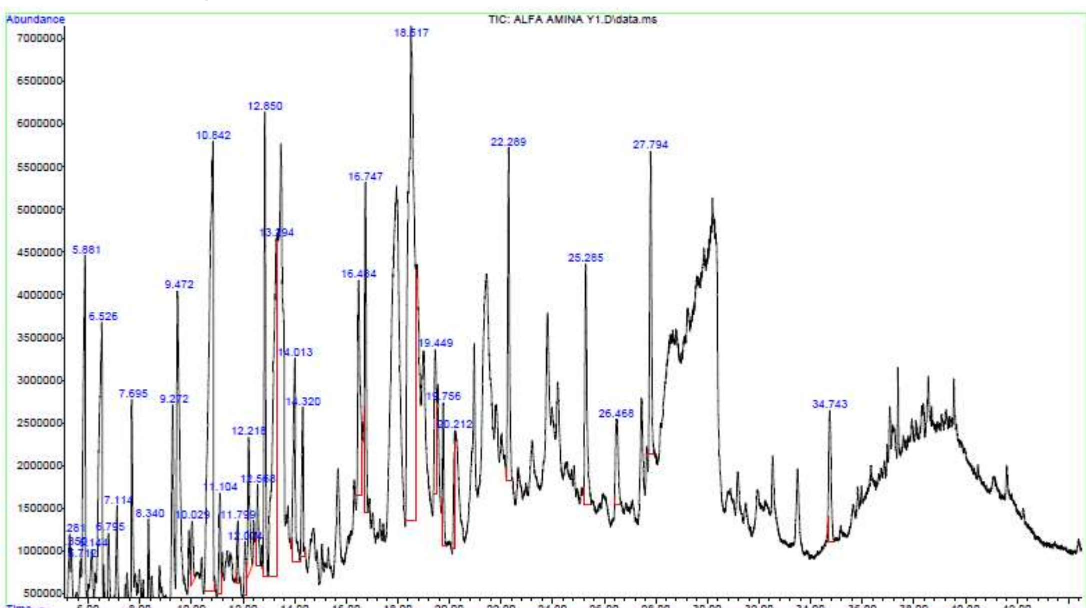

Figure 3: GC-MS Spectra of fast pyrolysis bio oil

INTERNATIONAL JOURNAL – ERT
VOL. 10 NO.5 DEC-2019 ISSN: 1074-4741

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