



## ABSTRACT

This paper reports a study of characterization of bio-oil produced from vacuum and fast pyrolysis of rice husk. Rice husk was characterized for proximate and ultimate analysis and the result indicates volatile matter of rice husk to be 70.66% with elemental compositions of carbon and

# C HARACTERIZATION OF BIO-OIL PRODUCED FROM VACUUM AND FAST PYROLYSIS OF RICE HUSK

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## INTRODUCTION

The growing demand for energy, chemicals, and materials from sustainable resources poses challenging efforts. Pyrolysis process converts biomass feedstock into three classes of products: a solid (or char), a liquid (also known as bio-oil from pyrolysis or simply bio-oil), and a gas (Undri, 2015). Biomass has been inward bound into our life and industries as a remarkable renewable resources used to provide second generation of Biofuels or chemicals (Huber *et al*, 2006)). Abundant amount and CO<sub>2</sub> neutrality with low sulfur and nitrogen contents make biomass a sustainable and eco-friendly energy source (Zeng *et al*, 2011; Dupont *et al*, 2014). It is recognized that biomass surpasses many other renewable energy sources, because of its abundance, high energy value and versatility. (European Commission, 1997; IEA, 2006). Also, biomass materials could be



oxygen as 42.68% and 42.41% respectively. Design expert software was used in planning the experiment to optimize process parameters such as temperature, particle size, retention time and N<sub>2</sub> gas flow rate. The optimum conditions for fast pyrolysis of rice husk with maximum bio-oil yield of 62.8wt% were at the temperature of 600°C, N<sub>2</sub> flow rate of 5 L/min, retention time of 60 min and particle size of 1.7mm. The optimum yield sample i.e. 1.7mm particle size was vacuum pyrolyzed and bio oil yield of 12.72wt% was obtained. The bio oils obtained at optimal conditions was characterized using GC-MS and FTIR to identify its compounds and functional groups. GCMS analysis of bio oils obtained from vacuum and fast pyrolysis showed a number of peaks with the compounds identified as acid derivatives, phenol derivatives, alcohol derivatives, furan derivatives etc. These studies have shown that rice husk can be used as a fuel and chemical feedstock.

**Keywords:** fast pyrolysis, vacuum pyrolysis, rice husk, bio oil, FTIR, GCMS.

proficiently utilized for the production of different value-added products as a substitute of the current common practice of burning them for energy generation purposes, especially in Africa, which is wasteful (Bridgwater, 2004).

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). Different types of thermo-chemical decomposition produce different product qualities and ratios by adjusting the oxygen content and process conditions. Fast pyrolysis is



optimized for high liquid yield production; gasification maximizes gas production; vacuum pyrolysis gives a more even spread of products; slow pyrolysis and torrefaction give char as main product; and finally combustion produces heat. Subject to the thermal setting and the final temperature, pyrolysis will yield mainly bio-char at low temperatures, less than 450 °C, when the heating rate is quite slow, and mainly gases at high temperatures, greater than 800 °C, with rapid heating rates. At an intermediate temperature and under relatively high heating rates, the main product is bio-oil (Zafar, 2018).

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. Traditional methods such as composting and incineration are not suitable to process these organic solid wastes as they contain small concentrations of nitrogen for composting and a considerable amount of solid grains and smoke would be released to pollute the environment during incineration (Paethanom and Yoshikawa, 2012). Therefore, a practical method should be to pyrolyze rice husk for providing bio-oil. Thus, the objective of this work is to find the optimum parameters for producing bio oil using vacuum and fast pyrolysis process. In addition, the bio-oils obtained at the conditions of maximum product yields were further analyzed to determine its possibility of being a potential source of renewable fuels and chemical feedstock.

## **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 3.1 presents the proximate and ultimate analysis of rice husk.

### Fast and Vacuum Pyrolysis

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 had a gas inlet for inert gas (nitrogen) which also had 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. To record the pyrolysis temperature, a K-type thermocouple was inserted inside the pyrolyzer in the reaction zone. The outlet pipe was 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 temperature in the reactor was reached, a 60min retention time was allowed for all the runs.

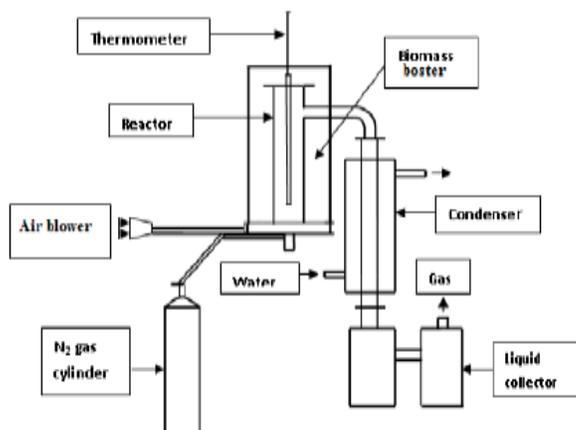




Figure 1: Schematic diagram of a fast pyrolysis setup

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 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. Fast pyrolysis experiments were conducted according to optimized results obtained from using design of experiment statistical software tool (design expert) and three operational variables (temperature, particle size and nitrogen gas flow rate) were considered.

The vacuum pyrolysis system consists of a vacuum pyrolyzer (reactor), a gear motor (stirrer), an electric heater, a condenser, a gas carbon separator, a vacuum pump, a water pump and an industrial gas burner. The system can handle 1-2 kg/h of biomass. Fire was set to the industrial gas burner in the furnace chamber with the aid of manhole. The pyrolyzer was then filled with 1kg of rice husk having a particle size of 1.7mm through the inlet at the top of the pyrolyzer. The inlet was closed tightly with the aid of a pipe wrench to block oxygen and maintain vacuum, the gas carbon separator outlet and bio-oil collector outlet was also closed. Then the water pump, vacuum pump and the heater on the G-C separator as well as the stirrer were all switched on. The vacuum pump was used to maintain atmospheric pressure in the reactor and to emit exhaust gas. The temperature was maintained at 300-500°C to decompose the biomass. The system was allowed to run continuously for two hours but at intervals of 30min, the valve from condenser was opened to collect the condensate (Bio-oil). After two hours the industrial gas burner was switched off to allow the system



cool to ambient temperature while the pumps, heater and stirrer are still running. The residue in the pyrolyzer is allowed a residence time of 2 hours before discharging. The liquid product condensed was weighed, so also the residue (char) obtained. The experimental setup is shown in fig 2.



Fig 2: vacuum pyrolysis unit



## 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 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



### 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 <sub>2</sub> 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 maximum bio oil yield of 62.8wt% was obtained using 1.7mm particle size of rice husk at the temperature of 600°C with N<sub>2</sub> 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<sub>2</sub> sweeping gas flowrate of 15L/min. Similarly, the maximum gas yield of 36.20wt% was achieved using 0.3mm particle



size of rice husk at the temperature of 600°C with N<sub>2</sub> sweeping gas flowrate of 25L/min.

### Effect of Retention Time on Pyrolysis Yields

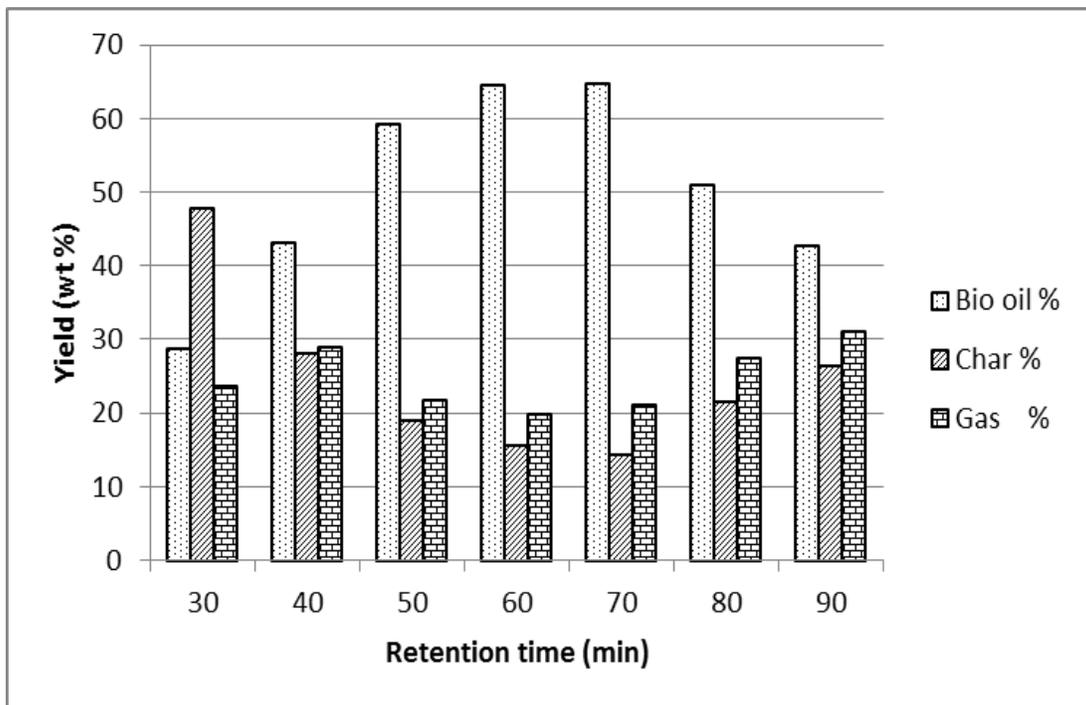


Chart 1- Products distribution as a function of retention time at a temperature of 600 °C, N<sub>2</sub> gas flow rate at 5L/min and feed particle size of 1.7 mm.

The effect of retention time of rice husk in pyrolysis reactor is presented in chart 1. The chart represents Products distribution as a function of retention time at a temperature of 600 °C, N<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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).

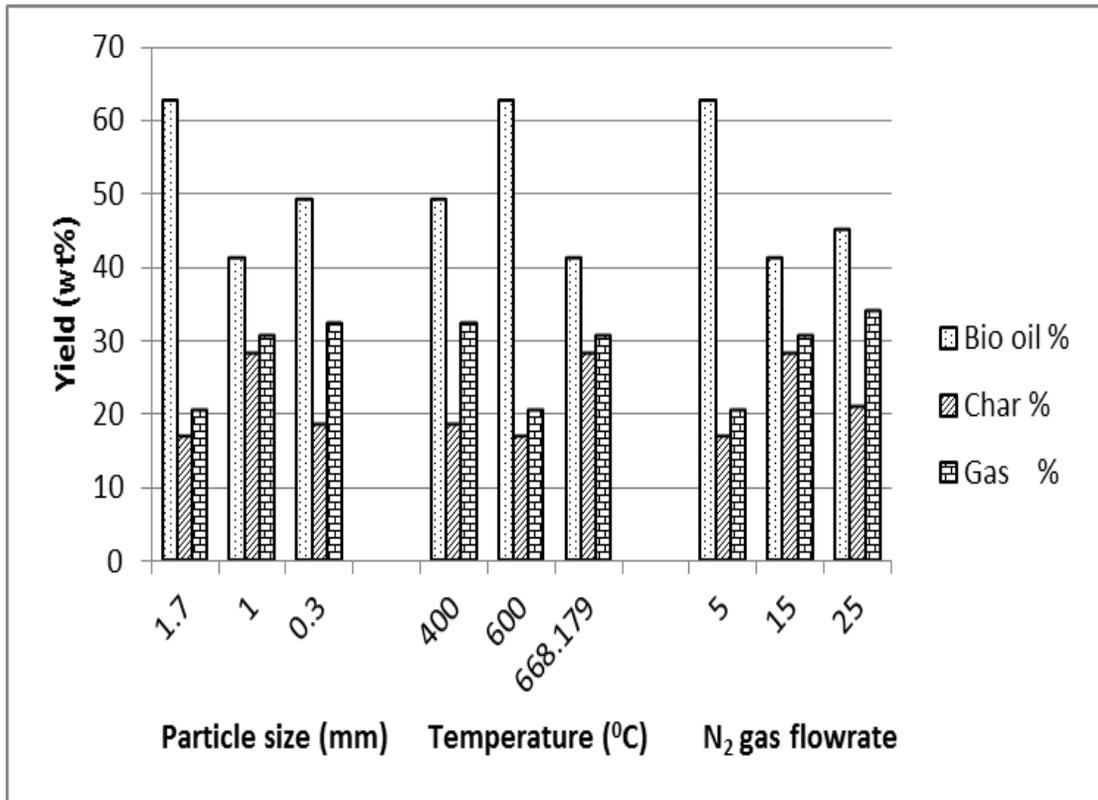


Chart 2: Effect of Particle size, Temperature and N<sub>2</sub> gas flowrate on pyrolytic products Yield

### Product Yield from Vacuum Pyrolysis of Rice Husk

The vacuum pyrolysis was carried out using sample particle size of 1.7mm. The pyrolysis oil obtained is a single phase almost homogenous liquid with dark brown colour and acidic odor. The result of mass balance shows that yield of pyrolysis liquid was 12.72wt% which is low whereas yield of char was 57.14wt% and yield of produced gas was 30.14wt% which is high. This result obtained was far below the bio-oil yield using fast pyrolysis for the same rice husk particle size. The product fractions of pyrolysis process depend on the operating parameters of the reactor (Balat et al., 2009). The pyrolysis liquid yield is low whereas with reference to gas is high due to design and



operating parameters of the vacuum pyrolysis system. Also, the water content in the pyrolysis bio oil is high. The decrease in bio oil yield and increase in water content in the bio oil depends on several pyrolysis parameters such as temperature, feed particle size and vapour residence time. The water content in the range of more than 40% in the bio oil indicates the secondary cracking reactions during pyrolysis resulting in the lower oil yield (Gerdes *et al.*, 2002).

### 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 while that obtained from vacuum pyrolysis of the same particle size is shown in figure 4. From 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 3.3

Table 3.3: FTIR Functional Groups and Bonds of Bio Oil

Wavenumber (cm <sup>-1</sup> ) experimental	Wavenumber (cm <sup>-1</sup> ) 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<sup>-1</sup> wavenumber in the range of 3300-



2500  $\text{cm}^{-1}$ . The presence of ketones and aldehydes is characterized by the strong and medium narrow absorbance peaks of  $\text{C}=\text{O}$  between the frequency range of 1625-1750  $\text{cm}^{-1}$ . The possible absorbance peak of  $\text{C}-\text{O}$  of wave number 1021  $\text{cm}^{-1}$  in the range of 1000-1300  $\text{cm}^{-1}$  represents alcohols, carboxylic acids, ethers and esters. The aromatic compounds are categorized by presence of the absorbance peak of 868  $\text{cm}^{-1}$  wavenumber in 680-860  $\text{cm}^{-1}$  range. The pronounced oxygenated functional groups of  $\text{O}-\text{H}$ ;  $\text{C}=\text{O}$ ;  $\text{C}-\text{O}$  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  $\text{C}=\text{O}$  bonds do not release energy during combustion. The presence of hydrocarbon groups  $\text{C}-\text{H}$ ;  $\text{C}=\text{C}$ ; and alcohols indicate that the liquids have a potential to be used as fuel.

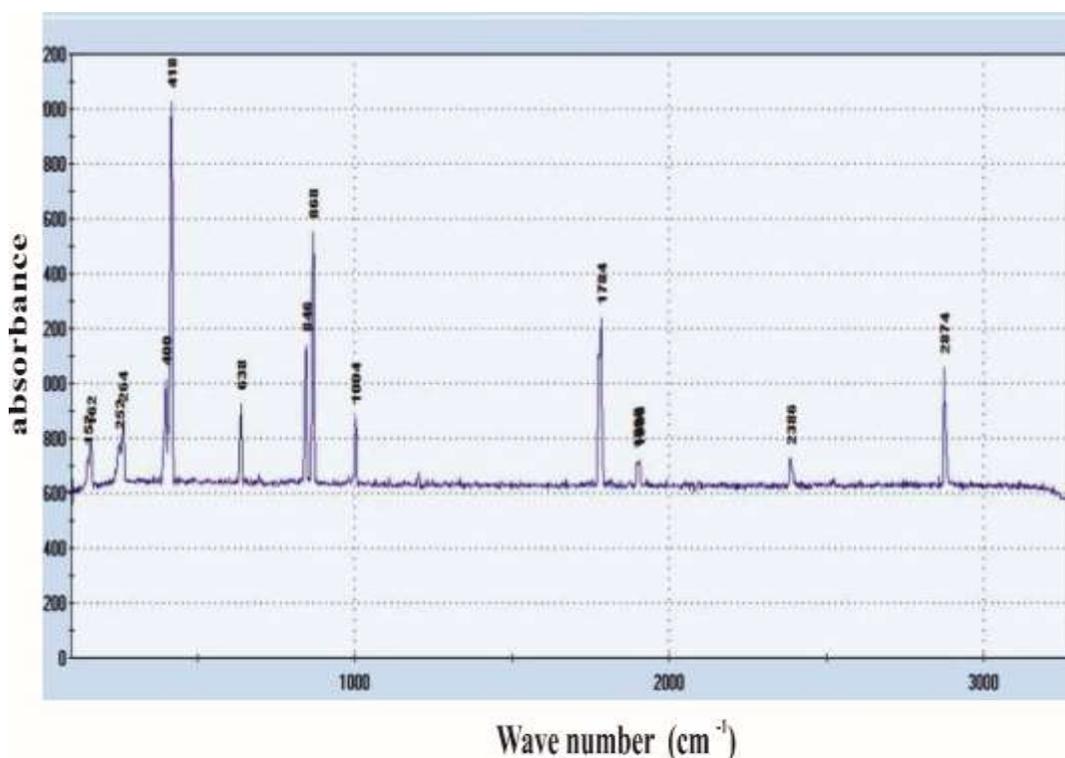


Figure 3: FTIR Spectra of vacuum pyrolysis bio oil





were 2.71%, 2.94%, 0.55%), Benzene derivatives with relative area at 0.97%, 1.74% and 1.92% in the bio oils. The major compounds identified in the bio-oils were phenolic compounds having the highest peak area. However, it was observed that the vacuum pyrolytic oil had more organic compounds and acid derivatives than the fast pyrolytic oil from the number of peaks observed to be 41 while that of fast pyrolytic was 34. This can be attributed to the fact that in fast pyrolysis, some of the volatiles must have left with the sweeping gas. Also, compared to fast pyrolytic oil which had only Butanoic and Carboxylic acid, organic acids such as Phosphonic acid, Butanoic acid, Carbonic acid, Carboxylic acid, 3-dione Benzoic acid and 2, 2-Dimethylglutaric acid were identified in vacuum pyrolytic oil. The high yield of phenolic compounds in the bio-oil is consistent with other results from the literature for the pyrolysis of rice husk (Lu *et al.*, 2011; Heo *et al.*, 2010).

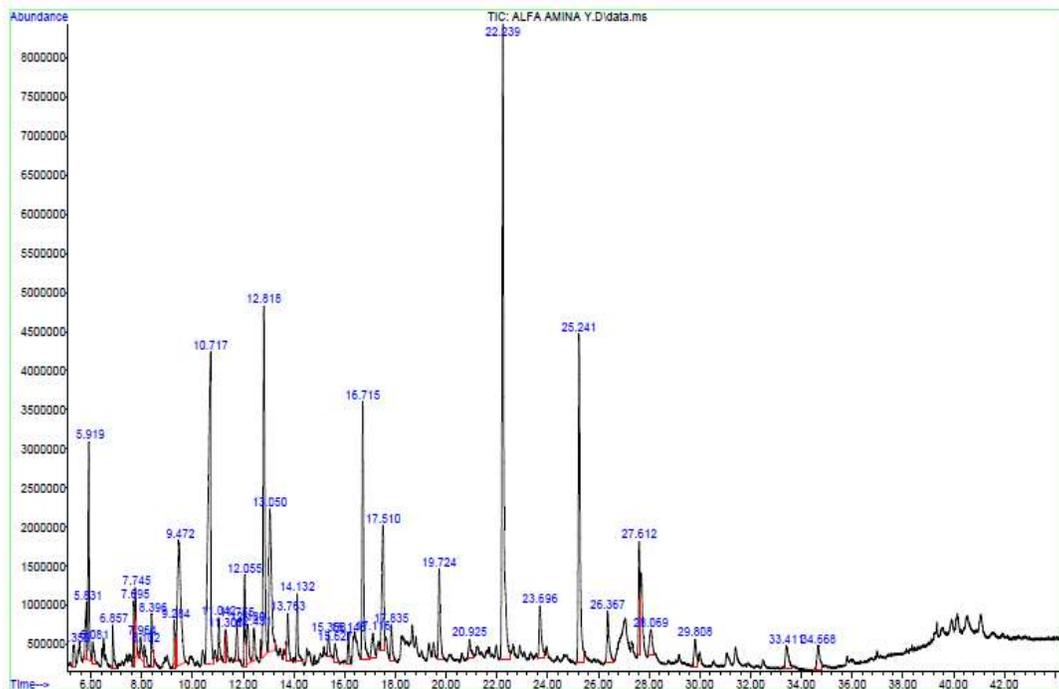


Figure 5: GC-MS Spectra of fast pyrolysis bio oil

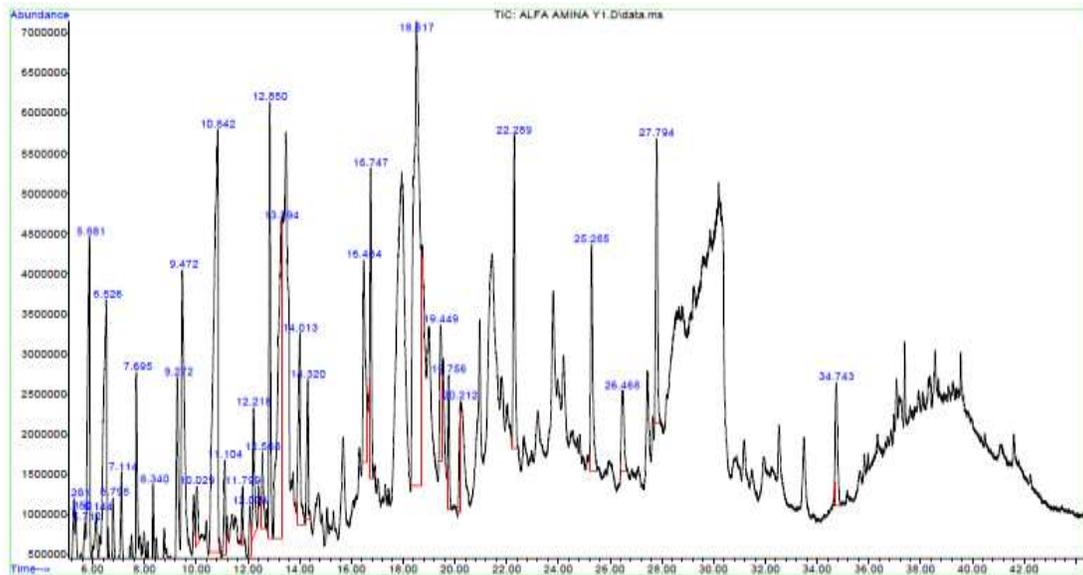


Figure 6: GC-MS Spectra of fast pyrolysis bio oil

## CONCLUSION

Based on the inefficient utilization of rice husk with respect to current technologies, pyrolysis was identified as a potential for sustainable energy and environmental security. The bio-oil production from fast and vacuum pyrolysis of rice husk shows that the optimum conditions for fast pyrolysis of rice husk with maximum bio-oil yield of 62.8% were at the temperature of 600°C, N<sub>2</sub> flow rate of 5 L/min, retention time of 60 min and particle size of 1.7mm. There are many factors that influence the pyrolysis process. However, from the FTIR and GC-MS analysis, it could be inferred that bio oil is a multicomponent mixture containing all kinds of organic compounds. 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. Thus, it can be said that the pyrolysis of RH can be considered as a potential raw material in chemical industries due to its high phenol



content and these findings have also suggested that it is possible to produce liquid fuels with better properties using the biomass sources. However, further characterization studies on pyrolysis liquid products from the solid wastes should be conducted to provide ways of utilizing the liquid in energy applications or as value added chemicals.

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