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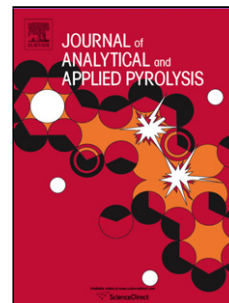
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CATALYTIC PYROLYSIS OF RICE HUSK FOR BIO-OIL PRODUCTION

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Catalytic pyrolysis experiments have been carried out on Brunei Rice Husk (BRH) to obtain bio-oil using a fixed-bed pyrolysis rig. ZSM-5, Al-MCM-41, Al-MSU-F and Brunei rice husk ash (BRHA) were used as the catalysts for the catalytic pyrolysis experiments and comparison was done to analyse the changes in the bio-oil properties and yield. Properties of the liquid catalytic and non-catalytic bio-oil were analysed in terms of water content, pH, acid number, viscosity, density and calorific value. The bio-oil chemical composition shows that ZSM-5 increases the production of aromatic hydrocarbons and light phenols, whilst Al-MCM-41 reduces the acetic acid production. The catalytic runs increased the calorific value and water content in the bio-oil, whilst viscosity, density and acid number is decreased.

Keywords: Brunei Rice Husk, Catalytic Pyrolysis, Fixed-bed, Bio-oil, Rice Husk Ash.

1. INTRODUCTION

Thermochemical conversion of biomass is rapidly becoming an alternative source for renewable energy and fuel production worldwide. For the process to be sustainable there must be sufficient biomass available as feedstock in order to satisfy the demand of emerging bioenergy industries. Several biomass feedstock have been utilised in the past ranging from agricultural wastes and residues to energy crops. The common factor amidst all the feedstock processing is the quality of the biofuel produced and the need to upgrade the fuel to meet standard specifications for different applications. Agricultural residues such as rice husks are abundant in rice growing countries such as Brunei, China and India. During the production of rice, rice husks are generated on site as a by-product in the milling factory. As rice is considered a staple food in most developing countries including Brunei, the by-products are available in large quantity to provide a source of alternative energy in the form of biofuel in addition to the current energy sector [1]. Although Brunei has a small land area, it is trying to achieve its aim of food security in rice production by growing high yielding variety of rice species [2]. One can expect that the volume of rice husks generated from rice milling will increase in the near future.

Bio-oils in general are dark brown, free-flowing organic liquids that are highly oxygenated, viscous, corrosive, relatively unstable and chemically complex. The chemical composition contains organic species groups which include organic acids, esters, alcohols, ketones, aldehydes, phenols, aromatic hydrocarbons, nitrogen compounds, furans and anhydrosugars [3-6].

Previous work on pyrolysis of rice husk has been carried out using either analytical [7-14] bench scale [15-19] or pilot scale method [20-22]. Lu et. al. showed in their work that the rice husk bio-oil is a valuable liquid fuel but is thermally unstable which may cause an increase in

the viscosity and water content, thus leading to phase separation [23]. Ji-lu studied the corrosivity of bio-oil towards stainless steel and copper and was shown to be mild, but the measured pH of the bio-oil was fairly acidic [20]. In another study by Lu et. al., it was suggested how the corrosivity of the bio-oil can be reduced by emulsification with diesel [57].

The challenge in biomass pyrolysis is to produce bio-oil of high quality either at source prior to full production or by upgrading the product. There are several methods of upgrading and improving bio-oil quality and one of these is the addition of catalysts into the pyrolysis process. The catalysts are expected to enhance the cracking reactions of the heavy molecules in pyrolysis products leading to the production of less viscous bio-oil and to induce reactions involving the removal of reactive oxygenated species, leading to the production of bio-oil of higher heating values and better stability. In catalytic pyrolysis there are various ways of incorporating catalyst to upgrade the pyrolysis vapours and hence the bio-oil produced. In-situ catalytic upgrading of biomass pyrolysis vapours by close-coupling the primary and secondary catalytic reactor is a promising route [24, 47]. The advantage of having such reactor configuration is that the reactor conditions can be independently controlled. Other configurations include co-feeding the biomass and catalyst in the same reactor, substitution of fluidising medium and close-coupling in-bed catalyst [25].

Pattiya et. al. studied the catalytic pyrolysis of cassava rhizome with ZSM-5, Al-MCM-41, Al-MSU-F and MI-575 in an analytical pyroprobe [26]. The study showed that all the catalysts have the potential to improve the viscosity and heating values of liquid biofuel, but increases the acidity of the bio-oil produced. French and Czernik also studied catalytic pyrolysis of biomass using commercial and laboratory-synthesised zeolite catalyst [27].

Studies on catalytic pyrolysis of rice husk are however quite limited. In an earlier work, William and Nugranad studied the catalytic pyrolysis of rice husk with zeolite ZSM-5 [16]. In a more recent work, Jeon et al., studied catalytic pyrolysis of waste rice husk over mesoporous materials [28] while Zhong et al., investigated the influence of red brick on fast pyrolysis of rice residue (husk and straw) in a fluidised bed reactor [22].

These studies highlight the use of zeolites and zeolite-like materials as an effective medium in catalytic pyrolysis process. Zeolites are crystalline aluminosilicates of natural or synthetic origin with highly ordered structures. They consist of SiO_4 and AlO_4 tetrahedral, which are interlinked through common oxygen atoms to give a three-dimensional network through which long channel runs [29]. Different types of zeolite have different structures or frameworks, which results in varying properties and applications. These properties and catalytic activities are related to their shape selectivity and acidity, and thus have advantages over conventional catalysts [16, 30]. The main zeolite catalyst used for upgrading biomass pyrolysis oils has been the hydrogen form of the zeolite, H-ZSM-5. In the temperature range of 350-450°C oxygenated compounds in contact with zeolite catalysts have been found to undergo a group of reactions including dehydration, decarboxylation, cracking, aromatization, alkylation, condensation, and polymerization. The product from catalytic pyrolysis using zeolites always produced a two-phase liquid (aqueous and organic) and gas, while coke deposits are known to be formed on the catalyst surface [27].

Mesoporous materials having zeolite-like structure [26] includes MCM-41 [31-35], SBA-15 [32] and MSU-S [36]. Al-MCM-41 significantly changed the composition of bio-oil, increasing the yields of phenols, hydrocarbons and polycyclic aromatics hydrocarbons (PAH), while

decreasing the yields of oxygenated carbonyl and acid compounds [34,37]. Al-MCM-41 also induced selective cracking and deoxygenation reactions of large molecules (derived from lignin) in pyrolysis vapours. Al-MSU-F type structure is a cellular foam framework of 150 Å pores size diameter. The presence of these very large pores in the structure lead to higher acidity expectation and induction of selective cracking of lignin oligomers from biomass vapours [26].

In this work, we have used commercial zeolite ZSM-5 and zeolites-like mesoporous. Al-MCM-41 and Al-MSU-F catalysts in the pyrolysis process to obtain bio-oil and compare their properties with non-catalytic pyrolysis experiments. Also as the alkali metals that naturally occur in ash in many biomass species and some wastes are known to have a catalytic effect we have used rice husk ash as one of the catalysts in the pyrolysis experiments. Rice husk ash is known to comprise of 90-97% silica, and has been used as a catalyst support and good synthesis precursor for zeolites catalysts [38-40].

2. EXPERIMENTAL

2.1. Materials

2.1.1. Feedstock

The feedstock used for the experiments is rice husk obtained from Brunei (BRH). Table 1 shows the characterisation data for the rice husk sample used. The proximate analysis was performed to measure the moisture, volatiles and ash contents of solid biofuels following the BS EN 14774-3:2009, BS EN 15148:2009 and BS EN 14775:2009 respectively [41-43]. The analysis shows that BRH has a high volatile matter and high ash content. The ultimate analysis describing the elemental composition of Carbon, Hydrogen, Nitrogen, Oxygen, Sulphur, and Chlorine in the sample was carried out by external laboratory using a Carlo-Erba 1108 elemental analyser. The gross heating value was determined using an oxygen bomb calorimeter model Parr 6100 according to ASTM D5865 [44]. The compositional analysis was determined using the Van Soest method [45-48]. This determine the lignocellulosic content of the rice husk, and the procedure includes the determining of neutral detergent fibre (NDF), acid detergent fibre (ADF) and acid detergent lignin (ADL) for evaluating the hemicellulose, cellulose and lignin contents in the biomass. The compositional analysis reveals that the rice husk is high in cellulose and lignin content.

2.1.2. Catalysts

The commercial catalysts used in these experiments are ZSM-5 obtained from Acros Organics, while Al-MCM-41 and Al-MSU-F were obtained from Sigma-Aldrich. Brunei rice husk ash (BRHA) was obtained by ashing the rice husk at 550°C for 3 hours. The catalysts were grounded and mixed with a montmorillonite clay binder at a ratio of 3:1, and for BRHA a ratio of 2:1 was used. The catalyst and binder were stirred in HPLC grade water at 60°C for 2 hrs. The catalyst/binder mixture was then coated on to a ceramic cordierite monolith support. The catalyst coated monolith are then dried to remove moisture, and calcined at 550°C for at least 3 hrs. The weight of the catalysts on the cordierite support is less than 1g, resulting in a feed-to-catalyst ratio of about 100:1. The monolith catalyst support and the catalyst-filled monolith are shown in figure 1.

2.2 Experimental pyrolysis setup

The catalytic pyrolysis rig is a close-coupled reactor configuration which consists of a primary fixed-bed reactor containing the biomass feed, coupled to a secondary fixed-bed reactor containing the catalyst. The primary reactor consists of a temperature controlled furnace containing a fixed bed quartz tube. The quartz tube is filled with the feed at the start of the experiment while nitrogen gas is passed continuously throughout the system as the carrier gas. A thermocouple connected to the furnace heating system is inserted into the quartz tube to measure the feed temperature. The secondary reactor containing the catalyst is heated up to 500°C at the start of the experiment. The condensation unit consists of the dry-ice condenser and a second condenser, acting as a cooling trap. The pyrolysis vapours are mostly condensed in the dry-ice condenser and is collected in oil-pot 1. The condensation medium is a mixture of dry-ice and acetone. The wet scrubber containing isopropanol is to remove excess condensable vapours or char fines before venting out the remaining gases. The pyrolysis rig setup diagram is shown in figure 2.

A gas injection is taken from the sampling line at a specific temperature to determine the composition of the uncondensed gases using a gas chromatography-thermal conductivity detector (GC-TCD). The GC used was HP 5890 Series II Gas Chromatograph with a 60/80 Carboxen-1000, 15' x 1/8" SS (2.1mm I.D) column. Helium is used as the carrier gas with a flowrate of 30 ml/min, and the calibration gases is a mixture of permanent gases which consists of hydrogen (H₂), nitrogen (N₂), methane (CH₄), carbon monoxide (CO) and carbon dioxide (CO₂). A volume of 100µl was injected at a single run. The initial oven temperature was held at 35°C for 5 minutes, and then ramped up to 225°C at a rate of 20°C/min.

Rice husks with a particle size of 355-849 µm was used for the experiments. The pyrolysis condition for the primary reactor is 450°C with a heating rate of 25°C/min. The secondary reactor, containing the catalyst is kept at a range of 490-540°C. A nitrogen gas flow of 50 cm³/min is maintained continuously throughout the experiment to purge the system.

2.3 Bio-oil analysis

GC-MS analysis of bio-oil was conducted using a Hewlett Packard HP 5890 Series II Gas Chromatograph with an Agilent auto sampler and coupled to an HP 5972 detector. Helium is used as the carrier gas with a DB 1706 non-polar capillary column. The initial oven temperature was 40°C and rising up to 290°C at a rate of 3°C/min. The injection temperature was held at 310°C with a volume of 5µl. Identification of the GC-MS peaks is based on the NIST mass spectra library. The dilution solvent used was ethanol and the dilution rate was 1:5.

The water content of the bio-oil was determined using a Karl Fisher Titrator V20 based on ASTM D1744 [49]. Acid number was determined using a Mettler Toledo G20 titrator based on ASTM D644-04 with a solvent mixture of toluene, 2-isopropanol and water, and potassium hydroxide solution (KOH) as the titrant. The pH was obtained using the Sartorius basic meter PB-11. Viscosity was measured according to the ASTM D445. The heating value was calculated via correlations using data obtained from ultimate analysis.

3. RESULTS AND DISCUSSION

3.1. Product yield

The mass balance obtained for the pyrolysis experiments is shown in table 2. The solid char and liquid bio-oil are obtained by weighing the components before and after experiments. The gases are obtained by difference, but are corrected with the gas values obtained from GC-TCD. A liquid bio-oil yield of up to 40% (by weight) was recorded for the catalytic experiments, which is marginally higher than yield from non-catalytic runs. The pyrolysis conditions can therefore be classified as intermediate pyrolysis due to the moderate temperature used and yield comparable to the patented Haloclean process [21]. From the mass balance, the char yield is consistent and comparable due to the invariable pyrolysis conditions for the primary fixed bed reactor. The significant change we observed was the increase in the gases yield for all the catalytic runs. This is confirmed by the increase in the CO₂ for almost all of the catalytic runs, except for Al-MCM-41 which increased the CO content. The liquid yield was found to be affected by ZSM-5 and BRHA with slight reduction compared to non-catalytic runs.

3.2. Bio-oil chemical composition

The chemical composition of the bio-oils was analysed using a GC-MS. The GC-MS chromatogram for typical rice husk sample pyrolysis oil is shown in figure 3, and the corresponding labelled peaks, chemical names, chemical formula and molecular weight are listed in table 3. The main pyrolysis products identified include acetic acids, furfural, guaiacol, ortho-cresol and para-cresol and levoglucosan. These chemicals originate from the degradation of cellulose, hemicellulose, lignin and extractives present in rice husk. Over 100 peaks were detected from the GC-MS, but only 42 peaks were judged to be crucial and selected for analysis. The bio-oil produced is classified into chemical groups, namely aromatic hydrocarbon, organic acids, furans, ketones, light phenols, heavy phenols and anhydrosugars. These are presented in table 4 showing the total peak areas for the different chemical groups for both non-catalytic and catalytic rice husk bio-oils.

It is interesting to note the varying effect of the different catalysts on bio-oil compositions. This suggests there is no uniformity in the catalyst properties and activities on bio-oil properties. A closer inspection of table 4 appears to suggest catalyst selectivity exist for certain chemical or functional groups. ZSM-5 was observed to be the most active catalyst for aromatics, furans and light phenols. Al-MCM-41 on the other hand increases the heavy phenols and decreases the amount of organic acids by considerable amounts.

The effect of catalyst selectivity on selected group of chemicals is given in table 5. Table 5 shows the peak areas for identified chemicals of interest that are known to affect specific bio-oil properties. Levoglucosan is one of the major products from the degradation of cellulose, besides water, char, CO and CO₂. All of the catalysts reduce the amount of levoglucosan present, but ZSM-5 shows the most reduction overall. This works confirms previous studies that showed levoglucosan is decreased or eliminated when subjected to catalytic cracking [14, 31].

Secondary degradation reactions by the catalysts help in the formation of other anhydrosugars and furans, such as furfural [50]. Furfural is produced from the pyrolysis of cellulose and hemicellulose [51]. The production of furfural is increased for all of the catalyst,

with ZSM-5 having the most effect. A study conducted by Adam et al. shows that Al-MCM-41 catalysts promote the furfural and furan production from pyrolysis of biomass [31]. The peak area for 2-methylfuran increases two-fold for Al-MCM-41 compared to the rest of the catalyst (table 5).

Acetic acid has the highest peak area detected amongst the other organic acids in the bio-oil. The peak area of acetic acid is mostly reduced with Al-MCM-41 catalyst, and BRHA catalyst having almost no effect on the reduction of acetic acid when compared to the non-catalytic run. This agrees with the study from Samolada et al., who reported a reduction in acetic acid content in bio-oil on using fresh Al-MCM-41 catalyst in a fixed bed reactor [52]. Adam et al. also reported that Al-MCM-41 increased the acetic acid production for fast pyrolysis, but observed a decreased for catalytic pyrolysis with a lower heating rate [31]. This result is in agreement with our study, as the heating rate in this work is moderate.

ZSM-5 appears to increase the production of phenols and cresols the most compared to the rest of the catalysts. Guaiacol and p-cresol is decreased by ZSM-5 and BRHA, but no significant change was seen for Al-MCM-41 and Al-MSU-F. The commercial catalysts showed a significant reduction of ketones, with ZSM-5 having the most reduction. BRHA on the other hand shows no variation in the amount of ketones.

The effect on aromatic hydrocarbons is shown in figure 4. Toluene and xylenes was seen to be the most affected by ZSM-5, with an increase in the peak areas compared to other catalysts. Benzene was not detected in the non-catalytic bio-oil, but is present in all the catalytic runs except for Al-MCM-41. The aromatics present in the non-catalytic runs are most likely due to the presence of alkali metals in the feedstock itself, which has a catalytic effect on its own during pyrolysis. Moreover, harmful polyaromatic hydrocarbon compounds were not detected in the rice husk bio-oil.

ZSM-5 was observed to be the most active catalyst, as it increases the aromatics, furans and light phenols content and decrease the ketones and anhydrosugars the most. Al-MCM-41 increases the heavy phenols and decreases the amount of organic acids the most while Al-MSU-F appears to mirror same activity with Al-MCM-41. BRHA can be seen to be the least active catalyst, but it decreases the amount of heavy phenols the most.

3.3. Bio-oil Properties

The physical properties of the bio-oil was measured and presented in Table 6. It shows the catalytic and non-catalytic bio-oils properties including the ultimate analysis, bio-oil pH and acid number, calorific values, bio-oil densities and viscosity, and water contents. The ultimate analysis was carried out externally by MEDAC Ltd., Surrey, UK for carbon, hydrogen, nitrogen and sulphur. Oxygen is obtained by difference. It was noted that the non-catalytic pyrolysis bio-oil is highly oxygenated, with 65 wt. % of oxygen present in the bio-oil. BRHA and Al-MSU-F was found to reduce the oxygen content compared to ZSM-5 and Al-MCM-41.

The carbon content for the non-catalytic rice husk bio-oil is 23.38 wt. %. Various authors reported fast pyrolysis for non-catalytic rice husk bio-oil to have higher carbon content values of 41.7 wt. % [19], 50.6 wt. % for the oil phase [16], 42.52 wt. % for upper phase and 57.87 wt. % lower phase respectively [22]. The difference might be due to the pyrolysis conditions,

in our case being intermediate pyrolysis. The carbon content for the catalytic runs shows that it decreases for ZSM-5 and Al-MCM-41, but increases for Al-MSU-F and BRHA.

Hydrogen content increases for all the catalytic runs, but slightly decreases for BRHA. Nitrogen and sulphur contents detected were very low in all of the bio-oils, showing their potential as a clean fuel when used for combustion purposes.

The acid number measured for non-catalytic pyrolysis oil was noticeably high with a value of 55 mg KOH/g but not unexpected. The use of catalyst reduces the value down to a range of 39-47 mg KOH/g, with ZSM-5 and BRHA having the least value. The pH of the bio-oil is noticeably acidic with a pH range of 2.7 to 3. There seems to be a vague correlation between the acid number and pH in this case. The pH measures the hydrogen ions in aqueous solution, and the pyrolysis oil obtained has an aqueous and an oil phase [53]. Nolte and Liberatore also concluded there was no correlation between pH and acid number in their work [54]. The measurement of acid number is much more relevant for measuring acidity compared to the pH, as it takes into account both phases of the pyrolysis bio-oil. Most of the acidity may arise from the presence of acetic acid, but other carboxylic acids, phenols and other acidic compounds will have a significant contribution.

The heating value is calculated from the ultimate analysis using the correlation from Parikh et al. [55]. However, there are assumptions needed to be considered such as the ash content of the bio-oil which is assumed to be 0.5% by weight. The values obtained takes into account the water content in the bio-oil. The higher heating value (HHV) increases for the entire catalytic runs regardless of the basis, except for ZSM-5 in wet basis (Table 6). This anomaly was also noted by Pattiya [56].

The measured viscosity, water content and density of the non-catalytic and catalytic rice husk bio-oil is also shown in table 6. The water content for the catalytic runs increases in the bio-oils. These indicate the catalysts are involved in the formation of water through reactions such as cracking and dehydration. The highest value of 55.56 % was obtained for ZSM-5, which indicates its stronger dehydration tendency compared to the other catalysts, due to its stronger acidity [52]. Oasmaa et al. reported that the density is a function of water content [58]. The density of the bio-oil decreases for the catalytic runs in comparison to the non-catalytic run, which can be attributed to the increase in the water content. Ji-lu found the density of rice husk bio-oil is 1190 kg/m³ at a water content of 25.2% [20], and Lu et al. obtained a value of 1140 kg/m³ at a water content of 28% [23]. In this study, the density of the non-catalytic pyrolysis oil is measured to be 1065 kg/m³ at 52.6% water content. The result from the viscosity measurements shows that the catalysts have an effect of reducing the viscosity on all of the runs. The low viscosity values for all, suggest that the viscosity is greatly influenced by the water content in the sample, as suggested by Nolte and Liberatore [54].

4. CONCLUSION

Catalytic pyrolysis experiments have been performed on rice husks and shown to improve some properties of the bio-oil in terms of the acidity, viscosity and heating values. ZSM-5 can be seen as a strong catalyst for the production of aromatic hydrocarbons and light

phenols, and Al-MCM-41 for reducing the acidity in the bio-oil. Significant changes in the peak area can be evaluated from the GC-MS, even though the catalyst-to-biomass ratio is low. The catalyst attached to a clay binder on monolith support is proven to work, although the effect of the binder towards the pyrolysis activity requires more research. The extent of catalyst coking by the pyrolysis vapours on the catalytic activity also needs to be investigated further. Poisoning of the catalyst should not be a problem as the sulphur content in the feedstock is very low. Since rice husk has very high ash content, the inorganic elements present will already have a catalytic effect on the feedstock itself. BRHA, therefore was used in this case as a cheaper alternative to the zeolite catalysts, and have shown to improve the bio-oil quality reasonably.

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REFERENCES

- [1] R. N. Lawrey, An economist's perspective on economic diversification in Brunei Darussalam, *CSPS Strategy and Policy Journal* 1 (2010) 13-28.
- [2] Department of Agriculture and Agrifood, Ministry of Industry and Primary Resources, Towards self-sufficiency in rice production Brunei Darussalam, www.agriculture.gov.bn [Accessed 1 June 2012]
- [3] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass Bioenerg.* 38 (2012) 68-94.
- [4] A.V. Bridgwater, Production of high grade fuels and chemicals from catalytic pyrolysis of biomass, *Catalysis Today* 29 (1996) 285-295.
- [5] D. Mohan, C. U. Pittman, Jr., P. H. Steele, Pyrolysis of wood/biomass for bio-oil: A critical review, *Energy Fuels* 20 (2006) 848-889.
- [6] H.B. Goyal, D. Seal, R.C. Saxena, Biofuels from thermochemical conversion of renewable resources: A review, *Renew. Sust. Energ. Rev.* 12 (2008) 504-517.
- [7] K.G. Mensaray, A.E. Ghaly, Thermal degradation of rice husk in nitrogen atmosphere, *Bioresource Technol.* 65 (1998) 13-20.
- [8] N. Worasuwanarak, T. Sonobe, W. Tanthapanichakoon, Pyrolysis behaviors of rice straw, rice husk and corncob by TG-MS technique, *J. Anal. Appl. Pyrol.* 78 (2007) 265-271.
- [9] S. Hu, A. Jess, M. Xu, Kinetic study of Chinese biomass slow pyrolysis: Comparison of different kinetic models, *Fuel* 86 (2007) 2778-2788.
- [10] L. T. Vlaev, I.G. Markovska, L.A. Lyubchev, Non-isothermal kinetics of pyrolysis of rice husk, *Thermochim. Acta* 406 (2003) 1-7.
- [11] W.-F. Chiang, H.-Y. Fang, C.-H. Wu, C.-Y. Chang, Y.-M. Chang, J.-L. Shie, Pyrolysis kinetics of rice husk in different oxygen concentrations, *J. Environ. Eng-ASCE* 134 (2008) 316-325.
- [12] H. Teng, H.-C. Lin, J.-A. Ho, Thermogravimetric analysis on global mass loss kinetics of rice hull pyrolysis, *Ind. Eng. Chem. Res.* 36 (1997) 3974-3977.

- [13] K.M. Isa, S. Daud, N. Hamidin, K. Ismail, S. A. Saad, F. H. Kasim, Thermogravimetric analysis and the optimisation of bio-oil yield from fixed-bed pyrolysis of rice husk using response surface methodology (RSM), *Ind. Crop Prod.* 33 (2011) 481-487.
- [14] Q. Lu, X. Zhu, W. Li, Y. Zhang, D. Chen, On-line catalytic upgrading of biomass fast pyrolysis products, *Chinese Science Bulletin* 54 (2009) 1941-1948.
- [15] W.T. Tsai, M.K. Lee, Y.M. Chang, Fast pyrolysis of rice husk: Product yields and compositions. *Bioresource Technol.* 98 (2007) 22-28.
- [16] P.T. Williams, N. Nugranad, Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. *Energy* 25 (2000) 493-513.
- [17] H.S. Heo, H.J. Park, J.-I. Dong, S.H. Park, S. Kim, D.J. Suh, Y.-W. Suh, S.-S. Kim, Y.-K. Park, Fast pyrolysis of rice husk under different reaction conditions, *J. Ind. Eng. Chem.* 16 (2010) 27-31.
- [18] E. Natarajan and E. Ganapathy Sundaram, Pyrolysis of rice husk in a fixed bed reactor, *World Academy of Science, Engineering and Technology* 56 (2009) 504-508.
- [19] S. Meesuk, J.-P. Cao, K. Sato, Y. Ogawa, T. Takarada, Fast pyrolysis of rice husk in a fluidised bed: Effects of the gas atmosphere and catalyst on bio-oil with a relatively low content of oxygen, *Energy Fuels* 25 (2011) 4113-4121.
- [20] Z. Ji-lu, Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system. *J. Anal. Appl. Pyrol.* 80 (2007) 30-35.
- [21] C.M. Rogerro, V. Tumiatti, A. Scova, C. De Leo, A. Binello, G. Cravotto, Characterization of oils from Haloclean® pyrolysis of biomasses, *Energy Sources: Part A* 33 (2011) 467-476.
- [22] R. Li, Z.-P. Zhong, B.-S. Jin, X.-X. Jiang, C.-H. Wang, A.-J. Zheng, Influence of reaction conditions and red brick on fast pyrolysis of rice residue (husk and straw) in a spout-fluid bed, *C. J. Chem. Eng.* 9999 (2011) 1-10
- [23] Q. Lu, Y. Xu-lai, Z. Xi-feng, Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk, *J. Anal. Appl. Pyrol.* 82 (2008) 191-198.
- [24] S.D. Stefanidis, K.G. Kalogiannis, E.F. Illiopolou, A.A. Lappas, P.A. Pilavachi, In-situ upgrading of biomass pyrolysis vapors: Catalyst screening on a fixed bed reactor, *Bioresource Technol.* 102 (2011) 8261-8267.
- [25] E.H Salter, Catalytic pyrolysis of biomass for improved liquid fuel quality, Ph.D, Aston University, (2001).
- [26] A. Pattiya, J.O. Titiloye, A.V. Bridgwater, Fast pyrolysis of cassava rhizome in the presence of catalysts, *J. Anal. Appl. Pyrol.* 81 (2008) 72-79.
- [27] R. French, S. Czernik, Catalytic pyrolysis of biomass for biofuels production, *Fuel Processing Technol.* 91 (2010), 25-32
- [28] M.-J. Jeon, S.-S. Kim, J.-K. Jeon, S.H. Park, J.M. Kim, J.M. Sohn, S.-H. Lee, Y.-K. Park, Catalytic pyrolysis of waste rice husk over mesoporous materials, *Nanoscale Research Letters*, 7 (2012).
- [29] J. Hagen, (2006). *Industrial Catalysis a practical approach*. Weinheim: Wiley-VCH.
- [30] A.V Bridgwater, Catalysis in thermal biomass conversion. *Appl Catal A-Gen* 116 (1994), 5-47.
- [31] J. Adam, M. Blaszko, E. Meszaros, M. Stocker, M.H. Nilsen, A. Bouzga, J.E. Hustad, M. Gronli, G. Oye, Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts, *Fuel* 84 (2005) 1494-1502.
- [32] J. Adam, E. Antonakou, A. Lappas, M. Stocker, M.H. Nilsen, A. Bouzga, J.E. Hustad, G. Oye, In situ catalytic upgrading of biomass derived fast pyrolysis vapours

- in fixed bed reactor using mesoporous materials, *Micropor. Mesopor. Mat.* 96 (2006) 93-101.
- [33] E. Antonakou, A. Lappas, M.H. Nilsen, A. Bouzga, M. Stocker, Evaluation of various types of Al-MCM-41 materials as catalysts in biomass pyrolysis for the production of bio-fuels and chemicals, *Fuel* 85 (2006) 2202-2212.
- [34] E.F. Iliopoulou, E.V. Antonakou, S.A. Karakoulia, I.A. Vasalos, A.A. Lappas, K.S. Triantafyllidis, Catalytic conversion of biomass pyrolysis products by mesoporous materials: Effect of steam stability and acidity of Al-MCM-41 catalysts. *Chem Eng J* 134 (2007) 51-57.
- [35] M.H. Nilsen, E. Antonakou, A. Bouzga, A. Lappas, K. Mathisen, M. Stocker, Investigation of the effect of metal sites in Me-Al-MCM-41 (Me = Fe, Cu or Zn) on the catalytic behavior during the pyrolysis of wooden based biomass. *Micropor. Mesopor. Mat.* 105 (2007) 189-203.
- [36] K.S. Triantafyllidis, E.F. Iliopoulou, E.V. Antonakou, A.A. Lappas, H. Wang, T.J. Pinnavaia, Hydrothermally stable mesoporous aluminosilicates (MSU-S) assembled from zeolite seeds as catalysts for biomass pyrolysis. *Micropor. Mesopor. Mat.* 99 (2007) 132-139.
- [37] C. Perego, A. Bosetti, Biomass to fuels: The role of zeolite and mesoporous materials, *Micropor Mesopor Mat.* 144 (2011) 28-39.
- [38] S. Wang, Application of solid ash based catalysts in heterogeneous catalysis, *Environ. Sci. Technol.* 42 (2008) 7055-7063.
- [39] A. M. Yusof, N.A. Nizam, N.A. Abd Rashid, Hydrothermal conversion of rice husk ash to faujasite-types and NaA-type of zeolites, *J Porous Mater* 17 (2010) 39-47.
- [40] M. M. Rahman, N. Hasnida, W.B. Wan Nik, Preparation of zeolite Y using local raw material rice husk as a silica source, *J. Sci. Res.* 1 (2009) 285-291.
- [41] British Standard Institution, BS EN 14774-3:2009 Solid biofuels – Determination of moisture content – Oven dry method – Part 3: Moisture in general analysis sample, London: BSI, 2010.
- [42] British Standard Institution, BS EN 15148:2009 Solid biofuels – Determination of the content of volatile matter, London: BSI, 2010.
- [43] British Standard Institution, BS EN 14775:2009 Solid biofuels – Determination of the ash content, London: BSI, 2010.
- [44] ASTM Standard D5865, Standard Test Method for Gross Calorific Value of Coal and Coke, ASTM International, United States, 2007.
- [45] FOSS Analytical AB, Determination of amylase treated Neutral Detergent Fibre using the Fibertec system according to AOAC 2002:04/ISO 16472:2005, 2003.
- [46] FOSS Analytical AB, Determination of Acid Detergent Fibre (ADF) and Acid Detergent Lignin (ADL) using Fibercap™ 2021/2023, 2003.
- [47] L. Du, P. Yu, B.G. Rosnagel, D. A. Christensen, J.J. McKinnon, Physicochemical Characteristics, Hydroxycinnamic Acids (Ferulic acid, p-coumaric acid) and their ratio, and in situ biodegradability: Comparison of genotypic differences among six barley varieties, *J. Agric. Food Chem.* 57 (2009) 4777-4783.
- [48] M. Carrier, A. Loppinet-Serani, D. Denux, J-M. Lasnier, F. Ham-Pichavant, F. Cansell, C. Aymonier, Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass, *Biomass Bioenerg.* 35 (2011) 298-307.
- [49] ASTM Standard D1744, Standard Test Method for Determination of Water in Liquid Petroleum Products by Karl Fisher Reagent, ASTM International, United States.

- [50] Y-C Lin, J. Cho, G. A. Tompsett, P. R. Westmoreland, G. W. Huber, Kinetics and mechanism of cellulose pyrolysis, *J. Phys. Chem. C* 113 (2009) 20097-20100.
- [51] P.J. De Wild, H. Reith, H.J. Heeres, Biomass pyrolysis for chemicals, *Biofuels* 2 (2011) 185-208.
- [52] M.C. Samolada, A. Papafotica, I.A. Vasalos, Catalyst evaluation for catalytic biomass pyrolysis, *Energy Fuels* 14 (2000) 1161-1167.
- [53] B. Bunting, A. Boyd, Pyrolysis oil properties and chemistry related to process and upgrade conditions for pipeline shipment, Oak Ridge National Laboratory, 2012.
- [54] M.W. Nolte, M.W. Liberatore, Viscosity of biomass pyrolysis oils from various feedstocks, *Energy Fuels*, 24 (2010) 6601-6608.
- [55] J. Parikh, S.A. Channiwala, G.K. Ghosal, A correlation for calculating HHV from proximate analysis of solid fuels, *Fuel* 84 (2005) 487-494.
- [56] A. Pattiya, Catalytic pyrolysis of agricultural residues for bio-oil production, Ph.D. Aston University (2007).
- [57] Q. Lu, J. Zhang, X. Zhu, Corrosion properties of bio-oil and its emulsion with diesel, *Chinese Science Bulletin* 53 (2008) 3726-3734.
- [58] A. Oasmaa, E. Leppamaki, P. Koponen, J. Levander, E. Tapola, Physical characterisation of biomass-based pyrolysis liquids, Application of standard fuel oil analyses, VTT Publications 306, 1997. ISBN 951-38-5051-X.

Table 1. Characterisation of Brunei Rice Husks (BRH)

Characterisation of Brunei Rice Husks	
Proximate Analysis (dry basis, wt %)	
Moisture	8.43
Volatile Matter	68.25
Ash	14.83
Fixed Carbon	16.92
Ultimate Analysis (dry and ash-free, wt %)	
Carbon	39.48
Hydrogen	5.71
Nitrogen	0.665
Sulphur	< 0.10
Chlorine	0.025
Oxygen	54.12
Heating Values (MJ/kg)	
HHV (dry basis)	17.34
LHV (dry basis)	16.10
Compositional Analysis (dry, ash and extractives free, wt %)	
Cellulose	41.52
Hemicellulose	14.04
Lignin	33.67
Extractives	10.77

Table 2. Mass balance yield (wt. %) from non-catalytic and catalytic pyrolysis of BRH

Run Name	No catalyst	ZSM-5	Al-MCM-41	Al-MSU-F	BRHA
Char (% by wt.)	41.92	42.27	43.15	43.31	42.27
Liquid (% by wt.)	39.61	38.29	39.98	39.59	38.29
Gases (% by wt.)	18.47	19.45	18.80	19.18	21.62
CH ₄ (vol. %)	2.06	2.86	1.72	1.49	4.65
CO (vol. %)	9.14	3.38	11.28	7.03	7.76
CO ₂ (vol. %)	75.40	83.19	74.20	78.80	76.33

Table 3. The selected BRH pyrolysis bio-oil chemicals detected from the GC-MS

Peak	Chemical name	Formula	Molecular Weight
1	2-methylfuran / Sylvan	C ₅ H ₆ O	82.10
2	Benzene	C ₆ H ₆	78.11
3	2,5-dimethylfuran	C ₆ H ₈ O	96.13
4	Acetic Acid	C ₂ H ₄ O ₂	60.05
5	2-methoxytetrahydrofuran	C ₅ H ₁₀ O ₂	102.13
6	Toluene	C ₇ H ₈	92.14
7	Propanoic acid	C ₃ H ₆ O ₂	74.08
8	Cyclopentanone	C ₅ H ₈ O	84.12
9	1-hydroxy-2-butanone	C ₄ H ₈ O ₂	88.11
10	Ethylbenzene & p-xylene	C ₈ H ₁₀	106.17
11	m-xylene	C ₈ H ₁₀	106.17
12	o-xylene	C ₈ H ₁₀	106.17
13	Styrene	C ₈ H ₈	104.15
14	Furfural	C ₅ H ₄ O ₂	96.09
15	Tetrahydro-2,5-dimethoxyfuran	C ₆ H ₁₂ O ₃	132.16
16	1-(acetyloxy)-2-propanone / Acetol acetate	C ₅ H ₈ O ₃	116.12
17	2-Cyclopenten-1-one, 2-methyl-	C ₆ H ₈ O	96.13
18	2-Furyl Methyl Ketone	C ₆ H ₆ O ₂	110.11
19	1,2-cyclopentanedione	C ₅ H ₆ O ₂	98.10
20	5-methyl-2-furancarboxaldehyde / 5-methylfurfural	C ₆ H ₆ O ₂	110.11
21	2,3-dimethyl-2-cyclopenten-1-one	C ₇ H ₁₀ O	110.16
22	3-Methyl-2-Cyclopentenone	C ₆ H ₈ O	96.13
23	2(5H)-Furanone	C ₄ H ₄ O ₂	84.07
24	3-methyl-1,2-cyclopentanedione	C ₆ H ₈ O ₂	112.13
25	Phenol	C ₆ H ₆ O	94.11
26	2-methoxyphenol / Guaiacol	C ₇ H ₈ O ₂	124.14
27	2-methylphenol / o-cresol	C ₇ H ₈ O	108.14
28	Maltol / Larixic acid	C ₆ H ₆ O ₃	126.11
29	4-methylphenol / p-cresol	C ₇ H ₈ O	108.14
30	3-methylphenol / m-cresol	C ₇ H ₈ O	108.14
31	2-methoxy-p-cresol / p-cresol	C ₈ H ₁₀ O ₂	138.17
32	2,4-Dimethylphenol / 2,4-xyleneol	C ₈ H ₁₀ O	122.16
33	4-Ethylphenol	C ₈ H ₁₀ O	122.16
34	4-Ethylguaiacol	C ₉ H ₁₂ O ₂	152.19
35	2,3-anhydro-d-galactosan	C ₆ H ₈ O ₄	144.13
36	1,4:3,6-dianhydro- α -d-glucopyranose	C ₆ H ₈ O ₄	144.13
37	o-coumaric acid	C ₉ H ₈ O ₃	164.16
38	2-Methoxy-4-vinylphenol / 4-Vinylguaiacol	C ₉ H ₁₀ O ₂	150.18
39	Isoeugenol	C ₁₀ H ₁₂ O ₂	164.20
40	Isovanillin	C ₈ H ₈ O ₃	152.15
41	Vanillyl methyl ketone	C ₁₀ H ₁₂ O ₃	180.20
42	Levogluconan	C ₆ H ₁₀ O ₅	162.14

Table 4. Total peak areas of the chemical groups for the non-catalytic and catalytic BRH bio-oil

Chemical Groups	Peak Areas (%)				
	No catalyst	ZSM-5	AI-MCM-41	AI-MSU-F	BRHA
Aromatic hydrocarbon	1.51	2.24	1.42	1.57	1.53
Organic Acids	16.06	15.49	14.17	15.51	16.16
Furans	8.99	9.63	9.47	9.57	9.48
Ketones	14.75	12.96	13.65	13.82	14.76
Light Phenols	12.77	14.44	12.60	12.56	12.66
Heavy Phenols	13.57	13.48	14.99	14.24	12.84
Anhydrosugars	3.65	2.04	2.88	2.34	2.75
TOTAL	71.27	70.27	69.16	69.59	70.16

Table 5. Total peak areas for selected chemicals from non-catalytic and catalytic rice husk bio-oil

Chemical Name	Peak Areas (%)				
	No catalyst	ZSM-5	Al-MCM-41	Al-MSU-F	BRHA
Acetic Acid	10.74	9.57	8.66	9.92	10.68
2-methylfuran / Sylvan	0.44	0.57	0.94	0.44	0.32
Furfural	6.54	7.13	6.80	6.84	6.87
3-methyl-1,2-cyclopentanedione	4.18	3.58	3.82	3.75	4.10
Phenol	2.97	3.78	2.86	2.73	3.06
Guaiacol	6.41	5.35	6.40	6.40	6.01
2-methylphenol /o-cresol	0.90	1.60	0.99	0.94	0.99
2-methoxy-p-cresol / p-creosol	3.26	2.65	3.30	3.16	2.92
Levoglucosan	2.35	0.98	1.68	1.34	1.45

Table 6. Properties of catalytic and non-catalytic BRH bio-oils

Ultimate Analysis	No Catalyst	ZSM-5	Al-MCM-41	Al-MSU-F	BRHA
C (%)	23.38	19.99	22.51	25.63	31.95
H (%)	10.39	11.38	11.34	10.67	10.16
N (%)	0.51	0.41	0.35	0.49	0.38
S (%)	<0.10	<0.10	<0.10	<0.10	<0.10
O (%) *	65.63	68.13	65.71	63.12	57.42
* By difference					
Acidity					
Acid number (mg KOH/g)	55.54	39	43.15	46.74	39.43
pH	3	2.74	2.83	2.69	2.79
Higher Heating Value (HHV)					
HHV-wet basis (MJ/kg)	13.61	13.33	14.41	14.98	17.17
HHV-dry basis (MJ/kg)	28.71	30.01	31.79	33.02	38.53
Kinematic Viscosity (cSt)	1.68	1.55	1.65	1.49	1.57
Water content (%)	52.6	55.56	54.66	54.64	55.43
Density (kg/m ³) @ 25°C	1065	1053	1058	1059	1052

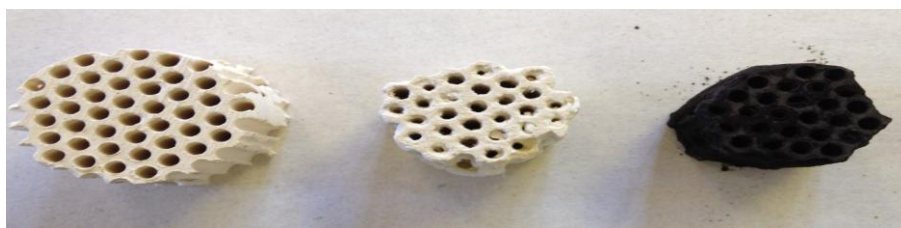


Figure 1. (From left to right) Monolith catalyst support, catalyst-filled monolith and coking on the catalyst after pyrolysis experiment

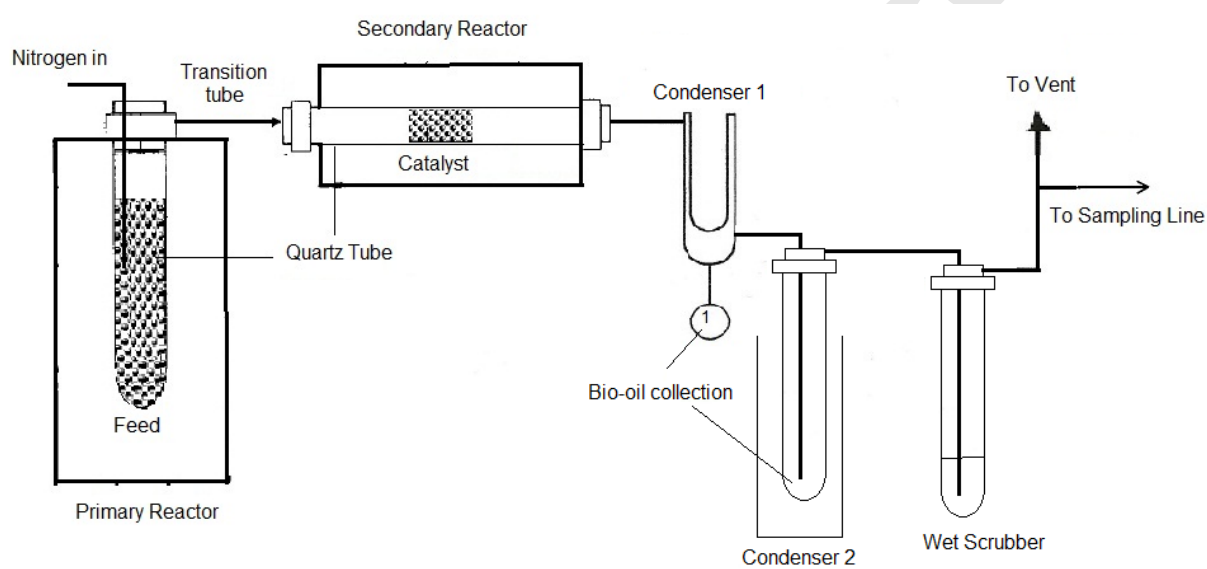


Figure 2. Schematic diagram of closed-coupled catalytic pyrolysis rig setup

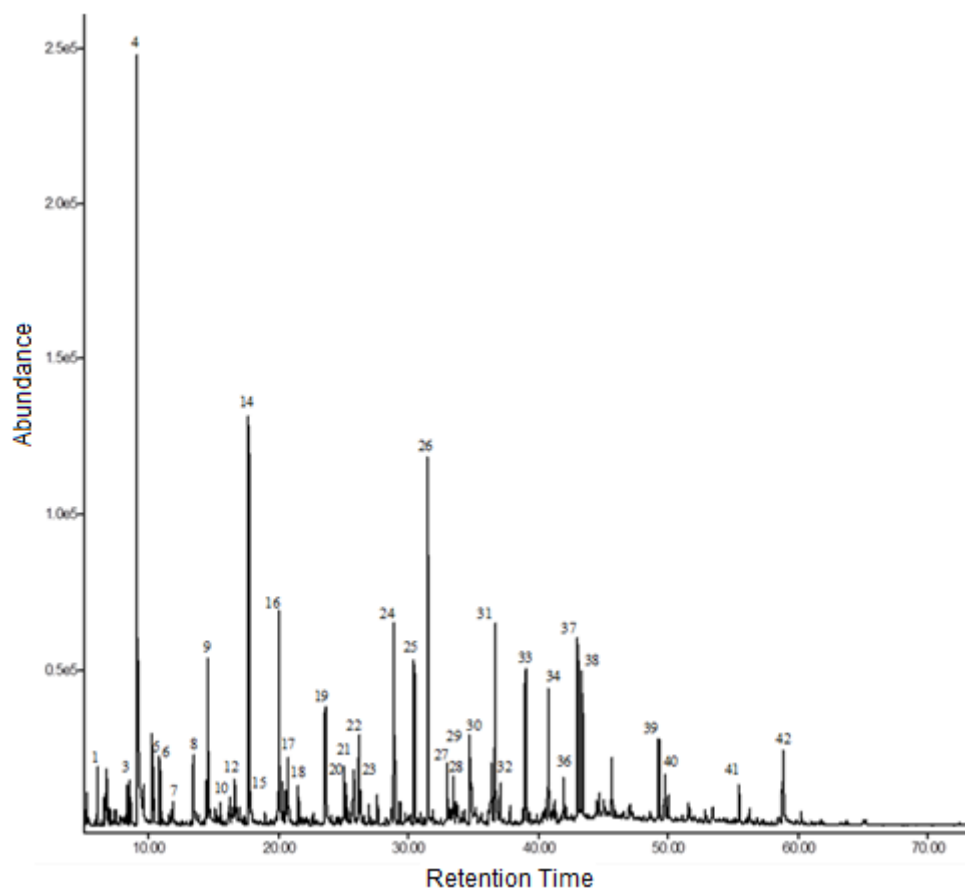


Figure 3. Shows a typical chromatograph of BRH pyrolysis oil

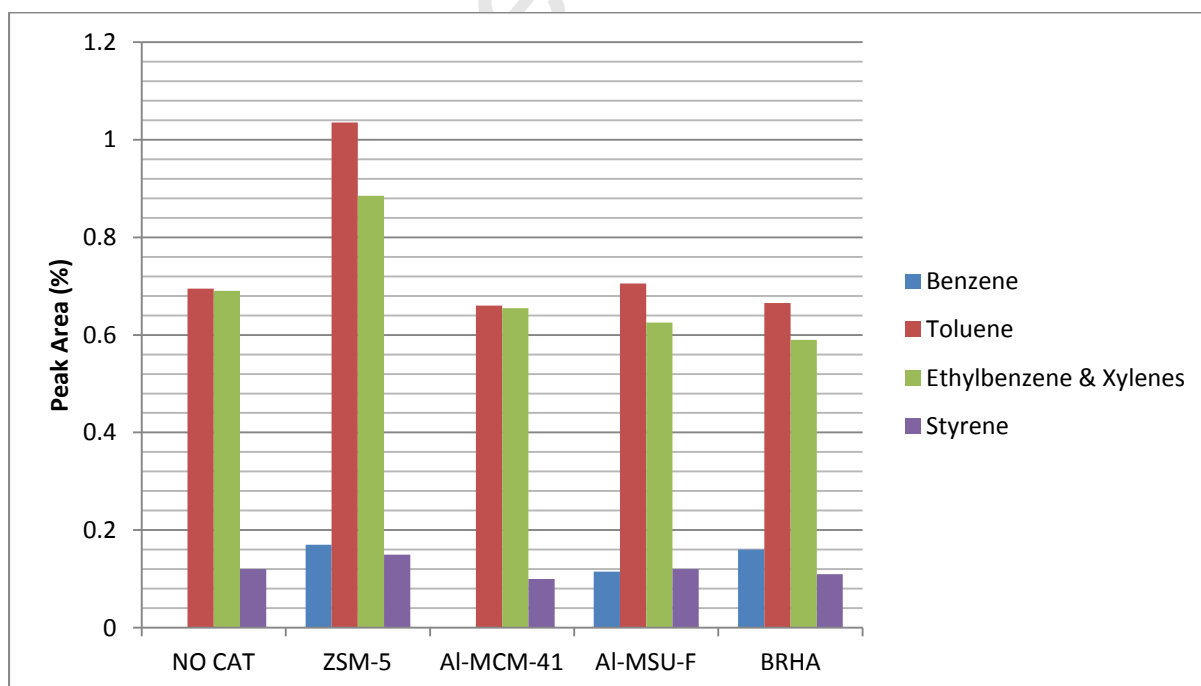


Figure 4. Effect of catalysts on aromatic hydrocarbons

Highlights:

- ZSM-5 is seen as a strong catalyst for the production of aromatic hydrocarbons and light phenols, and Al-MCM-41 for reducing the acetic acid in the bio-oil.
- The catalytic runs increased the calorific value and water content in the bio-oil, whilst viscosity, density and acid number is decreased.
- BRHA can be a cheaper alternative to the zeolite catalysts, and have shown to improve the bio-oil quality reasonably.

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