Comparative Performance of Catalytic and Non-Catalytic Pyrolysis of Sugarcane Bagasse in Catatest Reactor System

Syahirah Faraheen Kabir Ahmad¹, Umi Fazara Md Ali¹*, Khairuddin Md Isa², Alina Rahayu Mohamed², Omneswary Sataimurthi¹

¹Department of Environmental Engineering, Faculty of Engineering, University Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis
²Department of Chemical Engineering Technology, Faculty of Engineering Technology, University Malaysia Perlis, Padang Besar, Perlis 02100, Malaysia.
*email: umifazara@unimap.edu.my

Abstract. Catalytic pyrolysis is a favourable process used to enhance the quality of bio-oil. Based on reviews from previous research there are only scarce of studies on the comparison of catalytic and non-catalytic pyrolysis of biomass such as rice husk, olive husk and corncob. In this study, sugarcane bagasse was selected as it has not been explored much yet. The target of this research is to compare the impact of catalytic and non-catalytic pyrolysis of sugarcane bagasse in terms of the yield, properties, and also the compositions of bio-oil. Catalytic and non-catalytic pyrolysis was executed in catatest bed reactor at temperatures 400°C to 550°C with the aids of ZSM-5 zeolite catalyst. Bio-oil from catalytic and no-catalytic pyrolysis which gives the maximum yield was used to be studied further in terms of the properties and chemical compositions. The result shows that the maximum yield of bio-oil was accomplished from catalytic pyrolysis at temperature 500°C which was 21.4%. The properties and composition of bio-oil from catalytic pyrolysis shows better result compare to non-catalytic pyrolysis.

Keyword: Bio-oil, Biomass, Pyrolysis, Zeolite

1. Introduction
Recent concerns about depletion of oil have heightened the need for sustainable energy resources. Renewable sources such as biomass seem like a plausible alternative to be used to replace fuels in the future. There are several routes can be applied to transform biomass into bio-oil but the most well-known method is fast pyrolysis. This method can produce highest yield of bio-oil at following conditions (1) heating rate more than 100°C/min and high heating transfer rate, (2) biomass feed less than 1 mm, (3) temperature around 500°C, and (4) instant cooling of the pyrolysis vapours [1]. Many type of reactor have been used by researchers in fast pyrolysis process such as fixed bed [2-3], fluidized bed [4-5], spouted beds [6-7], ablative and vacuum pyrolyzers [8].

Catatest bed reactor is a fixed bed reactor usually used when catalyst is utilized. Catatest bed reactor is a cylindrical vessel filled with pellets catalyst and easy to operate. Catatest bed reactor is a prominent reactors used to produce bio-oil, bio-char and gas. Bio oil is a thick dark brown liquid which inhere different types of organic compounds such as alcohols, phenol, furans, organic acid, esters, aldehydes and others. Compound presence in the bio-oil is believed able to be used as an alternative to bio-fuel. However previous research shows that bio-oil is not capable to be used directly as fuel because it is highly oxygenated and chemically unstable. Bio-oils quality can be improved by reducing the oxygen content which can be achieved by adding catalyst [9].

Zeolite catalyst has been used in the pyrolysis process to reduce the oxygen content in the bio-oil [10-11]. There has been research that differentiate the product yields of catalytic and non-catalytic
pyrolysis from rice husks using ZSM-5 catalyst in a fluidized bed reactor [12]. The result shows that the influence of the catalyst was to convert the oxygen in the pyrolysis oil to largely H₂O at the lower catalyst temperatures and to largely CO and CO₂ at the higher catalyst temperatures.

In this paper, catalytic and non-catalytic pyrolysis of sugarcane bagasse was executed in cateat reactor system. The experiment was done two times separately, first in the presence of catalyst and the other one without catalyst. The main interest of this research was to pursuit the optimum temperature that gives highest yield of bio-oil from catalytic and non-catalytic pyrolysis of sugarcane bagasse. The bio-oil gained at this optimum temperature was investigated further in terms of their compositions and properties.

2. Method

2.1 Materials

2.1.1 Feedstock

Sugarcane bagasse was used as raw materials in this experiment. Sugarcane bagasse was collected along roadside of Jitra, Kedah, Malaysia. Prior to the experiment, sugarcane bagasse was dried in oven at temperature 80°C to remove external moisture. After that sugarcane bagasse was grinded in a cutting mill and sieved to obtain particle sizes of range 4.0 to 6.0 mm.

2.1.2 Catalyst

ZSM-5 zeolite used in this experiment was purchased from a commercial supplier. ZSM-5 zeolite is a high acidity catalyst which comes in pellets form with diameter about 0.2 to 0.3 cm.

2.2 Catatex B Reactors

Catalytic and non-catalytic pyrolysis experiments were done at difference temperature settings to investigate the effect of yield, chemical compositions and properties of the bio-oil extracted from sugarcane bagasse. Abundance of studies on pyrolysis of sugarcane bagasse has been executed at temperature range of 350°C to 650°C [13-14]. Hence current study of pyrolysis of sugarcane bagasse was also performed within this temperature range.

The pyrolysis process was executed in a catatex bed reactor as depicted in Figure 1. The reactor consists of a cylindrical tube reactor fitted with a thermocouple, a nitrogen cylinder, an electric heater, cold trap, water bath and product effluent. The tube reactor was filled with 2.0 g of sugarcane bagasse sample and 0.2 g of ZSM-5 zeolite catalyst which were mixed together physically. The temperature of the reactor which was heated by an electric furnace was supervised using an external PID controller. The tube reactor was insulated with glass wool to keep the temperature constant throughout the experiment. Water bath connected to the cold trap help to condense the vapour and quench it into liquid product (bio-oil). Non-condense gas was vented out.

Once the condenser was ready the sample and catalyst was inserted into the furnace. Nitrogen gas was pump into the reactor to maintain an inert condition throughout the process. Temperature was set in the PID controller and the heater was on. The heating rate of the heater was 50°C/min. After 15 minutes the heater was turn off to allow the reactor to cool down before collecting the bio-oil and char. Bio-oil and char were weighed and measured in weight percentage while the gas yield was calculated by difference between overall biomass fed and sum of bio-oil yield and char yield.
2.3 Products Analysis

2.3.1. GCMS

The compounds presence in catalytic and non-catalytic bio-oil were examined using Gas Chromatography Mass Spectrometer (GCMS). The model of GCMS used to analyze the bio-oil was QP2010 Series Gas Chromatograph equipped with 30 m length (0.25 mm I.D.) of Thermo Scientific Gas Chromatograph Column. Before the injection 250 mg/L of bio-oil was diluted with 2 mL methanol and 10 mL of dichloromethane. The GCMS method used in this study is the same method used by [16]. Roughly 32 minutes was taken to run each sample.

2.4 Properties of Bio-oil

The elemental analysis (CHON) of the bio-oil was done using Carlo-Erba, 628 series elemental analyzer. The gross calorific value of the bio-oil was determined by using Eq. (1). Viscosity of bio-oil was tested using Brickfield viscometer. Karl-fisher titration method was applied to identify the water content in the bio-oil. Other physicochemical properties such as density and pH value of bio-oil were also identified by using density meter and pH probe.

\[ HHV_{dry} = 0.2949C + 0.825H \]  

Eq. (1)

3. Result and Discussion

3.1 Impact of Temperatures on Outputs Yield

Table 1 indicates the influenced of temperature on the yield of bio-oil, char and gas gained from catalytic and non-catalytic pyrolysis of sugarcane bagasse at temperature range of 400°C to 550°C. Temperature is considered as most prominent criteria which influenced the products yield. In pyrolysis process, highest bio-oil yield usually is obtained at temperature within 350°C and 600°C. The bio-oil yield increases linearly along the temperature until it reach a supreme point and declining thereafter [17].

Current study also found similar trend of results. The bio-oil yield for catalytic and non-catalytic pyrolysis increase as the temperature incline from 400°C to 500°C and start decreasing as temperature reach 550°C. The sudden drop of bio-oil yield at higher temperature may due to secondary cracking of pyrolysis process in order to earn more gaseous and char product. This action causes the yield of bio-oil to decrease at high temperature [18]. The char yield for both catalytic and non-catalytic pyrolysis decrease rapidly as the temperature increasing. This may due to further break down of sugarcane bagasse lignin. Decreasing of char yield promotes the increasing of volatile matter which is transforms into liquid and gaseous product. Gas yield for catalytic and non-catalytic pyrolysis increased continuously as the temperature increased. The result obtained in this study is similar with previous
research [13-14]. From Table 1 it can be conclude that catalytic pyrolysis produce higher bio-oil yield compare to non-catalytic pyrolysis. Highest bio-oil yield was accomplished at temperature 500°C in catalytic pyrolysis which was 21.4%.

Table 1: Yield of products from catalytic and non-catalytic pyrolysis

| Temperature (°C) | Non-catalytic pyrolysis | Catalytic pyrolysis |
|------------------|------------------------|---------------------|
|                  | Bio-oil (%)            | Char (%)            | Gas (%)   | Bio-oil (%) | Char (%) | Gas (%) |
| 400              | 12.9                   | 54.8                | 32.3      | 16.4        | 43.5     | 40.1    |
| 450              | 14.3                   | 52.7                | 33.0      | 17.2        | 39.1     | 43.7    |
| 500              | 16.8                   | 48.7                | 34.5      | 21.4        | 33.8     | 44.8    |
| 550              | 3.67                   | 46.2                | 50.1      | 6.26        | 30.6     | 63.1    |

3.2 Chemical Compositions of Bio-oil at Optimum Temperature

3.2.1 Bio-oil Compositions for Non-catalytic Pyrolysis

The subsequent analysis was identifying chemical compounds presence in the bio-oil gained from the optimum temperature. The main purpose of this analysis was to compare similar components located in both catalytic and non-catalytic bio-oil. Bio-oil was evaluated using Gas Chromatography Mass Spectrometry (GC-MS). Bio-oil mainly consists of phenol, aldehydes, ketones, carboxylic acids, alcohols, esters, aliphatic hydrocarbon and aromatic hydrocarbon [19]. This compound is generated as result of decomposition of lignin and cellulose. From over 400 compounds recognized by GC-MS, only the first 100 compounds were examined. This is due to the concentration effect of oxygenated and aromatic compound found in the bio-oils and also the composition of the oxygenated compound in the bio-oil relies on the amount of lignocelluloses materials presence in the biomass.

The percentage of organic compounds presence in the bio-oil produced from non-catalytic pyrolysis of sugarcane bagasse was illustrated in Figure 2. Based on the chart the highest compounds presence in the bio-oil were acids (17.6%), phenol (16.3%), and furfural (12.0%). The results obtained in this study quite similar with previous research, which findings showed that dominant chemicals from non-catalytic pyrolysis of lignocellulosic biomass mainly consists of acids, furfural and phenol [16]. The percentage of acid and furfural are high due to secondary decomposition of hemicelluloses and hydroxymethyl furfural (HMF) around temperature 400°C [20]. Phenolic compound show high percentage because decomposition of aromatic compound from lignin start as the temperature increase from 400°C to 550°C [16].
3.2.2 Bio-oil Compositions for Catalytic Pyrolysis

**Figure 3** portrays the percentages of organic compounds exist in bio-oil produced from catalytic pyrolysis of sugarcane bagasse. Based on the chart the highest compound presences in the bio-oil were aromatic hydrocarbon (26.2%), phenol (14.8%) and furfural (13.0%). Presence of high amount of aromatic hydrocarbon is due to deoxygenation process. Deoxygenation process involves the conversion of oxygen into carbon dioxide. ZSM-5 zeolite catalyst helps in speeding up the deoxygenation process where most of the carbon dioxide is converted into benzene or toluene [21]. Catalytic pyrolysis was proven to be the most efficient process to produce good quality of bio-fuel as it reduces the content of oxygenated hydrocarbons.

3.2.3 Comparison of organic compound in bio-oil from non-catalytic and catalytic pyrolysis
Figure 4 shows the differences between percentage of organic compounds in bio-oil from direct pyrolysis and catalytic pyrolysis. In the figure below, organic compounds such as phenol, aldehydes, ketones, acids, alcohols, aliphatic hydrocarbon and sugar dominates in non-catalytic pyrolysis. Presence of catalyst in catalytic pyrolysis has triggered the increment of aromatic hydrocarbon and furfural drastically while decreasing other compounds. The decrease of other organic compounds in catalytic pyrolysis process may cause by the breakdown of molecules from long carbon chain.

![Comparison percentage organic compounds between non-catalytic and catalytic pyrolysis](Image)

**Figure 4**: Comparison percentage organic compounds between non-catalytic and catalytic pyrolysis

### 3.3 Properties of bio-oil

Table 2 shows the contrast between the properties of bio-oil from catalytic and non-catalytic pyrolysis of sugarcane bagasse.

| Properties          | Bio-oil with catalyst | Bio-oil without catalyst | Crude oil [22] |
|---------------------|-----------------------|--------------------------|----------------|
| C (wt%)             | 40.7                  | 31.7                     | 83-86          |
| H (wt%)             | 6.50                  | 5.25                     | 11-14          |
| N (wt%)             | 0.85                  | 0.96                     | <1             |
| O (wt%)             | 51.8                  | 61.9                     | <1             |
| S (wt%)             | 0.08                  | 0.12                     | <4             |
| pH value            | 3.4                   | 2.8                      | -              |
| Viscosity (cSt)     | 21.8                  | 21.5                     | 180            |
| Density (kg/m³)     | 1135                  | 1070                     | 860            |
| Water content (%)   | 12.3                  | 11.4                     | 0.1            |
| HHV (MJ/kg)         | 17.4                  | 13.7                     | 44             |

Carbon and hydrogen value in bio-oil from catalytic pyrolysis is much higher compare to bio-oil from non-catalytic pyrolysis. High value of carbon and hydrogen are illustrated in good quality fuel. The oxygen content in catalytic bio-oil is much lower compare to non-catalytic bio-oil. Decreasing of oxygen content in catalytic bio-oil caused the value of HHV to increase and this is favourable for good quality of fuel. Furthermore, low nitrogen and sulphur content in catalytic bio-oil is desirable. High nitrogen and sulphur fuel is not good for the environment as it produces oxides during combustions.
pH value of bio-oils from catalytic pyrolysis of sugarcane bagasse was slightly higher compared to non-catalytic. pH value of bio-oil normally between 2.0–3.8 because the existence of organic acids, commonly acetic and formic acid. The presence of these acids compound in bio-oil will compromise the storage and transport process.

Viscosity of bio-oils usually is between 35-1000cP at 40°C depending on the feedstock as well as the operating conditions. In this research, the value of viscosity for bio-oil from catalytic pyrolysis was 21.80 cSt which also slightly higher compared to non-catalytic. However the value is much lower compared to viscosity of crude oil. This may due to the presence of large amount of water in the bio-oil which resulting in the increment of the oil fluidity.

The density of bio oil for catalytic pyrolysis was 1135 kg/m³ while for non-catalytic was 1070 kg/m³ which was slightly higher than the crude oil.

Water contents of bio-oil from catalytic pyrolysis of sugarcane bagasse was slightly higher compared to non-catalytic which was 12.3 wt%. Previous research has reported that most of water content in bio-oil is within 15-30 wt% relying upon the original moisture in biomass and parameter of pyrolysis process [23]. Water content in bio-oil was considerably low which may due to the drying of sugarcane bagasse prior to the pyrolysis process. Low water content in bio-oil from this research indicates this bio-oil has potential as a good combustion fuel.

Typically, bio-oil has a heating value in between 40–50% of conventional petroleum fuel [24]. The heating value of catalytic bio-oil was higher compared to non-catalytic which was 17.4 MJ/kg. However, the heating value was considered lesser than the crude oil (44 wt %). The lower heating value maybe because effect of water and oxygenated compounds presence in the bio-oil.

4. Conclusion

Fast pyrolysis of sugarcane bagasse was executed in catatet bed reactor to investigate the effect of catalytic and non-catalytic pyrolysis on the yield, properties and also composition of the bio-oil produced. This study concludes that in terms of the yields and compositions of bio-oil, catalytic pyrolysis is better compared to non-catalytic pyrolysis as it gives the highest bio-oil yield at temperature 500°C which was 21.4%. The use of ZSM-5 zeolite catalyst improves the composition of bio-oil by increasing the aromatic hydrocarbon and lowering the oxygen content of bio-oil which gives plausible potential to be implemented as fuel. By taken consideration of overall performances, it can be summarized that some of bio-oil properties produce from catalytic pyrolysis of sugarcane bagasse such as elemental composition, viscosity and heating value showed better quality to be used as substitution for fuel in comparison to non-catalytic bio-oil.

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5. References

[1] Tsai WT, Lee MK, Chang YM. Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *Journal of Analytical and Applied Pyrolysis*. 2006; 76: 230–237.
[2] Ro D, Kim YM, Lee IG, et al. Bench scale catalytic fast pyrolysis of empty fruit bunches over low cost catalysts and HZSM-5 using a fixed bed reactor. *Journal of Cleaner Production*. 2018; 176: 298–303.
[3] Moralı U, Yavuzel N, Şensöz S. Pyrolysis of hornbeam (Carpinus betulus L.) sawdust: Characterization of bio-oil and bio-char. *Bioresources Technology*. 2016; 221: 682–685.
[4] Ly HV, Kim SS, Woo HC, et al. Fast pyrolysis of macroalga Saccharina japonica in a bubbling fluidized-bed reactor for bio-oil production. *Energy*. 2015; 93: 1436–1446.
[5] Jeong JY, Lee UD, Chang WS, et al. Production of bio-oil rich in acetic acid and phenol from fast pyrolysis of palm residues using a fluidized bed reactor: Influence of activated carbons. *Bioresources Technology*. 2016; 219: 357–364.
[6] Alvarez J, Lopez G, Amutio M, et al. Characterization of the bio-oil obtained by fast pyrolysis of sewage sludge in a conical spouted bed reactor. Fuel Process. Technol. 2016; 149: 169–175.
[7] Alvarez J, Lopez G, Amutio M, et al. Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor. Fuel. 2014; 128: 162–169.
[8] Luo G, Chandler DS, Anjos LCA, et al. Pyrolysis of whole wood chips and rods in a novel ablative reactor. Fuel. 2017; 194: 229–238.
[9] Nilsen MH, Antonakou E, Bouzga A, et al. 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. Microporous and Mesoporous Materials. 2007; 105: 189–203.
[10] Wang Y, Wang J. Bioresource Technology Multifaceted effects of HZSM-5 (Proton-exchanged Zeolite Socony Mobil-5) on catalytic cracking of pinewood pyrolysis vapor in a two-stage fixed bed reactor. Bioresour. Technol. 2016; 214: 700–710.
[11] Zhang B, Zhong Z, Chen P, et al. Microwave-assisted catalytic fast pyrolysis of biomass for bio-oil production using chemical vapor deposition modified HZSM-5 catalyst. Bioresour. Technol. 2015; 197: 79–84.
[12] Williams PT, Nugranad N. Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. Energy. 2000; 25: 493–513.
[13] Varma AK, Mondal P. Pyrolysis of sugarcane bagasse in semi batch reactor: Effects of process parameters on product yields and characterization of products. Ind. Crops Prod. 2017; 95: 704–717.
[14] David GF, Justo OR, Perez VH, et al. Thermochemical conversion of sugarcane bagasse by fast pyrolysis: High yield of levoglucosan production. J. Anal. Appl. Pyrolysis. 2018;133: 246–253.
[15] Isa KM, Daud S, Hamidin N, et al. Thermogravimetric analysis and the optimisation of bio-oil yield from fixed-bed pyrolysis of rice husk using response surface methodology (RSM). Ind. Crop. Prod. 2011; 33(2): 481–487.
[16] Ghorbannezhad P, Dehghani Firouzabadi M, Ghasemian A. Catalytic fast pyrolysis of sugarcane bagasse pith with HZSM-5 catalyst using tandem micro-reactor-GC-MS. Energy Sources, Part A Recover. Util. Environ. Eff. 2018; 40(1): 15–21.
[17] Akhtar J, Amin NAS. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. Renew. Sustain. Energy Rev. 2011; 15(3):1615–1624.
[18] Horne PA, Williams PT. Influence of Temperature on the Products from the Flash Pyrolysis of Biomass. Fuel. 1996; 75(9): 1051–1059.
[19] Aysu T, Durak H, Güner S, et al. Bio-oil production via catalytic pyrolysis of Anchusa azurea: Effects of operating conditions on product yields and chromatographic characterization. Bioresour. Technol. 2016; 205: 7–14.
[20] Lu Q, Dong C, Zhang X, et al. Selective fast pyrolysis of biomass impregnated with ZnCl2 to produce furfural: Analytical Py-GC/MS study. J. Anal. Appl. Pyrolysis. 2011; 90(2): 204–212.
[21] Karagöz S, Kawakami T, Kako A, et al. Single shot pyrolysis and on-line conversion of lignocellulosic biomass with HZSM-5 catalyst using tandem micro-reactor-GC-MS. RSC Advances. 2016; 6(52):46108–46115.
[22] Lyu G, Wu S, Zhang H. Estimation and comparison of bio-oil components from different pyrolysis conditions. Frontiers in Energy Research. 2015; 3:1–11.
[23] Islam MR, Haniu H, Islam MN, et al. Thermochemical Conversion of Sugarcane Bagasse into Bio-Crude Oils by Fluidized-Bed Pyrolysis Technology. Journal of Thermal Science and Technology. 2010; 5(1): 11–23.
[24] Jahirul M, Rasul M, Chowdhury A, et al. Biofuels Production through Biomass Pyrolysis—A Technological Review. Energy. 2012; 5(12): 4952–5001.