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EFFECT OF BIOMASS TYPES ON BIO-OIL CHARACTERISTICS IN A CATALYTIC FAST PYROLYSIS PROCESS WITH A Ni/ZSM-5 CATALYST

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ABSTRACT

The application of bio-oil for biofuel has been limited due to its low heating value, high acidity and high oxygenate content. Pursuant to the urgency of obtaining access to sustainable energy from renewable resources, the studies for bio-oil upgrading have been recently placed in high priority. This study is aimed at identifying the effect of biomass types on bio-oil product characteristics. The conversion of several types of biomass, i.e. rice straw, rubberwood *(Hevea brasiliensis)*, and palm Empty Fruit Bunches (EFB) to bio-oil by-products was investigated in a Catalytic Fast Pyrolysis (CFP) reactor using a Ni/ZSM-5 nickel nitrate and zeolite catalyst at 550^{o}C and at atmospheric pressure. The results show that Ni/ZSM-5 catalyst has actively enhanced the de-oxygenation reaction process and aromatic production. The composition of aromatic compounds in bio-oil from rubberwood, rice straw, and EFB are 10.25 wt%, 7.8 wt%, and 5.98 wt%, respectively. In the absence of a catalyst, bio-oil from rice straw contains no aromatics.

Keywords: Aromatic; Bio-oil; Catalytic fast pyrolysis; Ni/ZSM-5

1. INTRODUCTION

In line with global trends, crude oil is one of primary energy resources in Indonesia. Recently, crude oil supply contributes at least 49% of the total national energy supply (Dewan Energi Nasional, 2013). With increased energy demand, however, the growth of the crude oil supply hardly could be fulfilled. In fact, the production of crude oil in Indonesia tends to decline annually. As an illustration, the production has declined from 517 million barrels in 2000 to 346 million barrels in 2009 (Pusdatin ESDM, 2014).

Recently studies in the energy sector in Indonesia are being focused on reducing dependency on crude oil resources. Several types of renewable energy are being explored, especially biomass wastes. Indonesia's biomass potential is estimated at 146.8 million ton/year which can generate around 470 million gigajoules/year (GJ/year). Those biomass resources are composed mainly of: rice straw (120 million GJ/year), rubberwood (170 million GJ/year), and palm oil (67 million GJ/year) (Zentrum fur Rationell Energianwendung und Umwelt GmbH, 2000).

One of crude oil substituents in the future is bio-oil, which can be produced from biomass. Nowadays the application of energy from biomass in Indonesia is limited to around 3.25% of its available potential, being mostly for electricity and cooking (Kementrian Energi dan Sumber Daya Mineral, 2011). Environmentally, the use of waste to energy would be advantageous, since the process helps to reduce the amount of untreated wastes.

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Apart from its ideal application, bio-oil quality is still questionable for biofuel. This is due to the high content of oxygenate compounds in bio-oil as well as low heating value, high acidity, and high viscosity characteristics (Muthia, 2011). To overcome such limitations, some studies were carried out to improve the bio-oil quality by using a catalytic fast pyrolysis process. The Ni catalyst was selected due to higher yield of bio-oil with lower oxygenate compounds (Rahman, 2013). The use of Ni metal is able to enhance the de-oxygenation process via dehydration, de-carboxylation, and de-carbonylation simultaneously (French & Czernik, 2010).

Biomass is composed of cellulose, hemicellulose, and lignin. According to the research conducted by Stefanidis et al. (2014), in the pyrolysis process, cellulose in biomass would form levoglucosan ($C_6H_{10}O_5$) via transglycosylation which then can be converted into other products, mainly aromatics and phenols in the presence of a catalyst. Xylan (hemicellulose) could be converted to a wide range of products, primarily phenols, ketones, and acids. The catalytic process, the amounts of acids and ketones would decrease and form aromatics and phenols. Lignin would form phenolic complexes as it hardly can be converted to any other product.

This study is aimed at identifying the effect of biomass types on the characteristics of bio-oil products in a catalytic fast pyrolysis reactor. Three types of biomass, i.e. rice straw, rubberwood, and palm empty fruit bunches (EFB), were selected due to their high availability in Indonesia.

2. RESEARCH METHODOLOGY

In this research, bio-oil was produced from biomass via a catalytic fast pyrolysis process. The pyrolysis process was carried out at 550^{o}C and an atmospheric pressure using a fluidized bed reactor. Initially, a blank test of bio-oil production (without a catalyst presence) was done by using rice straw as the biomass feedstock. Secondly, a catalytic fast pyrolysis was carried out by using rubberwood, rice straw, and EFB as the biomass feedstocks, in which the mass ratio of catalyst to feed was 5:1. The biomass was added to the reactor with the mass flow of 1 g/min and particle sizes less than 0.6 mm.

ZSM-5 was obtained from the Zeolyst International. The mass ratio of Si/Al was 50. Ni/ZSM-5 was synthesized by the wet impregnation method. ZSM-5 was mixed with a saturated nickel nitrate solution in order to load 5 wt% of nickel onto ZSM-5. The nickel nitrate solution was prepared by adding 5.21 g of nickel nitrate hexahydrate solution to 71.67 ml of distilled water. The nickel nitrate hexahydrate solution was obtained from Sigma Aldrich. A measure of 20g ZSM-5 was added to the solution and then mixed for 5 hours at 80^{o}C. The solid phase and remaining nickel nitrate solution were separated accordingly. Drying was then applied to the solid phase. Calcination was done at 550^{o}C over a period of 6 hours with a heating rate at 5^{o}C/min. The Ni/ZSM-5 catalyst was characterized with X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF).

Figure 1 shows the catalytic fast pyrolysis system. To operate the reactor, the feeder was filled with biomass. Quartz and the catalyst were then loaded in the reactor. The furnace temperature was set at 550^{o}C and the condenser was turned on. Nitrogen as an inert gas was delivered from the bottom part of reactor. When temperature was stable at 550^{o}C, the electric motor in feeder was turned on so that the biomass was loaded into the reactor. Once in the reactor, biomass would be converted into three phases, i.e. solid (char and coke), liquid (bio-oil), and gas phases. After passing through the condenser, the primary gas changed into a liquid. The product yield and its contents were analyzed. The liquid contents were observed by using Gas Chromatography-Mass Spectrometry (GC-MS). The gas compositions were examined with Gas Chromatography with a Thermal Conductivity Detector (GC-TCD).

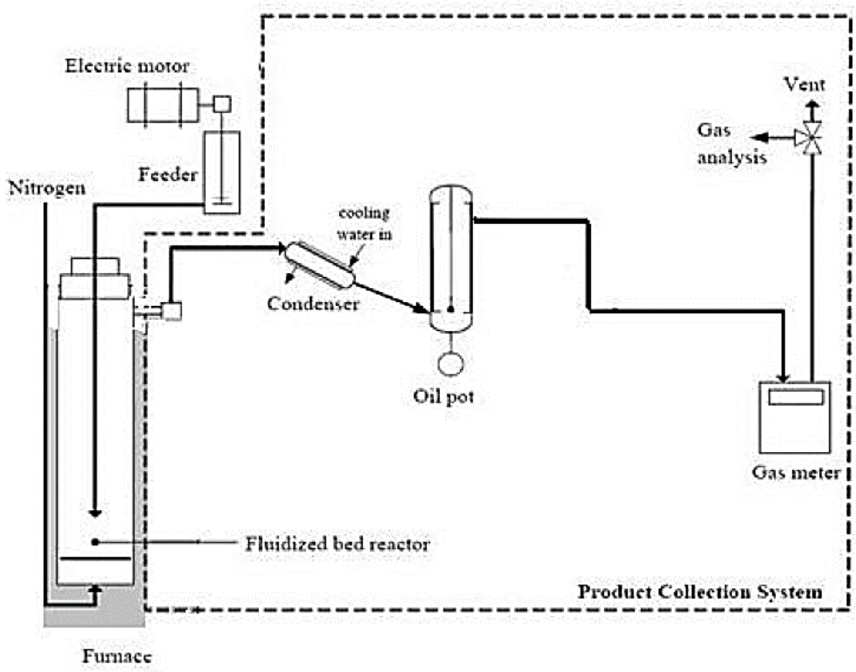

Figure 1 Catalytic fast pyrolysis system (Muthia, 2011)

3. RESULTS AND DISCUSSION

3.1. Synthesis of Ni/ZSM-5 Catalyst

Figure 2 points out the XRD profile of the synthesized Ni/ZSM-5 which matches the literature. According to the Joint Committee on Powder Diffraction Standards (JCPDS) 01-07301519, the peaks at 2θ = 37.3; 43.4; 63; 75.6; and 79.6, respectively correspond to NiO. Based on JCPDS 00-044-0002, the peaks at 2θ = 8.0; 8.9; 9.1; 14.9; 20.9; and 23.2, respectively indicate the presence of ZSM-5 (Vafeian et al., 2013). The peak's presence at 2θ = 5^o–10^o could not be characterized due to the ability of XRD to read and analyze from the peak at 2θ = 10^o.

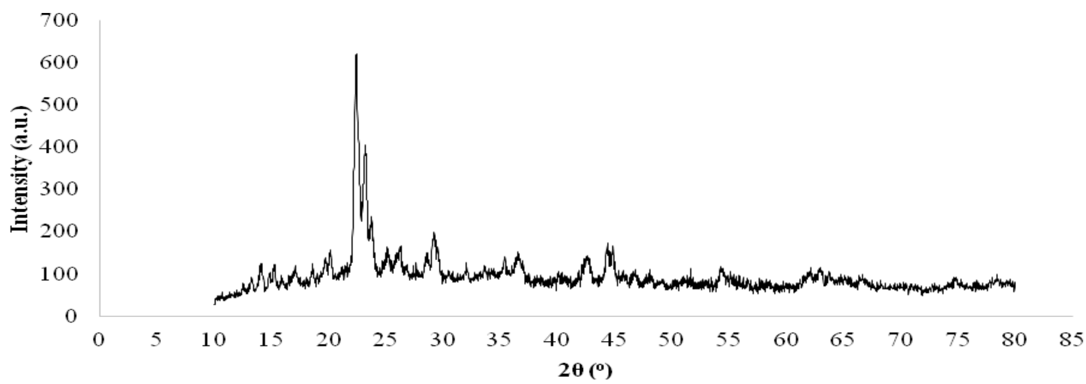

Figure 2 XRD profile of synthesized Ni/ZSM-5

Table 1 presents XRF analysis of the synthesized Ni/ZSM-5. The presence of Ni (5.56 wt%) is calculated based on the amount of NiO.

Table 1 XRF analysis of synthesized Ni/ZSM-5

Compound	Concentration (wt%)
SiO_2	88.16
NiO	7.09
Al_2O_3	3.27
P_2O_5	0.49
SO_3	0.39
Cl	0.36
Fe_2O_3	0.12
TiO_2	0.04
CuO	0.02
ZrO_2	0.02
Cr_2O_3	0.01
CoO	0.01

3.2. Bio-oil Production

In this section, the characteristics of bio-oil will be discussed, consisting of bio-oil colors, yields of products, and components of products. Figure 3 points out the colors of bio-oil. The colors of bio-oil vary from reddish to blackish brown. In the absence of a catalyst, the bio-oil color tended to be blackish brown (Figure 3a). With the catalyst's presence inside the reactor, the color of bio-oil was reddish brown (Figures 3b, 3c, and 3d). With time, the color of the bio-oil turned darker which was most possibly caused by a polymerization reaction.

(a) (b) (c) (d)

Figure 3 Bio-oil product from: (a) rice straw, non-catalytic; (b) rice straw, Ni/ZSM-5; (c) rubber wood, Ni/ZSM-5; and (d) EFB, Ni/ZSM-5

The yields of products and components distribution of gas products for different types of biomass are provided in Figure 4 andFigure 5, respectively. Figure 4 implies that the amount of liquid product (bio-oil) decreases, which is followed by the increase of the amount of gas when Ni/ZSM-5 catalyst was loaded into the reactor. This indicates the role of Ni/ZSM-5 catalyst to trigger cracking and de-oxygenation which eventually enhanced gas production (French & Czernik, 2010). This is proved with the presence of more CO and CO_2 in the gas product of the catalytic process (Figure 5). The total production of CO and CO_2 increases from 15.18 vol% to 27.35 vol%.

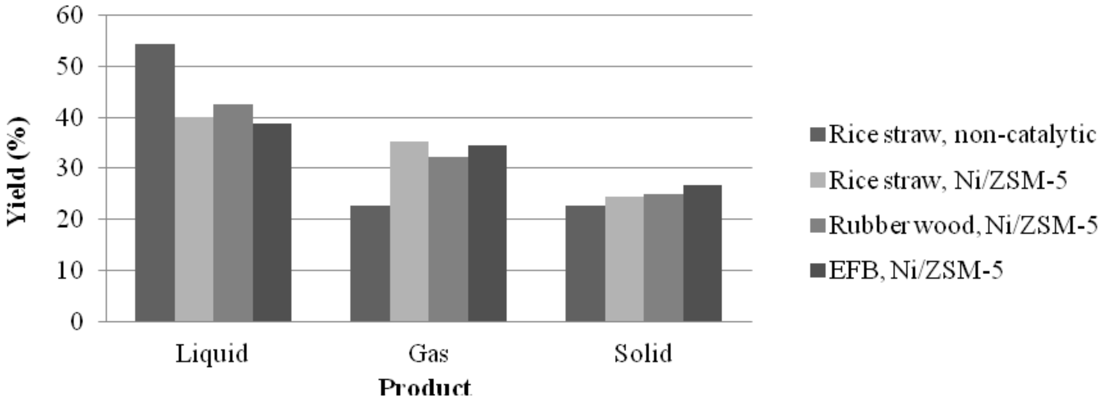

Figure 4 Yields of products

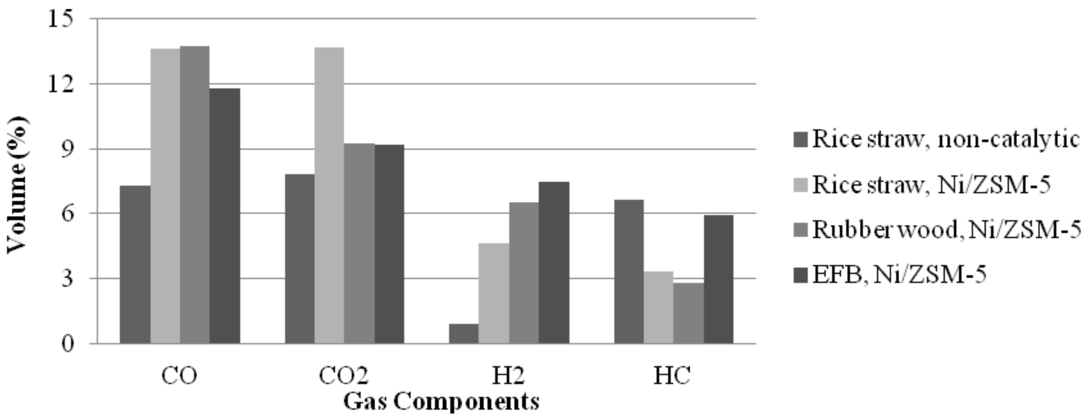

Figure 5 Gas components of fast pyrolysis products

The distribution of bio-oil components is shown in Figure 6. Bio-oil is mainly composed of phenol, acids, and ketones for all variants.

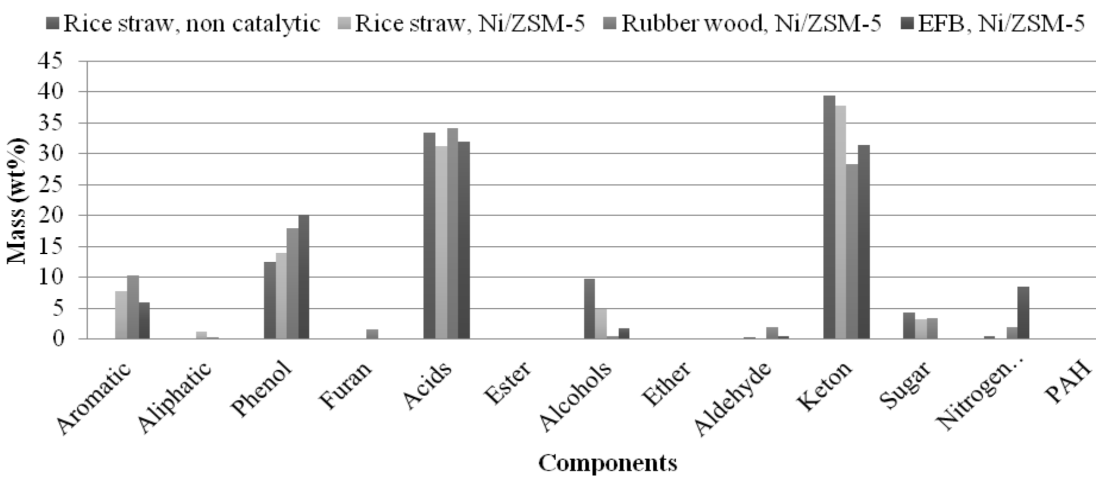

Figure 6 Distribution of bio-oil components based on its functional groups

In the absence of any catalyst, the bio-oil product from rice straw contains no aromatic and aliphatic compounds. Meanwhile for the catalytic process, aromatic content of 7.8 wt% and small amount of aliphatic of 1.21 wt% were detected. The presence of aromatic and aliphatic compounds is followed by the decrease of acids, alcohols, and ketones. This implies that the Ni/ZSM-5 catalyst is selective in the cracking and de-oxygenation of acids, alcohols, and ketones into mainly aromatics and gas. Phenol was the only compound with oxygenate that was not reduced. C-O bond in phenol was resistant to the ZSM-5 catalyst and it is even difficult to be converted to other products in presence of any catalyst (Stefanidis et al., 2014).

According to Figure 6, the highest aromatic content is obtained in the bio-oil from rubberwood. This is due to the highest content of cellulose and hemicellulose in the rubberwood compared to those in rice straw and EFB (Table 2). Among those three types of biomass, the highest phenol content is found in the bio-oil from EFB due to the fact that phenolic compounds are mainly generated from lignin which is largely found in EFB.

Table 2 Biopolymer contents of biomass (Fisafarani, 2010; Omar et al., 2010)

Biomass types	Content (wt%, dry base)		
	Lignin	Cellulose	Hemicellulose
Rice straw	12.87	40.54	20.80
Rubber wood	22.68	47.89	26.88
EFB	29.20	23.70	21.60

4. CONCLUSION

The effect of biomass types on bio-oil characteristics has been successfully investigated. The use of the Ni/ZSM-5 catalyst reduces the yield of bio-oil and increases gas production. The increase of CO and CO_2 production when the Ni/ZSM-5 catalyst was added in the reactor leads to the result that Ni/ZSM-5 offers a significant contribution to cracking and de-oxygenation process. Ni/ZSM-5 is able to crack and de-oxygenate acids, alcohols, and ketones mainly into aromatics and gases. In the catalytic process, aromatic contents in bio-oil from rubberwood, rice straw, and EFB are 10.25 wt%, 7.8 wt%, and 5.98 wt%, respectively. In a comparison of the biomass types, the highest aromatic content is obtained in the bio-oil from rubber wood due to the highest fraction of cellulose and hemicellulose compared to those data in rice straw and EFB. The highest phenol content is found in the bio-oil from EFB due to the higher fraction of lignin in EFB.

5. ACKNOWLEDGEMENT

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