Catalytic Pyrolysis of Palm Empty Fruit Bunch

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Catalytic Pyrolysis of Palm Empty Fruit Bunch over Activated Natural Dolomite Catalyst: Product Distribution and Product Analysis

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Abstract. In this study, an activated natural dolomite catalyst is used as catalyst for the palm empty fruit bunches (PEFB) pyrolysis to produce bio-oil. The research was conducted in fixed bed reactors operating in batches by varying several parameters, which are temperature (400-600°C) and nitrogen gas flow rate (100-300 mL.min^{-1}). The results show that the catalytic pyrolysis process using an activated natural dolomite catalyst obtains a maximum liquid yield of 35.87% when using a 500°C catalytic pyrolysis temperature and the rate of nitrogen gas is 100 cm^3/minute, while the yield of gas and solids is 53.12% and 11.76%, respectively. The use of the dolomite activation catalyst influences the product distribution of pyrolysis and the bio-oil chemical compounds.

Introduction

The transportation sector contributes 94% of the total global demand for fuel. On the other hand, the demand for biofuels is gradually increasing significantly to reduce dependence on fossil fuels, government policies, and the availability of abundant raw materials and awareness of environmental preservation. Biofuel has various advantages compared to fossil fuels, including renewable, low greenhouse gas emissions, and sustainable. In last few decades, biomass has gain much pay attention from researchers as the main raw material for producing biofuels in order to overcome various problems of energy supply and environmental protection due to the impact of the use of fossil fuels [1]. Biomass is consists of lignocellulosic material, with the main components being cellulose, hemicellulose, and lignin.

Indonesia is the largest producer of palm oil in the world since 2008. The processing of palm oil fresh fruit bunches to produce Crude Palm Oil (CPO) will generate Palm Empty Fruit Bunch (PEFB) as a solid waste [2]. From each processing of 1 ton of EFB, the resulting solid waste is 144 kg of 64 kg mesocarp fiber shells and 210 kg of oil palm empty fruit bunches (PEFB) [3]. Indonesia's CPO production in 2017 reached 42 million tons and in 2018 it is estimated to reach 45 million tons. This number will continue to increase with the increase in Indonesia's FFB production. Thus, biomass solid waste generated will be more and more and need to be addressed so as not to cause environmental pollution. Biomass from palm byproducts can be used as a source of renewable energy.

Pyrolysis is one of the most promising technologies for the biomass conversion into bio-oil, biochar and gas products through thermochemical process [4] Bio-oil is obtained from biomass pyrolysis at a temperature range of 350 to 600°C in the absence of oxygen during the process. Bio-oil is an organic liquid that is dark brown in color and has high viscosity [5]. The bio-oil chemical composition is composed of several different chemicals, such as aldehydes, esters, acids, alcohols, phenols, ketones, aromatics, and oligomers. The compounds contributes to the properties of bio-oil. Bio-oil has a low heating value because it contains water of 15-30% by mass; oxygen compound 35-50% by mass; and high acidity in the range of 2-3 pH values. The properties of bio-oil including density, viscosity, acidity, compound content, acidity, and heating value can be significantly improved by upgrading process.

Biomass is decomposed into gas bio-oil, and bio-char products through pyrolysis in the temperature range of 400-600°C in an inert environment. The use of fixed bed reactors for pyrolysis has been used in several studies. During the pyrolysis process, the devolatilization of the biomass structure becomes steam which is then condensed into bio-oil. Oxygenate compounds, such as phenols, ketones, furans, acids, and anhydrosugars are the result of the breakdown of lignin and cellulose which are the main components of biomass. Oxygenate compounds contribute to several undesirable properties in bio-oil, such as low heating value, high acidity, corrosiveness, instability, and. Therefore, the bio-oil quality could be improved by reducing the content of oxygenate compounds through deoxygenation and cracking reactions with the help of catalysts. The deoxygenation process is carried out through the stages of dehydration, decarboxylation, and decarbonylation. Several metal oxide catalysts, such as ZnO [6], MgO [7], CaO [7], ZrO_2 [8], TiO_2 [9], SiO_2 [10], Al_2O_3 [11], and others have been studied to improve the quality of bio-oil through the catalytic pyrolysis process. The catalytic pyrolysis process is a promising method because it provides many advantages, including the absence of hydrogen consumption and the process conditions at atmospheric pressure.

Dolomite is an abundant and inexpensive natural mineral ingredient. Dolomite contains metal oxides in the form of Calcium Oxide (CaO) and Magnesium Oxide (MgO). The application of dolomite as a catalyst has received great attention, especially for the process of gasification of biomass at high temperatures to reduce the formation of tar. Reducing the formation of tar is accomplished by various stages, namely cracking of vapors formed, reforming compounds with high molecular weight, and improving yield and quality of synthetic gases. Moreover, dolomite can also be utilized as a catalyst to increase the quality of bio-oil by cracking heavier organic matter into lighter fractions and reducing the oxygenate compounds formed. Berrueco et al. [2014] use dolomite as a catalyst to reduce tar yield by 51%, in the gasification process of cypress trees carried out at a temperature of 750°C [12]. Yu et al. [2009] have also learned that tar conversion of 65-75% can be achieved when using a dolomite catalyst at a reaction temperature of 700°C [13].

In this research, natural dolomite is used as a catalyst for the PEFB catalytic pyrolysis process to increase bio-oil properties. The research was conducted in fixed bed reactors operating in batches by varying several parameters, which are temperature (400-600°C) and nitrogen gas flow rate (100-300 mL.min-1).

Experimental

Materials. Palm Empty Fruit Bunches (PEFB) were obtained from oil palm plantations in the Pangkalan Bun area, South Kalimantan Province, Indonesia. Before the pyrolysis process, PEFB is dried in the sun and cut into small sizes and the drying process is continued in an oven at 105°C for a day and night. PEFB was then ground and sieved to a size between 50–100 mesh. Moisture content from dry PEFB is measured to ensure that the water content is less than 10% by mass.

Catalyst Preparation. Natural dolomite which will be used for the catalytic pyrolysis process was obtained from Klaten Regency, Central Java Province, Indonesia with a particle size of 60-80 mesh (180-250 μm). Before being used as a catalyst, natural dolomite was calcined at 900°C for 3 hours. During the calcination process, carbonates are broken down into CaO and MgO. he results of the measurement of the specific surface area of the activation dolomite catalyst using the Brunauer-Emmett-Teller (BET) equation were obtained at 10.58 m^2/g. Crystallography of the activated dolomite catalyst structure was identified using an X-Ray Diffractometer (XRD) with a CuKα radiation source and operated at a scanning speed of 5 °/min from 5 to 80°. Figure 1 shows the XRD diffraction pattern of natural dolomite and dolomite catalyst activation. The diffraction pattern of natural dolomite shows an intense peak at 2θ= 30.8; 33.5; 35.5 and 37.4° corresponding to $CaMg(CO_3)_2$, the other peak at 2θ = 41.3°; 50.6°; and 51.2° indicate CaO_2 compatibility. Furthermore, the activated dolomite XRD pattern showed diffraction peaks associated with the presence of CaO (2θ = 32.6°; 37.5°; 54.2°; and 67.4°) and MgO (2θ = 43.3° and 74.8°).

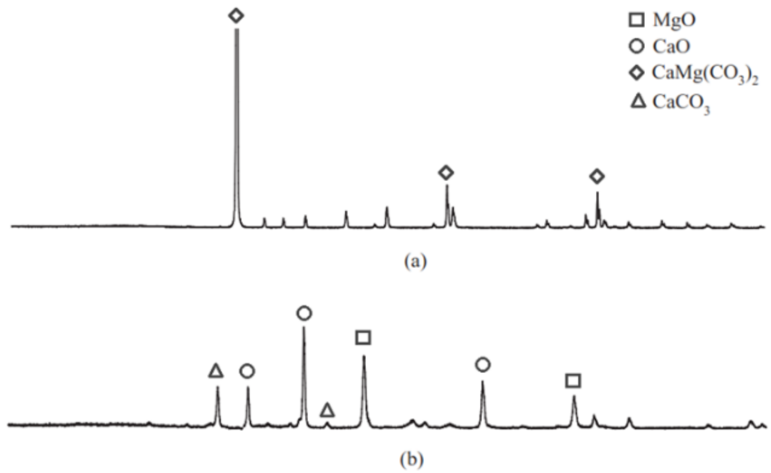

Fig. 1. XRD patterns of (a) natural dolomite; and (b) activated dolomite

Catalytic Pyrolysis Experiments. Pyrolysis experiments are carried out in a fixed bed reactor made of stainless steel which are operated below at atmospheric pressure. The reactor is placed into a cylindrical furnace that is electrically heated. The furnace is equipped with a thermocouple to monitor temperature and is controlled by a temperature controller. At first 10 grams of PEFB are placed inside the reactor. Before the temperature is raised, Nitrogen (N_2) gas is flowed into the reactor to remove oxygen. Then, the furnace is raised at a temperature of 10°C/min to reach 400°C. The temperature is kept stable for 2 hours and during heating, N_2 gas flows into the reactor at a rate of 100 mL/min. The gases formed from pyrolysis flow out together with N_2 gas from the top of the reactor. The gas passes through a condenser which functions to condense the gas. Liquid products or bio-oil condensation from condensers are collected in Erlenmeyer flasks and their recovery is measured. Experiments carried out by doing variations on various parameters, namely temperature (400-600°C), the ratio of the mass of biomass to the catalyst (0.5-2.0), and the flow rate of nitrogen gas (100-300 $cm^3.min^{-1}$). Bio-oil obtained under experimental conditions that provide maximum oil yields is characterized by physical and chemical properties. The chemical composition of bio-oil is analyzed using gas chromatography-mass spectrometry (GC-MS).

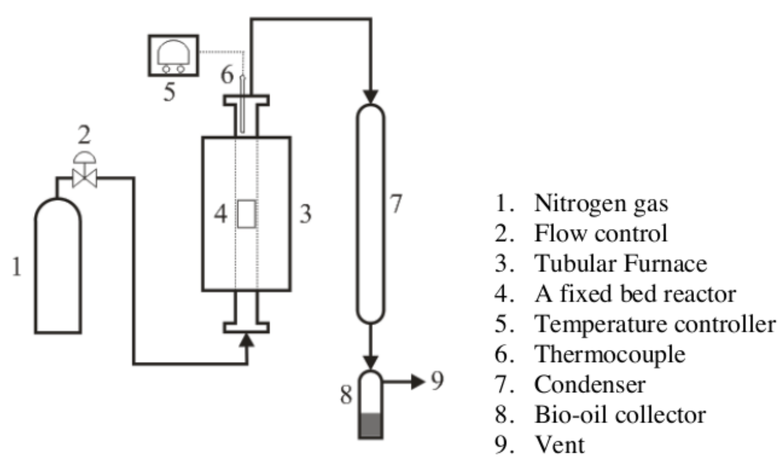

Fig. 2. Catalytic Pyrolysis Experiments Apparatus

Results and Discussion

Effect of Pyrolysis Method. Fig. 3 shows the comparison of the product distribution on pyrolysis using activated dolomite as a catalyst and the non-catalyzed process for PEFB pyrolysis with the same operating conditions i.e., nitrogen gas flow rate of 200 mL/min, pyrolysis temperature 600°C as non-catalytic pyrolysis. The percentage of gas obtained is determined by the difference between the number of feed samples with the amount of liquid and charcoal products obtained. The use of activated dolomite catalysts gives a higher percentage of gas products compared to the results of non-catalytic gas pyrolysis products. However, on the other hand, bio-oil products and charcoal in the non-catalytic process show a greater percentage compared to pyrolysis using activated dolomite catalysts.

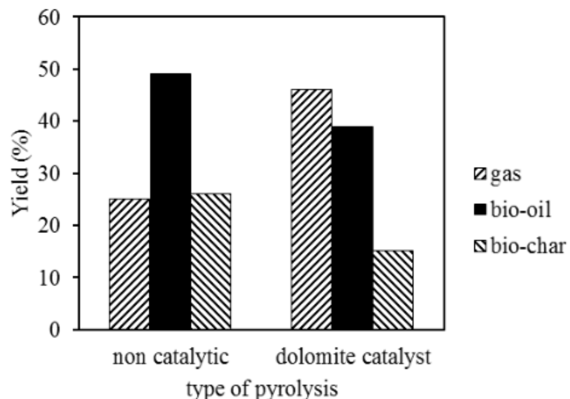

Fig. 3. Effect of Pyrolysis Type on the Product Distribution

Effect of Temperature. To study the effect of temperature on the results of the distribution of PEFB catalytic pyrolysis products with dolomite catalysts the activation of the experiment was carried out by varying the temperature of 400, 500 and 600°C at a constant flow rate of nitrogen gas at 200 mL/min and the ratio of mass of biomass to catalyst 1.0. The distribution of PEFB catalytic pyrolysis products with temperature variations is shown in Fig. 4. Char acquisition decreases with an increase in temperature from 400 to 600°C. Decreased char acquisition is caused by PEFB decomposition and secondary decomposition of residual charcoal due to increasing temperatures. The acquisition of bio-oil and gas has increased with all the high temperatures as shown in Fig. 4. This is related to the secondary decomposition activity of volatile products formed by pyrolysis. The acquisition of a slightly higher gas product is likely due to a water gas shift reaction from pyrolysis catalyzed by activation dolomite.

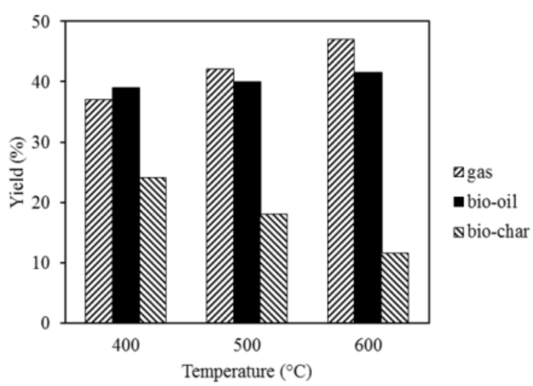

Fig. 4. Effect of Temperature on the Product Distribution of PEFB Catalytic Pyrolysis

Effect of Nitrogen Gas Flow Rate. The effect of nitrogen gas flow rate on the distribution of PEFB pyrolysis products was observed by varying the magnitude of the N2 flow rate at values of 100, 200 and 300 mL/min with the catalytic pyrolysis temperature maintained stable at 600°C. The results of the influence of nitrogen gas flow rate on the distribution of PEFB pyrolysis products are shown in Fig. 5. Gas yield decreases slightly when the nitrogen gas flow is increased from 100 to 200 mL/min and then increases with a further increase in flow rate to 300 mL/min. The bio-oil yield is different from the results obtained from the gas yield. At a nitrogen gas flow rate of 200 mL/min, the highest bio-oil product results are obtained. This indicates that the flow rate can increase the activity of activated dolomite catalyst during the pyrolysis process.

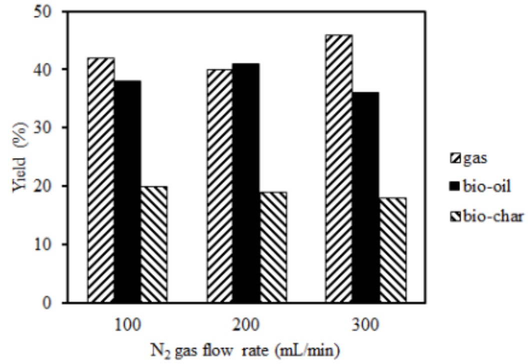

Fig. 5. Effect of Nitrogen Gas Flow Rate on the Product Distribution of PEFB Catalytic Pyrolysis

The GC–MS Analysis of the Bio-oil. Bio-oil characterization using gas chromatography-mass spectrometry (GC-MS) was carried out to determine the content of complex and heterogeneous compounds. The classification of the distribution of major vegetable oil product compounds in PEFB pyrolysis and catalytic pyrolysis can be seen in Fig. 6. Bio-oil from non-catalytic and catalytic pyrolysis contains several hydrocarbon compounds (acids, alcohols, aldehydes, ketones, and esters), aromatics, and oxygenates. The use of dolomite catalyst can increase the productivity of aliphatic hydrocarbon compounds (alkanes and alkenes), esters and alcohols. On the other hand, the amount of acid and alcohol content decreases when the dolomite catalyst is activated. However, the content of aromatic compounds in the form of phenols has increased slightly.

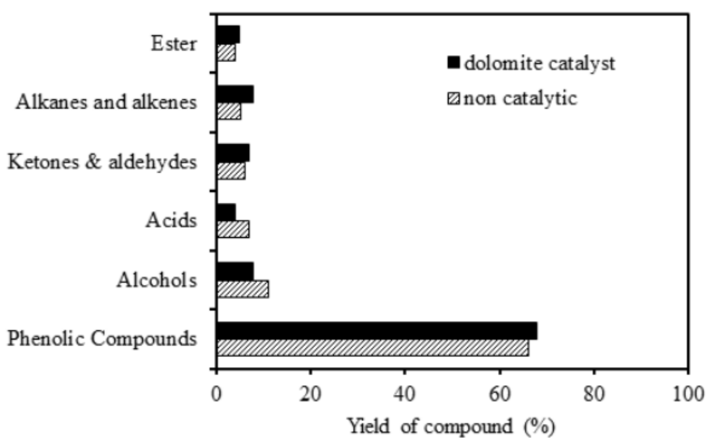

Fig. 6. Classification of major bio-oil product compound distribution in pyrolysis and catalytic pyrolysis of PEFB

Conclusions

In this study, the catalytic pyrolysis experiments of PEFB were conducted in a fix-bed reactor over the Activated Dolomite catalyst. The research was conducted in fixed bed reactors operating in batches by varying several parameters, which are temperature (400-600°C) and nitrogen gas flow rate (100-300 $mL.min^{-1}$). The optimal yield of bio-oil could be achieved at the pyrolysis temperature of 500 °C. Higher nitrogen flow rates were more favorable for the production of the bio-oil. The GC–MS analysis shows the use of dolomite catalyst can increase the content of esters, keton, aldehyde, alcohols and phenolic compounds in the bio-oil.

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References

[1] N. Abdullah, H. Gerhauser, Bio-oil derived from empty fruit bunches, Fuel 87 (2008) 2606-2613.

[2] C. Berrueco, D. Montané, B. Matas Güell, G. del Alamo, Effect of temperature and dolomite on tar formation during gasification of torrefied biomass in a pressurized fluidized bed, Energy 66 (2014) 849-859.

[3] T. Kan, V. Strezov, T.J. Evans, Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters, Renewable and Sustainable Energy Reviews 57 (2016) 1126-1140.

[4] C. Liu, H. Wang, A.M. Karim, J. Sun, Y. Wang, Catalytic fast pyrolysis of lignocellulosic biomass, Chemical Society Reviews 43 (2014) 7594-7623.

[5] T. Mochizuki, D. Atong, S.-Y. Chen, M. Toba, Y. Yoshimura, Effect of SiO2 pore size on catalytic fast pyrolysis of Jatropha residues by using pyrolyzer-GC/MS, Catalysis Communications 36 (2013) 1-4.

[6] V. Nair, R. Vinu, Production of guaiacols via catalytic fast pyrolysis of alkali lignin using titania, zirconia and ceria, Journal of Analytical and Applied Pyrolysis 119 (2016) 31-39.

[7] N.M.N. Qadi, A. Hidayat, F. Takahashi, K. Yoshikawa, Co-gasification kinetics of coal char and algae char under CO2 atmosphere, Biofuels 8 (2017) 281-289.

[8] L. Santamaria, A. Arregi, J. Alvarez, M. Artetxe, M. Amutio, G. Lopez, J. Bilbao, M. Olazar, Performance of a Ni/ZrO2 catalyst in the steam reforming of the volatiles derived from biomass pyrolysis, Journal of Analytical and Applied Pyrolysis 136 (2018) 222-231.

[9] B. Sutrisno, A. Hidayat, Pyrolysis of palm empty fruit bunch: Yields and analysis of bio-oil, MATEC Web Conf. 154 (2018).

[10] T. Yoshizaki, Y. Shirai, M.A. Hassan, A.S. Baharuddin, N.M. Raja Abdullah, A. Sulaiman, Z. Busu, Improved economic viability of integrated biogas energy and compost production for sustainable palm oil mill management, Journal of Cleaner Production 44 (2013) 1-7.

[11] Q.Z. Yu, C. Brage, T. Nordgreen, K. Sjöström, Effects of Chinese dolomites on tar cracking in gasification of birch, Fuel 88 (2009) 1922-1926.

[12] X. Zhao, M. Wang, H. Liu, C. Zhao, C. Ma, Z. Song, Effect of temperature and additives on the yields of products and microwave pyrolysis behaviors of wheat straw, Journal of Analytical and Applied Pyrolysis 100 (2013) 49-55.

[13] Y. Zhou, Z. Chen, H. Gong, L. Chen, H. Yu, W. Wu, Characteristics of dehydration during rice husk pyrolysis and catalytic mechanism of dehydration reaction with NiO/γ-Al2O3 as catalyst, Fuel 245 (2019) 131-138.

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