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Production Biofuels from Palm Empty Fruit Bunch by Catalytic Pyrolysis Using Calcined Dolomite

ARIF Hidayat[1,a*], MUFLIH Arisa Adnan[1,b] and HENI Dewajani[2,c]

[1]Chemical Engineering Department, Universitas Islam Indonesia, Indonesia

[2]Chemical Engineering Department, Politeknik Negeri Malang, Indonesia

[a]arif.hidayat@uii.ac.id, [b]175210102@uii.ac.id, [c]heny.dewajani@polinema.ac.id

*arif.hidayat@uii.ac.id

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Abstract. In this study, Palm Empty Fruit Bunch (PEFB) was utilized to produce bio-oil through non-catalytic and catalytic pyrolysis process. A fixed-bed reactor was applied to conduct pyrolysis experiments at atmospheric pressure. Comparison of bio-oils obtained from non-catalytic and catalytic pyrolysis wih different pyrolysis temperature was studied in terms product yield. The maximum bio-oil yield of 52.4% was obtained at pyrolysis temperature of 600 °C. Furthermore, based on Gas Chromatography-Mass Spectrophotoscopy (GC-MS) analysis, the percentage of phenolic compounds in bio-oil products from catalyzed pyrolysis showed more higher compared with the non-catalyzed pyrolysis.

Introduction

The biofuel production from renewable sources was urgently needed to eliminate dependency of fossil fuels. This is also driven by a diminishing of petroleum reservoirs and an increase in fuel consumption due to population growth. The issues that mention above encourage the researcher to pursue alternative fuels from biomass. In the other hand, the government started more stringent to implement the regulation related to environmental protection becomes due to increasing of greenhouse and exhaust gas emissions. Bio-oil that derived from biomass is renewable, harmless, abundantly supply and sustainable. Thus, bio-oil considered as a potential candidate to substitute petroleum fuels.

The thermo-chemical processes, such as direct combustion, gasification, pyrolysis, and torrefication are genereally applied for converting biomass to bio-oil. Pyrolysis is the lignocellulosic biomass conversion into biochar, bio-oil and gaseous products through a thermo-chemical process by heating in without oxygen presence. The main lignocellulosic biomass components composed hemicellulose, cellulose, and lignin. The lignocellulosic biomass thermally degraded to produce bio-char, bio-oil and gaseous products within temperature ranges of 300–500 °C. Pyrolysis is conducted at lower temperatures as compared to gasification (>700 °C) and direct combustion (>900 °C) [1]. The atmospheric pressure can be applied on pyrolysis process (0.1–0.2 MPa) to produce bio-oil. Generally, pyrolysis process is classified into slow, fast and flash pyrolysis. The classification was based on the rate of heating and residence times of biomass in the pyrolysis reactor. The slow and fast pyrolysis were the most used for pyrolysis process. Many biomass have been exploited as biomass feedstock for pyrolysis process such as rice husk [2], corn cob [2], palm oil empty fruit bunch [3], wheat straw [2], sugarcane bagasse [4], coffee hulls [5], cotton stalk [6], saw dust [7], etc.

Palm Empty Fruit Bunch (PEFB) is biomass wastes that generated from palm oil refining plant. Conventionally, PEFB was applied as a fuel to produce steam in boiler. The remaining ash that remained from combustion was utilization as fertilizer or soil conditioner in palm oil plantation. In addition, PEFB is also widely used as organic fertilizer by composting in the fields for supplementary fertilizer. However, the usage as mention above could overcome the problem regarding on PEFB disposal, there is still a huge of PEFB available that can be applied for bio-oil production as alternative renewable energy source. Since 2015, Indonesia becomes the biggest of palm oil producer in the world. In 2015, palm oil production reached 18.8 million tons which continue increase year to year.

At a rough estimate, when fresh fruit bunch produced one ton of crude palm oil, it would generate 1.3 ton PEFB which consist of fibers, kernels and shells [8]. This huge amount of biomass has potential as raw materials for bio-oil production.

The bio-oil quality from pyrolysis process can be improve using several operating parameters, such as temperature, pressure, residence time, type of reactor, catalytic addition and type of feedstock. Addition of catalyst accelarate the cracking reaction so that the bio-oil quality could be upgraded. The catalyst will promote the breaking of carbon bonds on heavy hydrocarbons as well as the reduction of oxygenated compounds [9]. It will enhance the number of light hydrocarbons and aromatics compounds. Therefore, the produced bio-oils will consist of much low molecular weight hydrocarbons and less oxygenated substances that contribute the reduction bio-oils viscosity and give better stability [10]. Furthermore, the bio-oils heating value will increase compared to raw bio-oils.

Many researchers have been intensively investigated different catalysts for the biomass pyrolysis process application and bio-oil upgrading. The H-ZSM-5, H-Y, and mordenite as a microporous zeolite catalysts type have investigated in the biomass pyrolysis catalytic cracking to upgrade bio-oil [11]. On the other report, the mesoporous catalysts that include metal oxides [12], MCM-41 [13], and noble metal supported catalysts [14, 15] are tested in biomass pyrolysis process. Utilization natural mineral as the catalyst for high-quality bio-oil production has been attained more concern in last few years. The development of catalyst derived from natural mineral is gained more attention due to their relatively inexpensive, high porosity, reusable, allow easy recovery, show chemical inertness both in acidic and basic conditions, and environmentally friendly. This work was aimed to study the catalytic pyrolysis of PEFB using dolomite. The dolomite catalysts were prepared through the calcination process. The catalysts properties were evaluated by the N_2 adsorption/desorption isotherms and X-Ray Diffraction. The product yield and bio-oil characteristics were also determined using GC/MS instrument.

Experimental Method

Materials and Catalysts Preparation. Dry PEFB biomass was achieved from palm oil plantation in Pangkalan Bun, Central Kalimantan Province, Indonesia. PEFB was reduced in particle size by grinding and followed by sieving to get uniform size. Dolomite is purchased from Klaten district, in Central Java Province, Indonesia. The dolomite was sieved and conducted the calcination process at 900 °C for 2 h using muffle furnace. The calcined dolomite was utilized in PEFB pyrolysis as catalyst.

Pyrolysis Experiments. The PEFB pyrolysis was applied in a fixed-bed reactor under N_2 flow at atmospheric pressure. The N_2 flow as carrier gas was kept stable at 200 mL/min. The temperature of the PEFB pyrolysis was also maintained constantly at 500 °C with heating rate 10 °C/min. The experiments were conducted catalytically using raw dolomite and calcined dolomite as catalyst. By Bio-oil product was collected from the bottom of condenser and measured its volume. The bio-oil chemical composition analyzed using GC/MS instrument.

Results and Discussions

Catalysts Characterization. The N_2 adsorption/desorption isotherms of raw and calcined dolomite were shown in Fig. 1. The calcination process at high temperature will encourage devolatilization of CO_2 which increases the formation of mesopore structure. The isotherm curve shows the pore structure of calcined dolomite with extensively connected channel-like pores. Hence, the pore size and shape is in an irregular distribution. A typical type IV isotherm was shown in both raw and calcined dolomite, indicating a typical hysteresis loop for type H2 where nitrogen desorption is due to pore narrowing. The higher amount of nitrogen uptake in calcined dolomite compared to natural dolomite indicates a wide mesopore network. Furthermore, the amount of adsorbed N_2 increased sharply at a relative pressure of> 0.8 in a narrow pore size distribution. The calcination of raw dolomite formed a mesoporous structure with surface area of 45 $m^2.g^{-1}$, larger than specific surface area of raw dolomite (13 $m^2.g^{-1}$). The increasing of surface area will facilitate more active sites that be necessary for catalytic pyrolysis.

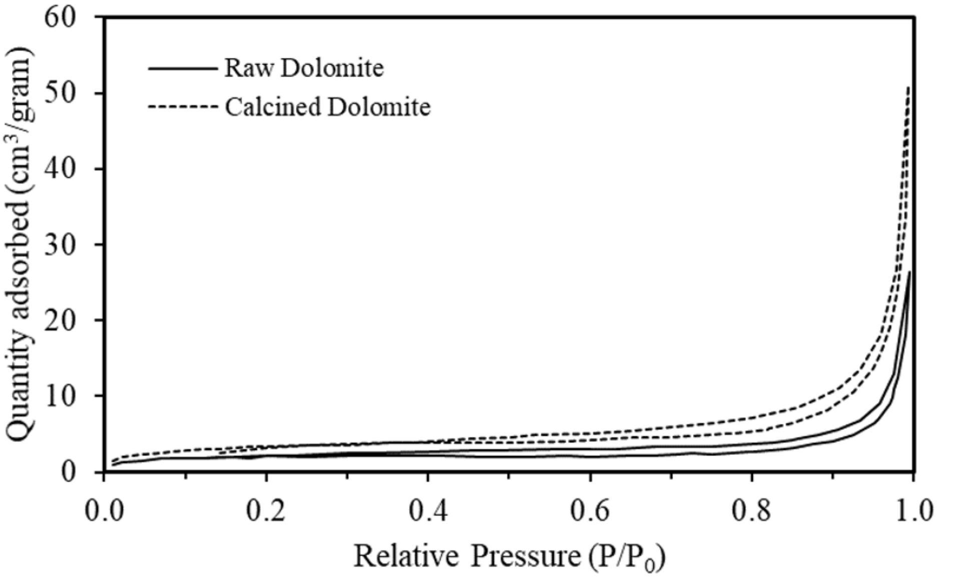

Fig. 1. The N_2 Adsorption/Desorption Isotherms of Raw and Calcined Dolomite.

Fig. 2 (a) and 2. (b) exhibited the XRD analysis for raw and calcined dolomite. It can be seen that the crystal structure and phase change no significantly occurred after the calcination process. The peaks at 2θ 30.8°, 41.2°, and 50.8° indicated the presence of $MgCa(CO_3)_2$ peaks structure on raw dolomite. The CaO crystalline phase was detected are at 2θ = 28.6°, 32.4°, 37.3° and 54°. Meanwhile, the MgO peaks existed at 2θ = 42.9° in both raw and calcined dolomite. The porosity and morphology of calcined dolomite were changed from the raw dolomite due to calcination process which drive the physical and chemical modification

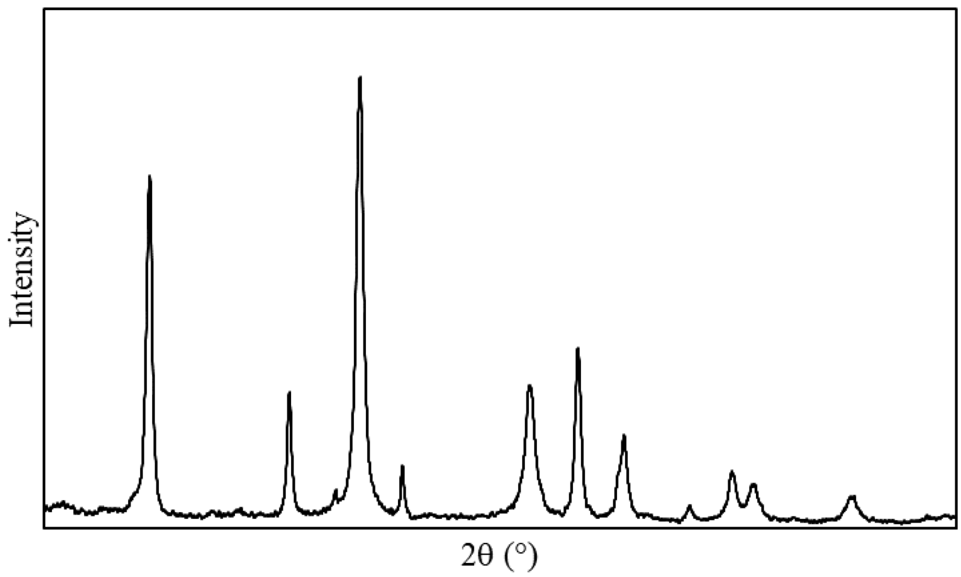

Fig. 2.(a). The XRD Analysis for Raw Dolomite.

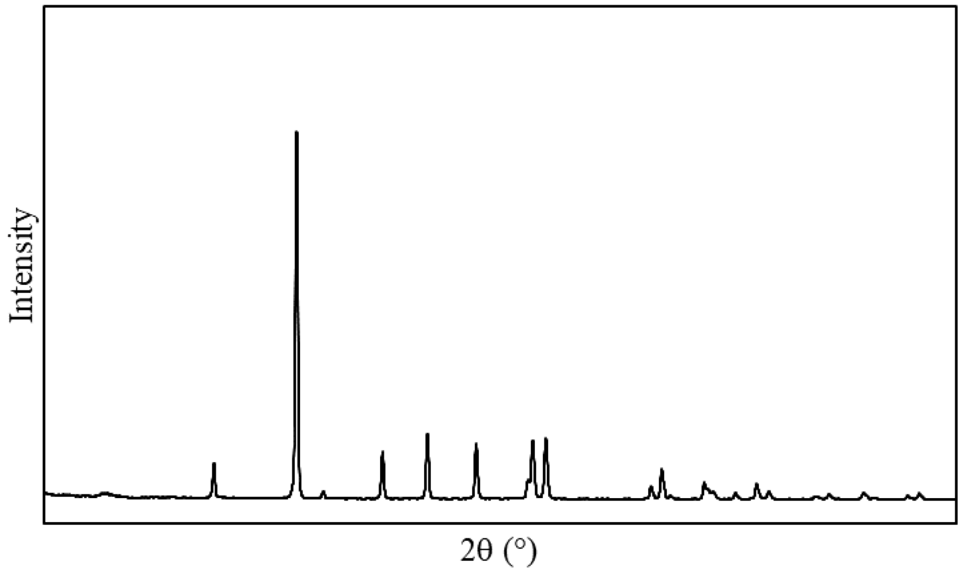

Fig. 2.(b). The XRD Analysis for Calcined Dolomite.

Pyrolysis Experiments.

Effect of Temperatures on Product Yield. The temperature was differed from 400 to 600 °C to investigate the effect on products yield distribution. Fig. 3 shows the products yield distribution on catalytic pyrolysis of PEFB using calcined dolomite as catalyst. The yield of char was found to be increasing when the pyrolysis was operated at low temperature (400 °C). The highest yield percentage (31.2%) was obtained at 400 °C. Meanwhile, the gas yield was tend to increase with increasing temperature. It could be possible to promote by the secondary cracking of volatile components form the non-condensable gas. A high pyrolysis temperature also promotes in enhancing decomposition of char. The bio-oil yield achieved a maximum percentage of 46.9% at 600 °C. At high temperature, the primary decomposition of PEFB constituents and secondary decomposition of char will occur more faster compared to low temperature.

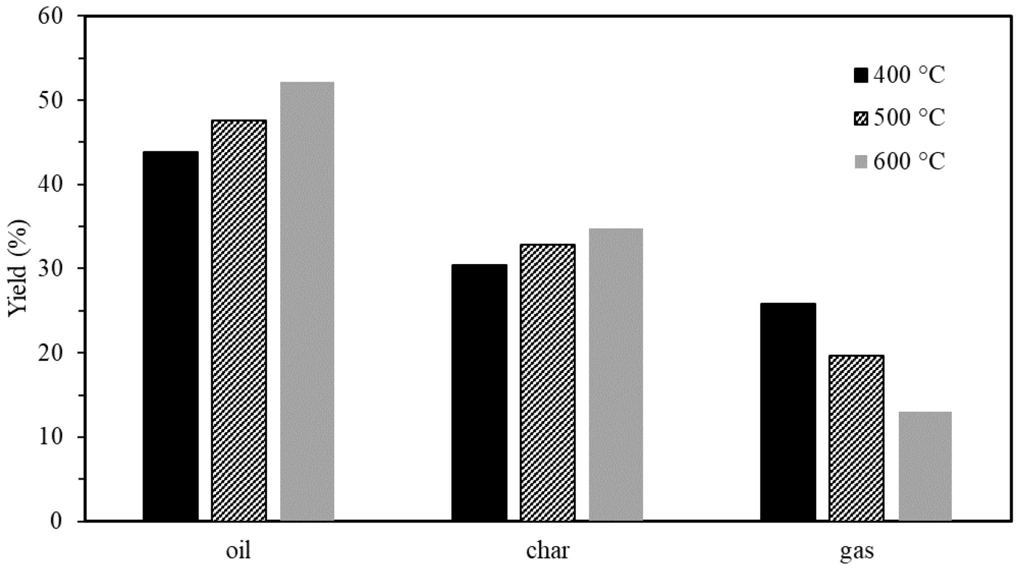

Fig. 3. Effect of Temperatures on Product Yield Distribution on PEFB Pyrolysis.

Comparison of Products Yield between PEFB Catalytic and non-catalytic Pyrolysis. The comparison of products yield distribution between catalytic and non-catalytic pyrolysis are exhibited Fig. 4. The PEFB catalytic pyrolysis applied the raw and calcined dolomite as catalyst. The pyrolysis were conducted at similar operating conditions were of 150 cm^3/min N_2 gas flow rate and 600 °C temperature. When using catalyst, the bio-oil yield showed higher percentage compared with the non-catalytic pyrolysis. The similar results were obtained on the gas yield. The decomposition of main constituents of biomass (lignin, cellulose, and hemicelluloses) was occured more faster when using catalyst. Meanwhile, the char yield was found in lower percentage on the catalytic pyrolysis using calcined dolomite catalyst

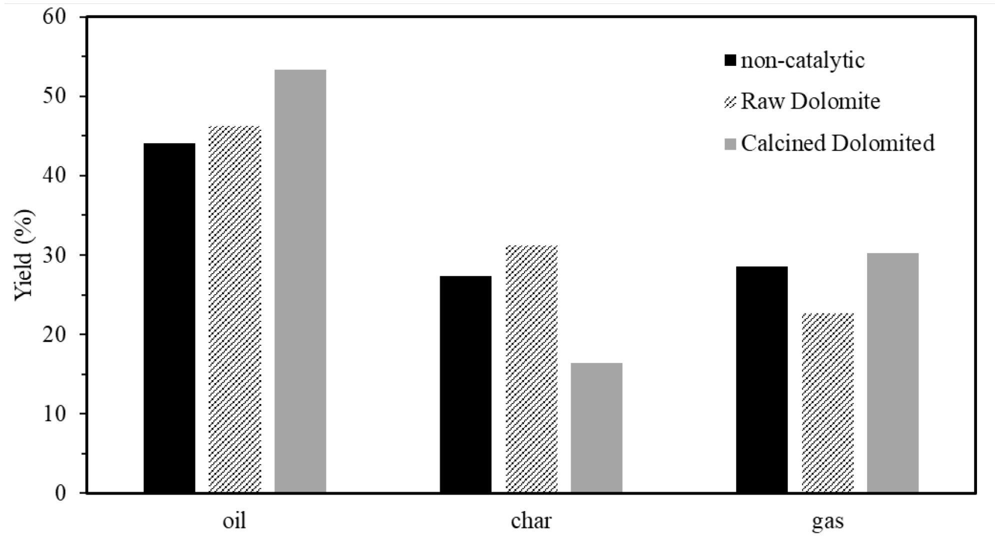

Fig. 4. Comparison of Products Yield between PEFB Catalytic and non-catalytic Pyrolysis.

Product Characterization. The product characterization of PEFB bio-oil was identified using GC/MS. The bio-oils of both the catalytic and non-catalytic pyrolysis were categorized and classified as phenols, alcohols, acids, ketones and aldehydes, aliphatic hydrocarbons, and esters. Various organic compounds were generated by the thermal decomposition of lignin, cellulose, and hemicellulose at high temperature. The phenolic compounds were increased in the presence of catalyst. The presence of catalyst promoted the secondary reaction of volatile components and assisted the decarbonylation and decarboxylation reactions to form hydrocarbons.

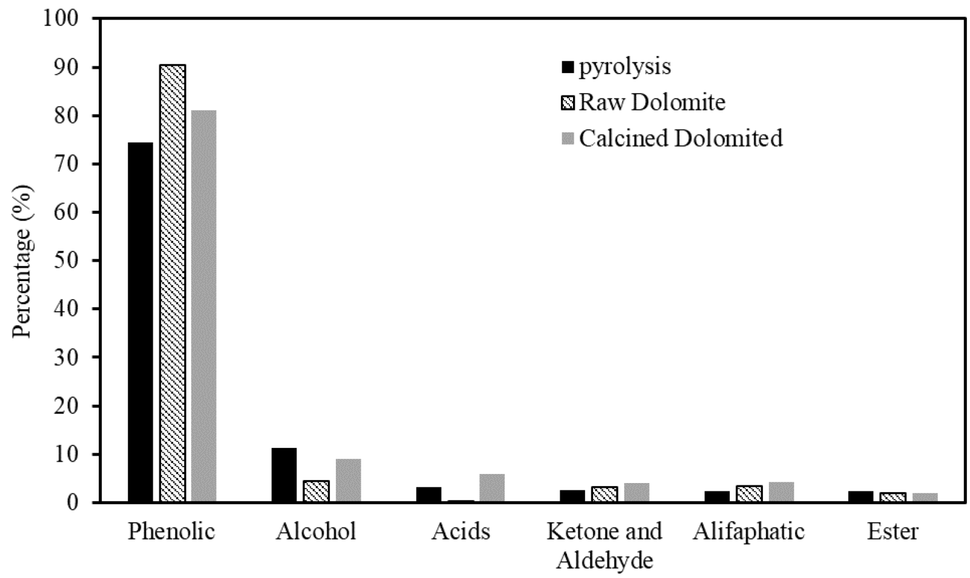

Fig. 5. Product Characterization of PEFB Catalytic and non-catalytic Pyrolysis.

Conclusions

The raw and calcined dolomite catalysts was examined in the pyrolysis of palm oil empty fruit bunch (EFB). The catalyzed pyrolysis performed significant effect in bio-oil yield. The operating conditions i.e. temperature and addition catalyst was evaluated to investigate the impact on the product yield and bio-oil composition. The maximum bio-oil yield of 52.4% was obtained at pyrolysis temperature of 600 °C. The percentage of phenolic compounds in bio-oil products from catalyzed pyrolysis showed more higher compared with the non-catalyzed pyrolysis

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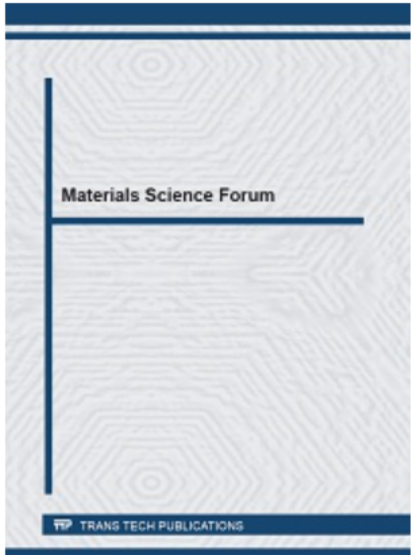

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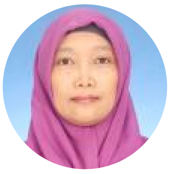

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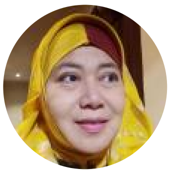

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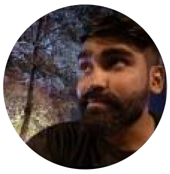

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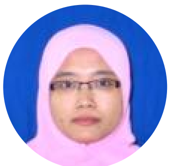
Dr. Sharifah Adzila Binti Syed Abu Bakar
Advanced materials, Biocompatible Materials, Biomaterials
Universiti Tun Hussein Onn Malaysia (UTHM)
Malaysia



Ts. Dr. Zakiah Binti Kamdi
Material sciences, Advanced materials
Universiti Tun Hussein Onn Malaysia (UTHM)
Malaysia

Dr Sarwono
King Saud University
Saudi Arabia

Dr Nguyen Hoc Thang
Materials Engineering, Inorganic Chemical Engineering, Environmental Engineering
Ho Chi Minh City University of Food Industry
Vietnam

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