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Integration of pyrolysis – tar decomposition over porous low grade iron ore

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Abstract. The objective of this research was to investigate the effect of low grade iron ore as catalyst on pyrolysis process of using palm empty fruit bunch. The process was conducted in fixed bed reactor at 450-600 °C. During experiment, the biomass placed within the first stack underwent pyrolysis process was pyrolyzed to produce char, tar and gases. Tar vapor and gases passed through the catalyst bed located within the second stack to conduct catalytic reaction. Furthermore, the vapor left the reactor and entered the cooling system. The catalyst after experiment was weighed to calculate total carbon deposited into catalyst pores. The results showed that the presence of low grade iron ore catalyst increased the gas yield with the yield reduction of liquid fraction. The gas yield was also increased with increasing temperature.

1. Introduction

Fossil fuels as primary energy source in the world are ultimately unsustainable, and directly related to air pollution, land, water degradation and climate changes. Those are the largest greenhouse gas emitters in the world, contributing 3/4 of all carbon, methane and other greenhouse gas emissions. Burning coal, petroleum and other fossil fuels at extremely high temperatures (combustion) as the primary process to produce electricity leads to heavy concentrations of pollutants in our air and water. The process also cause the increasing surface temperature of the earth and climate change [1]. Furthermore, the sources of fossil fuel are always declining with the increasing demand; the price was also influenced by the political and economic situation of the world. It is estimated that the petroleum and coal will run out in 40-60 and 100 years, respectively [2]. This situation encourages the researchers to discover the renewable and sustainable resources of environmental and friendly fuels. One of the renewable resources that are promising for substitution of fossil fuel in the future is biomass such as palm empty fruit bunch (PEFB).

PEFB, a by-product of the palm oil industry, is being recognized as one of the most potential kinds of biomass for energy production. The conversion of PEFB to renewable fuels and chemicals has attracted the attention of the researchers. In thermochemical processes including gasification, pyrolysis and direct combustion, the biomass can be converted to energy [3,4]. Pyrolysis has several advantages which are simple reactor configuration, faster reaction time, more liquid products (less energy for product separation) and high adaptation to various biomass [5].

Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures without the participation of oxygen that produce char as main product and volatile matter, tar and gases as by-products [6]. Thermal decomposition during the process generate char product with high fixed carbon



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and heating value. However, condensation of tar components will arise several problems and decrease overall efficiency of pyrolysis process. Therefore, complete conversion of tar into a major portion of the gaseous product has been a most important engineering subject. It can also greatly enhance the process efficiency and reduce the implementation or operating cost. Catalytic tar decomposition is one of the promising method to increase the efficiency of pyrolysis process [7]. Several materials were studied by a number of researchers as potential catalyst such as Ni, Pt, Rh, and Pd; however, the deactivation of catalyst due to carbon deposition is main problem [8-10]. Another option of tar decomposition is to apply a catalyst or catalyst-like solid that can be used as material or fuel even after loss of activity, as example tar decomposition over charcoal. After reaction, charcoal and deposited carbon could be utilized as fuels. The use of low grade iron ore as catalyst will make carbon deposited into the pores can be used for the reduction process in the steel industry. Automatically, the reduction reaction of iron ore to iron can be faster at lower temperatures. Thus, the main objective of the research is to investigate the effect of low-grade iron ore as catalyst on pyrolysis process of using palm empty fruit bunch.

2. Material and Method

2.1. Raw Material

Biomass used in this study was palm empty fruit bunch (EFB), while low grade iron ore was obtained from Sebuku Island, Kotabaru, South Kalimantan, Indonesia. The compositions of low-grade iron ore were 51.41 % of total Fe, 7.214 % of Al_2O_3 , 3.042 % of SiO_2 and 0.4803 % of NiO.

2.2. Experimental Procedures

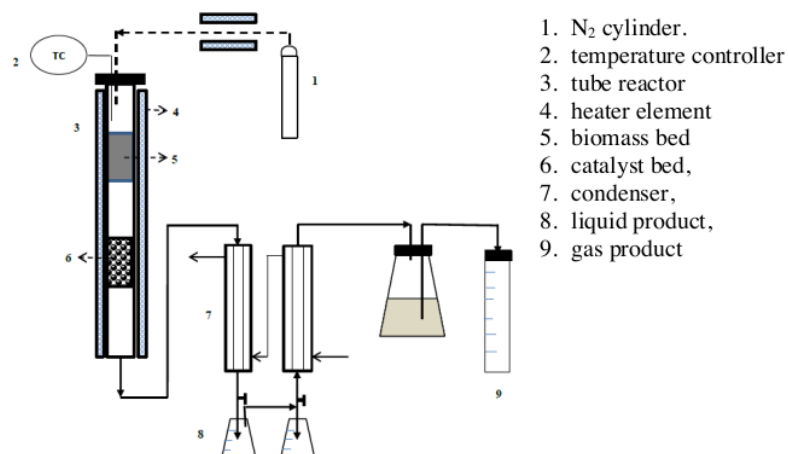


Figure 1. Experiment Apparatus For Pyrolysis-Tar Decomposition Integration

As shown in Figure 1, a reactor tube used in these experiments was equipped with electrical furnace to heat-up the reactor at elevated temperature. The reactor was also equipped with thermocouple and a condenser set to change condensable vapor to liquid. The experiment was conducted at temperature of 450 to 600°C and at atmospheric pressure with certain amount of pyrolysis agents. In order to ensure the homogenous system inside the reactor, the pyrolysis agents was flowed for a while before heating-up. The reactor was heated and kept constant at experimental temperature of pyrolysis process. Biomass placed within the first stack underwent pyrolysis process during heating up to produce char, tar and gases. Tar vapor and gases passed through the catalyst bed located within the second stack and

then occurring catalytic reaction. By flowing the N₂ through top of the reactor system, subsequently, the vapor left the reactor from bottom of the reactor and then entered the cooling system.

3. Introduction

3.1. Porous Low Grade Iron Ore

3.1.1. Analysis of BET

From the BET analysis, the specific surface area of low quality of the iron ore catalysts is shown in Table 1. From the table, it can be seen that there is an increase of the catalyst surface area about 3 times after calcination. After the catalyst was used to decompose the tar, the outer surface area of the catalyst decreased because the catalyst pores begin to be filled with carbon sourced from the tar decomposition reaction. As shown in the table, the average diameter of iron ore pores decreased from 5.23 nm to 2.88 nm after calcination. According to the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC) [11], the adsorbent of pores is classified into three groups: micro-pore (size <2 nm), meso-pore (2-50 nm) and macro-pore (> 50 nm). The size of the pores formed has an effect on porosity, the specific of total specific surface area is available for adsorption and thus it is possible to diffuse into solids. From the results of the analysis, it can be seen that low-quality iron ore after calcination has an average pore diameter value in the meso-pore region.

Table 1. Bet Analysis Result Of Porous Low Grade Iron Ore

Iron Ore	Surface Area (m ² /g)	Average Diameter (nm)
original	24.27	5.23
After calcination	86.91	2.88
After tar decomposition	23.90	4.23

The pore size distribution in iron ore catalysts can be seen in Fig. 2. From the figure, the pore distribution changes in the original iron ore, after activation and after the decomposition process. The new pores was significantly added at pore sizes of 1 - 4 nm, once the iron ore activation process was carried out by heating at 450 °C. This addition is due to the loss of impurities found in the original iron ore after the activation process. The figure also shows that there was a decrease in the pore size distribution of 1-4 nm in iron ore after it was used for the tar decomposition process. This confirms that the carbon from the tar decomposition process fills the pores of the iron ore.

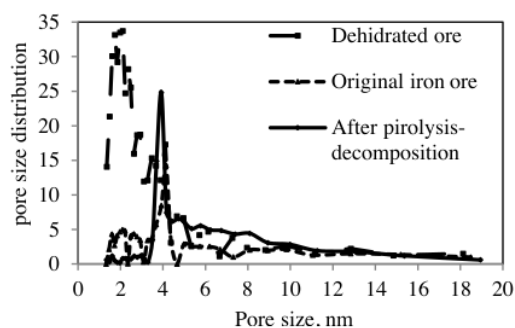


Figure 2. Pore Size Distribution Of Iron Ore Of Original, Dehydrated And After Decomposition

3.1.2. Analysis of SEM (Scanning Electron Microscope)

Figure 3 shows the SEM results from iron ore, iron ore after calcination and after pyrolysis-tar decomposition process. From the those figures, there changes in the morphological structure of iron ore. Figure 3 shows the original iron ore which still appears to be closed by an OH group of FeOOH [12]. After heating to 450 °C, the OH group will emerge in the form of H₂O vapor and the iron ore compound changes from FeOOH to Fe₂O₃.

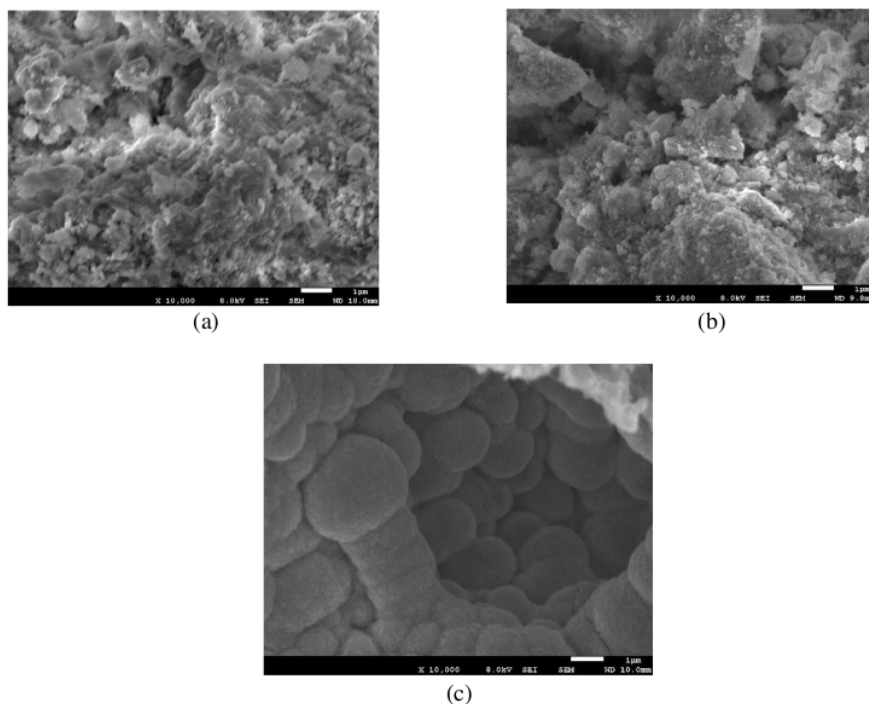


Figure 3. Sem Analysis: (A) Original Iron Ore; (B) Iron Ore After Calcination; (C) Iron Ore After Tar Decomposition Process

3.2. Pyrolysis – Tar Decomposition Integration

3.2.1. Catalyst Influence On Product Distribution

Figure 4 shows the product distribution at different temperatures in the pyrolysis of EFB biomass when porous iron ore was used as catalyst. The distribution of pyrolysis products (gas, char and the whole liquid product before phase separation) was analyzed in terms of their yield (wt.%, g of product/g of biomass fed).

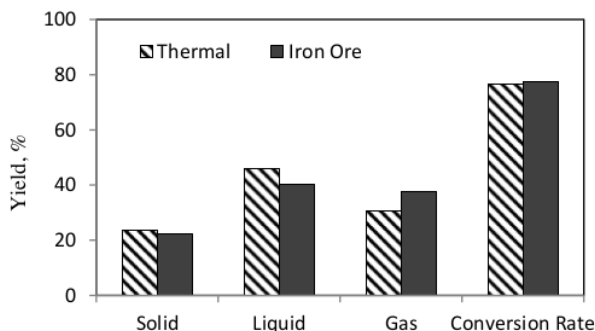
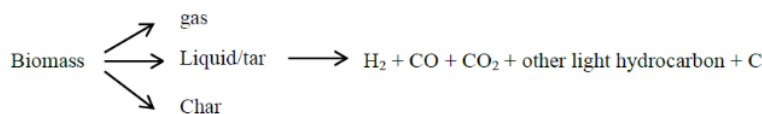


Figure 4. Effect of low grade iron ore catalyst at 550 °C

Figure 4 shows the yields of pyrolysis product and total conversion of EFB during pyrolysis in the absence and presence of supported low-grade iron ore. It can be seen that the yield of gas was significantly improved at the presence of iron ore. Since the liquid fraction decreased with almost the same order of magnitude, it appears that the gas fraction mostly increased with the cracking of higher molecular weight molecules at the catalyst surface. The char yield was registered with a very small reduction. Thus, the presence of iron ore catalyst improved the rate of conversion (1%) and the gas yield (7%) while the liquid yield decreased (6%). The decrease in liquid yield and the increase in gas indicate that low grade iron ore has the catalytic ability in the process of decomposition of the pyrolysis tar, as in the following reaction:



3.2.2. Temperature Influence on Product Distribution

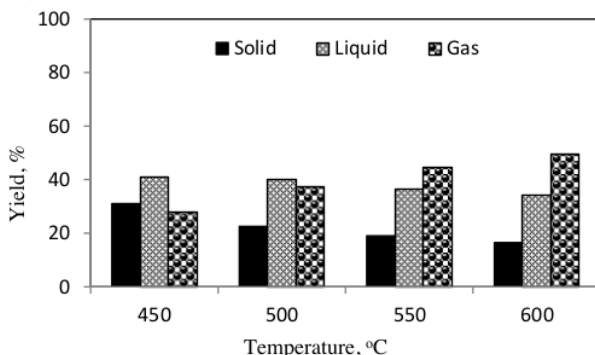


Figure 5. Effect of temperature on yield of product

As observed in Figure 5, temperature clearly affected to the three products obtained in catalytic tests. Gas product was improved with temperature while solid and liquid decreased. The increase in gas yield and the decrease in liquid yield indicate that the rate of tar decomposition reaction increases along with the increasing temperature. In addition, at elevated temperature, tar conversion increased and then occurred the decomposition to the gas product easier. By increasing the temperature, liquid

dominated by heavy compounds was converted into compounds of light hydrocarbons like methane (CH₄), hydrogen (H₂), carbon dioxide (CO₂) and carbon monoxide (CO) [7].

4. Conclusion

The integrated pyrolysis – tar decomposition of biomass over porous low-grade iron ore has been performed in a tube reactor. The proposed system ore was promising candidate for tar decomposition and offered also solution for problem related with energy and environment. The results showed that the presence of low-grade iron ore catalyst reduced the yield of liquid fraction with a consequent increase in the gas yield. It has been also observed that with the increasing of temperature, gas product increased but liquid and solid decreased.

5. Acknowledgment

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