The Characteristic of Coal Oil from Catalytic Coal Gasification

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Abstract

In this work, the catalytic gasification process of coal was studied at different operating temperatures and catalyst weights. The purpose of this study was to study the characteristics of coal oil produced through the gasification process using Nickel Molybdenum (NiMo) catalyst. The effect of adding NiMo catalyst with variations in weight of 0%, 5%, 10% and 15% for different gasification temperatures (375 – 385 °C, 430 – 440 °C, and 475 – 485 °C) were studied on coal with a calorific value of 6,400 kcal/kg. The process was done in fluidized bed reactor under atmospheric pressure and an air flow rate of 2 liters/minute was flow for 60 minutes. The results showed that NiMo is effective as a catalyst in the gasification of coal at 430 – 440 °C, the addition of 15% weight of catalysts produced coal oil with a yield of 9.35% and the composition of hydrocarbon consists of 59.75% of aromatics, 26.42% of aliphatics, and 7.34% of phenolics. Compared to coal oil without catalyst give a yield of 6.56% with 57.33% of aromatics, 17.44% of aliphatics, and 16.03% of phenolics. This showing that NiMo catalysts have a high selectivity to increase aromatic and aliphatic hydrocarbons in coal oil.

Keywords: Catalytic, Coal, Gasification, NiMo

INTRODUCTION

National energy needs are projected to increase to 4.9% per year in 2015-2050. The increasing energy requirements are directly proportional to the increasing number of economic growth, population, energy prices, and government policies. Based on the energy utilization sector, national energy needs are dominated by the transportation and industrial sectors until 2050 [1]. Coal is one of the most used energy sources, but only 21% of total coal production is used to meet national energy needs and the rest is exported [2].
Coal is an organic material derived from the process of plant decay that occurs in the soil and is affected by high pressure and temperature over millions of years. The utilization of coal can be divided into 2 (two) types, as fuel (industry, power plants, and households) and as raw materials for briquettes, liquefaction, gasification, coal upgrading, and metal processing. Coal gasification was one of the coal utilization technologies by converting coal thermochemically into the synthesis gases (CO and H₂), CH₄, and CO₂. Gasification products were intermediate products which can be further processed into various products such as fertilizer raw materials (NH₃), dimethyl ether fuel (DME), chemical raw materials (methanol, ethylene, etc.) and synthetic natural gas.

Catalytic coal gasification is the process of converting coal into synthesis gas by involving a catalyst in the process in order to increase the yield of synthesis gas. It has advantages of low operating temperature, high energy conversion efficiency, and a variety of reaction pathways towards the production of desired gases. Fan, et al. [3] studied about catalytic gasification of sub-bituminous coal in a fixed-bed reactor with eggshell as catalyst under atmospheric pressure at temperatures 700 – 900 °C. Chen, et al. [4] was done catalytic coal gasification using Ca(OH)₂ in a fluidized bed reactor under 1.5 MPa and temperature of 800 °C.

The utilization a catalyst in the process can be minimized tar production by converting tar to H₂, CO, CH₄, and CO₂ [5]. Several types of catalysts such as Ni, Rh based catalysts [6], dolomite [7], Y-Zeolite, and olivine [8], have been studied in the catalytic gasification process. Chang [9] concluded that Y-Zeolite has good activity in partial oxidation. Ribeiro, et al. [10] added copper to the Y-Zeolite catalyst to form a CuNaHY Y-Zeolite catalyst and used in the gasification process. Asadullah, et al [11] concluded that Ni catalysts have the ability between 80% - 100% to convert synthetic gas. Then, the next study from Asadullah, et al [12] using Rh/CeO₂ catalysts was able to convert carbon to gas between 68% - 100%. And the research by Tristantini et al. [13] conducted gasification of lignite coal charcoal using K₂CO₃ catalyst.

The synthesis gases were more used as an energy source for electricity generation, industrial raw materials, manufacturing of DME, and chemicals. Coal oil production process through condensation of synthesis gas is the development of gas utilization technology from the gasification process that will be carried out in this study, where the gasification process is done by using NiMo catalysts.

MATERIALS AND METHODS

Materials

The study was done using coal with a calorific value of 6,400 kcal/kg (BB64) from PT. Bukit Asam, South Sumatera, Indonesia and Nickel Molybdenum (NiMo) commercial. The instruments used were a reactor, furnace, compressor, condenser, computer, grinder, Erlenmeyer, pycnometer, beaker glass, and measuring glass.

Methods

The gasification process took place in a fluidized bed reactor with dimensions of OD = 170 mm, ID = 100 mm, and h = 400 mm. The heat source of the reactor is obtained from an electric furnace with temperature is set at 375 – 485 °C and atmospheric pressure. The coal is grinded (MKS-ML 100 Herb Grinder) to a size of ± 300 mesh, and NiMo catalyst is activated at 500 °C for 5 hours. BB64 powder is put into the reactor and the catalyst is loaded into the catalyst bed with variation in weights of 0%, 5%, 10%, and 15%. Air with a flow rate of 2 LPM flowed into the reactor during the process within 60 minutes. In this process, the outlet gas through the top of the reactor is condensed and is stored inside the Erlenmeyer. The coal oil products were analyzed for density (ASTM D 1298), specific gravity, αAPI gravity (ASTM D 1298), GC-MS (ISQ Series Trace™ 1300) and calorific value (ASTM D 5865-11).

RESULTS AND DISCUSSION

Effects of Catalyst Weight Addition on Coal Oil Yield at Temperatures Variations

The proximate and ultimate composition of coal with a calorific value of 6,400 kcal/kg are shown in Table 1 and 2. The catalytic coal gasification produced an insoluble mixture of coal oil and water, as presented in Figure 1 and 2, due to differences in density between coal oil and water. For the upper layer, the form of coal oil products with a lower density is compared to the water in the lower layer. These two liquid mixtures are separated based on the principle of differences in density by using a separating funnel.

The synthesis gases were more used as an energy source for electricity generation, industrial raw materials, manufacturing of DME, and chemicals. Coal oil production process through condensation of synthesis gas is the development of gas utilization technology from the gasification process that will be carried out in this study, where the gasification process is done by using NiMo catalysts.
The addition of 15% by weight of the catalyst gave coal oil yield decreased to 33.63%. The effect of the addition of catalyst weight percent on coal oil yield at the process temperature of 375 – 385 °C is inversely proportional. The more amount of catalyst added, the less yield of coal oil is produced. It can be caused by several factors: first, the catalyst used acts as an inhibitor. An inhibitor is a substance that can slow the rate of chemical reactions in a process. The more amount of catalyst added, the slower the reaction of product formation. As a statement from Sunarno, et al. [14], the optimum NiMo catalyst ratio is 2.5% at 330 °C with a yield of 68.60% and the addition of 3.5% catalysts gave a decrease in yield to 55.60%. Second, the gas formed may have a lower freezing point than the condensation temperature, it causes a lot of gas is not condensed. Third, the influence of the composition of the moisture of raw materials, as shown in Table 1, the total of inherent moisture in coal was 4.45%. It was not given a big effect to yield. The free moisture factor has a greater influence of moisture formed in the product where H₂ has more possibilities to react with air and the more moisture (H₂O) can be formed. Last but not least, the reactor configuration was used where the reactor showed an increase in yield at temperatures above 400 °C.

At temperatures of 430 – 440 °C, coal oil’s yield showed a significant increase. The highest yield increase was indicated by the addition of 5% catalysts which was 8.81%. The yield was increased to 42.53% by adding 15% catalysts compared to without catalyst. The effect of the addition of catalyst weight percent on coal oil yield at the process temperature of 430 – 440 °C is directly proportional. The more amount of catalyst added, the more yield of oil is produced. The yield increase due to the endothermic properties of the main reactions to the formation of synthesis gases namely water gas, boudouard, and methane reforming [15]. The higher the temperature, the gas formation reaction will shift to the right, which means that more gas will be formed and can be condensed into the oil.

At temperatures of 475 – 485 °C, coal oil yields showed an increase but not significantly. The yield of coal oil of 7.35% without catalyst and the addition of 15% by weight of the catalyst can increase yield to 8.03%. The effect of the catalyst added to yield under temperature 475 – 485 °C is directly proportional, even though was not significant. This occurs due to the more amount of catalyst used, the more short-chain hydrocarbon components are produced which cannot be condensed at room temperature [16]. The catalyst activity is influenced by the temperature at which the higher temperature, the more amount of components were adsorbed on the surface of the
catalyst. A higher temperature will be increased the molecular kinetic energy, and the adsorption balance will be moved towards desorption. Therefore, a higher temperature can reduce the performance of the catalyst [17]. However, as shown in Figure 3 indicates if the addition of catalyst greater than 15%, the yield of coal oil will increase.

![Figure 3](image)

**Figure 3.** The effect of adding the weight percent of the catalyst to the yield of coal oil at process temperature variations

The comparison above concluded that in order to obtain a high coal oil yield at temperatures of 375 – 385 °C, there is no need to add catalysts or by adding catalyst with ratios smaller than 5%. The addition of 5%, 10% and 15% NiMo catalysts give a high increase to yield under temperature 430 – 440 °C. As the statement from Indra [18], Ni metal is very selective for terminating the C - C and C - H chains. The combination of Ni and Mo metals can cause a breakdown of the oxygen chain bound in C - H.

**Effect of Catalyst Weight Addition on Coal Oil Density at Temperatures Variations**

The effect of adding a catalyst to the density of coal oil at process temperature variations is presented in Figure 4. The density value obtained from the smallest to the highest was 0.842 gr/cm³ – 0.904 gr/cm³. The effect of adding NiMo catalyst to the density of coal oil at the variation of process temperature was inversely proportional. The more amount of catalyst used, the smaller density of coal oil produced. At temperatures of 375 – 385 °C, the density of coal oil without a catalyst was 0.904 gr/cm³ and the addition of 15% catalysts gave the density of coal oil decreased to 0.878 gr/cm³. At temperatures of 430 – 440 °C, the density of coal oil with without a catalyst was 0.880 gr/cm³ and the addition of 15% catalysts causes the density of coal oil decrease to 0.842 gr/cm³. At temperatures of 475 – 485 °C, the density of coal oil without a catalyst was 0.882 gr/cm³ and the addition of 15% catalysts caused the density of coal oil decrease to 0.858 gr/cm³.

![Figure 4](image)

**Figure 4.** The effect of weight addition of catalyst on coal oil density in process temperature variations

The addition of NiMo catalyst in the gasification process has a greater influence on coal oil products under temperatures of 430 – 440 °C. Where the addition of 5% catalysts can produce coal oil with a density of 0.856 gr/cm³. While at a temperature of 475 – 485 °C, it required 15% catalysts to get coal oil with a density of 0.858 gr/cm³.

**Effect of Catalyst Weight Addition on Coal Oil °API Gravity Value and Classification Oil at Temperatures Variations**

The relationship between specific gravity and °API gravity is inversely proportional. The lower specific gravity of oil, the higher °API gravity. It means that the higher °API gravity, the lighter oil will be classified. The lighter of oil produced, the shorter carbon chain so that it is easier to crack into fuel. The comparison of the °API gravity and classification of coal oil is shown in Table 3. Coal oil produced from catalytic gasification is included in the light-medium group.

The effect of adding a catalyst to °API gravity of coal oil under the variation of temperature process shown in Figure 5. The percentage of catalysts added to the value of °API gravity oil is directly proportional. The more amount of catalyst used, the greater the value of °API gravity of coal oil produced.

At temperatures of 375 – 385 °C, the coal oil produced has a gravity °API value of 23.16 - 27.69. These values indicated that the coal oil produced is classified to the medium oil group.
Table 3. The comparison of °API gravity value and classification of coal oil in variations in process temperature and the weight percent of catalysts

<table>
<thead>
<tr>
<th>No</th>
<th>Temp (°C)</th>
<th>Mass of Catalyst (%wt)</th>
<th>°API</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>375 – 385</td>
<td>0</td>
<td>23.16</td>
<td>Medium</td>
</tr>
<tr>
<td>2</td>
<td>375 – 385</td>
<td>5</td>
<td>25.39</td>
<td>Medium</td>
</tr>
<tr>
<td>3</td>
<td>375 – 385</td>
<td>10</td>
<td>25.91</td>
<td>Medium</td>
</tr>
<tr>
<td>4</td>
<td>375 – 385</td>
<td>15</td>
<td>27.69</td>
<td>Medium</td>
</tr>
<tr>
<td>5</td>
<td>430 – 440</td>
<td>0</td>
<td>27.33</td>
<td>Medium</td>
</tr>
<tr>
<td>6</td>
<td>430 – 440</td>
<td>5</td>
<td>31.73</td>
<td>Light</td>
</tr>
<tr>
<td>7</td>
<td>430 – 440</td>
<td>10</td>
<td>32.49</td>
<td>Light</td>
</tr>
<tr>
<td>8</td>
<td>430 – 440</td>
<td>15</td>
<td>34.41</td>
<td>Light</td>
</tr>
<tr>
<td>9</td>
<td>475 – 485</td>
<td>0</td>
<td>26.97</td>
<td>Medium</td>
</tr>
<tr>
<td>10</td>
<td>475 – 485</td>
<td>5</td>
<td>29.13</td>
<td>Medium</td>
</tr>
<tr>
<td>11</td>
<td>475 – 485</td>
<td>10</td>
<td>30.61</td>
<td>Medium</td>
</tr>
<tr>
<td>12</td>
<td>475 – 485</td>
<td>15</td>
<td>31.36</td>
<td>Light</td>
</tr>
</tbody>
</table>

This shows that the addition of the weight percent of the catalyst at a temperature of 375 – 385 °C did not give a change in the oil group to the coal oil produced. At temperatures of 430 – 440 °C, the coal oil produced has an °API gravity value of 27.33 - 34.41.

Figure 5. The effect of addition of catalyst percent on °API gravity oil coal in process temperature variations

These values indicated that the coal oil produced is classified into the medium to light oil group, and is dominated by light oil groups. The addition of 5% of the catalyst gives an °API gravity value of 31.73 and belongs to the light oil group. At temperatures of 475 – 485 °C, the coal oil produced has a gravity °API value of 26.97 - 31.36. These values indicated that the coal oil produced is classified into the medium to the light group, is dominated by medium oil groups. Light oil is obtained by adding 15% of the catalyst and giving an °API gravity value of 31.36.

The comparison of the value of °API gravity above, explained that the addition of the weight percent of the catalyst has a greater influence on the group of coal oil produced under temperatures of 430°C – 440 °C which produces a group of light oils. It was happened due to a NiMo catalyst have a good performance in breaking long carbon chains into short carbon chains under these operating conditions. The shorter carbon chain, the easier the oil will be to crack into a fuel fraction.

The Composition of Coal Oil

Gas Chromatography-Mass Spectroscopy (GC-MS) is an analytical instrument used to determine the number and components of hydrocarbons in coal oil from catalytic gasification using NiMo catalysts. NiMo catalyst is one type of catalyst used to produce oil with a high composition of aromatic compounds [19]. GC-MS analysis was carried out on 3 samples from temperature 430 – 440 °C with catalyst weight of 0%, 5%, and 15%. The results of GC-MS analysis for three samples are shown in Table 4 and Figure 6, 7 and 8. The result of GC-MS, the composition of coal oil consisted of the composition of aromatic, aliphatic, phenolic, alcohol and other hydrocarbons.

Table 4. The hydrocarbon composition of coal oil (T = 430 – 440 °C)

<table>
<thead>
<tr>
<th>No</th>
<th>Composition (%)</th>
<th>0%</th>
<th>5%</th>
<th>15%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aromatics</td>
<td>57.33</td>
<td>48.31</td>
<td>59.75</td>
</tr>
<tr>
<td>2</td>
<td>Aliphatics</td>
<td>17.14</td>
<td>22.86</td>
<td>26.42</td>
</tr>
<tr>
<td>3</td>
<td>Phenolics</td>
<td>16.03</td>
<td>22.99</td>
<td>7.34</td>
</tr>
<tr>
<td>4</td>
<td>Alcohols</td>
<td>7.85</td>
<td>1.67</td>
<td>3.84</td>
</tr>
<tr>
<td>5</td>
<td>Others</td>
<td>1.65</td>
<td>4.17</td>
<td>2.65</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 6. The chromatogram of coal oil with 0% catalyst
Coal oil without catalyst treatment is dominated by aromatics of 57.33%, aliphatics of 17.14% and phenolics of 16.03%. The addition of 5% catalysts produced coal oil which was dominated by aromatic hydrocarbons as much as 48.31%, aliphatics of 22.86% and phenolics of 22.99%. While the addition of 15% catalyst produced coal oil which was only dominated by aromatic hydrocarbons of 59.75% and aliphatic of 26.42%, as presented in Figure 9. This result is in accordance with the statement of Murti, et al. [18] that the use of NiMo catalysts gives high selectivity to aromatic hydrocarbons and in line with the results of Sugianto's research, et al. [20] which produced coal oil with a phenolic component of 54.56% from the addition of 1% NiMo catalyst. This shows that the more the amount of NiMo catalyst used, the aliphatic and aromatic hydrocarbon composition will be increased.

The NiMo catalyst has selectivity to increase the aliphatic hydrocarbon composition in which the greater the percent weight of the NiMo catalyst used, the aliphatic composition will increase. As is known, aliphatic compounds are combustible compounds that are used as the main constituent components of fuel. From the results of the study, it can be seen that the best weight percent of catalyst is 15% because it is able to produce a much smaller and phenolic aliphatic hydrocarbon composition. Comparison of the composition of the fraction of aliphatic hydrocarbons is shown in Figure 10.

The composition of aliphatic hydrocarbons from coal gasification is composed of C6 to >C30 chains. In the treatment without a catalyst, the aliphatic hydrocarbon composition was dominated by the C15 - C20 fraction of 4.91% and >C30 at 6.55%. The addition of 5% NiMo catalyst showed the dominant fraction was C15 - C20 which was 15.44%. The addition of 15% NiMo catalyst showed that the dominant fractions were C6 - C12 which was 11.70% and C15 - C20 which was 6.78%. This shows that the addition of 5% NiMo catalyst to coal oil production process at temperatures of 430–440 ºC has a better performance in breaking the long carbon chain into short carbon chains C15 - C20 fractions. While the addition of 15% NiMo catalyst has a better performance in breaking the long carbon chain into a short carbon chain C6 - C12 fraction.

Compared with Muis's research [21] which produced coal oil made from sub-bituminous coal at a temperature of 400 – 475 ºC using 3% by weight catalyst γ-Al2O3 to produce coal oil products with 60.07% short chain hydrocarbon compositions C7 - C12 which still binds to the O and S elements, the NiMo catalyst can be said to have better performance because the coal oil products produced without S elements.
Calorific Value of Coal Oil

Calorific value is the amount of energy released when the fuel is burned perfectly in a combustion process. The tool used to analyze calorific value is the bomb calorimeter. Analysis of the heating value was carried out on 3 (three) types of samples from temperature conditions 430 – 440 °C with catalyst weight of 0%, 5%, and 15%. The comparison of the calorific value of the addition of catalyst weight percent is shown in Figure 11.

Figure 8 shows the calorific value produced in coal oil with a treatment without a catalyst was 8,158.54 cal/gram. The addition of 5% the catalysts was not given a significant increase in the calorific value of the coal oil, which was 8,166.71 cal/gram. The addition of 15% the catalyst shown that the calorific value of coal oil increases to 8,309.25 cal/gram. It can be known that the effect of adding the weight percent of the catalyst to the calorific value of coal oil is directly proportional. The greater the weight percent of the catalyst added, the greater the calorific value of the coal oil. Compared with the Frątczak study [22] which produced coal oil using 1% Molybdenum catalyst and get a calorific value of 6,393.90 cal/gram, the coal oil from this study has a greater calorific value and has a potential to be developed as a source of material alternative fuel.

CONCLUSION

Based on the result of the research and the data analysis that has been done, it can be concluded that NiMo catalyst has a high performance under temperature 430 – 440 °C to give an increase of coal oil yield. The addition of 15% catalysts gives a yield of 9.35% with the composition of hydrocarbon consists of 59.75% of aromatics, 26.42% of aliphatics, and 7.34% of phenolics. NiMo catalyst has high selectivity in breaking long carbon chains into aromatic and aliphatic compounds.

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