Syngas production process from catalytic cracking of glycerol based on modified zeolite catalyst Ni/ZSM-5

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Abstract. Increased biodiesel production has an effect on increasing the availability of glycerol, where glycerol is a by-product of biodiesel production. So far, the use of glycerol is less than optimal where only a small portion is used as an additive in the food industry. So it needs efforts to utilize glycerol becoming a more valuable product. Based on its characteristics, glycerol is potentially converted with catalytic cracking process produced gas that are enrich in H$_2$, CO which is known as synthesis gas (Syngas). Syngas is the main ingredient in the petrochemical industry, besides syngas can also be used as an alternative fuel do to its heating value. The main objective of this research is to study the conversion of glycerol to syngas with the catalytic cracking process, the effect of the ratio of catalyst to glycerol and reaction temperature on product yield. This research was carried out in a semi batch reactor filled with Ni/ZSM-5 catalyst which was flowed by Nitrogen gas at 350, 400, 450 and 500°C reaction temperature variations with catalyst ratio of 0, 3, 4 and 5% (w/w). Gas products were analyzed using Gas Chromatography (GC) to determine the composition of the constituent gases which are CO, CO$_2$, H$_2$ and the catalyst characterization was carried out by the BET, XRD and AAS methods. The highest yield was obtained at a process temperature of 500 °C with catalyst ratio of 3 wt % which produced 49.45% of Syngas with the hydrogen selectivity of 20.94%.

1. Introduction
Biodiesel is one of the alternative fuels to replace biofuels which are currently being produced. In the process of production biodiesel a by-product is produced in the form of glycerol as much as 10% [1]. Government policies related to renewable energy that encourage increased biodiesel production have an impact on the abundance of glycerol produced. Currently, glycerol is widely used in the production of cosmetic, medicine and even as a flavor enhancer in food. Glycerol has not been used optimally compared to its availability, therefore it is necessary to make some efforts to utilize it so that glycerol does not only become waste from the biodiesel production process. Glycerol can be used to produce syngas which in the process does not need to be reacted with other chemicals.

Syngas or commonly called synthesis gas is a gas mixture with the main components are hydrogen gas (H$_2$) and monoxide gas (CO), while the side components are carbon monoxide gas (CO$_2$) and methane gas (CH$_4$). Syngas can be used as fuel for internal combustion engines and diesel combustion engines. In addition, syngas is also used as raw material for producing ethanol through the Fischer-Tropsch process and urea production process [2].
In the syngas production process, glycerol can be converted through several processes using the utilization of a catalytic, for example the reforming and catalytic cracking process. About 95% of hydrogen is still produced from fossil fuel sources through the pyrolysis or steam reforming process, and only about 5% is produced through renewable sources, including through the electrolysis of water [2]. However, using some of these processes still requires a lot of heat. In addition to the above processes, syngas can be produced by catalytic cracking of glycerol which does not require high temperatures.

Several previous studies on the conversion of glycerol to syngas have been carried out, such as an experiment by Shahirah et al. [3]. In this study, syngas was produced from cracking of glycerol using a praseodymium-Ni/Al₂O₃ catalyst. The research includes catalyst synthesis and catalyst characteristics. The reaction was carried out using a stainless steel fixed bed reactor with operating conditions 973 K – 1073 K and at atmospheric pressure. The results of this study obtained a hydrogen yield of 29.04% [3]. In addition, other research by Harun et al. [4] has converted glycerol to hydrogen using the dry reforming method using an Ag-Ni/Al₂O₃ catalyst. Research includes catalyst preparation, glycerol dry reforming, and product analysis. Ni(NO₃)₂.6H₂O solution and AgNO₃ solution were used to impregnate Al₂O₃. The reaction was carried out using a fixed bed reactor with operating conditions 873 K – 1173 K. The results of this study obtained a glycerol conversion 40.70% and H₂ yield 32% [4].

In this study, the conversion of glycerol to syngas was carried out using a catalytic cracking process where this process does not require a high temperature of around 300°C-500°C compared to the steam reforming process which uses temperatures above 600°C. While the catalyst was modified using nickel metal impregnation so that it became Ni/ZSM-5 to increase the active site of the catalyst. Nickel is a transition metal that has one empty d orbital, so it can bind the split carbon atoms of glycerol [5].

2. Materials and methods
This experiment consists of preparation catalyst and catalytic cracking reaction. In catalyst preparation, ZSM-5 catalyst were prepared by wet impregnation. ZSM-5 mixture with an aqueous solution of Ni(NO₃)₂.6H₂O stirred at 80-85°C for 3 h and dried at 120°C for 6 h. The prepared catalysts were calcination at 10°C/min to 600°C for 2 h in the air atmosphere. For the reduction process, the catalysts were reduced with flowing 5 ml/min hydrogen at 600°C for 2 h, and get the Ni/ZSM-5 catalyst. Prior used to the catalytic cracking, the catalysts is mixed with kaolin (5 wt. %) in order to more easily when formed into pellets. The explanation of the catalyst preparation used to experimental has been presented in previous paper [5].

Catalytic cracking gliserol performed in a fixed bed reactor as in figure 1 and heated at the temperature reaction of 350-500°C. The catalyst is placed in the reactor which contacted with glycerol vapor. Product were analyzed using GC-MS and the catalyst were characteristic using BET, XRD and AAS.

![Figure 1. Equipment scheme.](image-url)
3. Results and discussion

3.1. Characteristic catalyst

3.1.1. BET characteristic catalyst. One of method to estimate the type of pores obtained from the impregnation process of Ni metal on the catalyst is to analyze the absorption pattern of nitorgen (N$_2$). The $N_2$ absorption pattern of the ZSM-5 and Ni/ZSM-5 catalyst is shown in figure 2.

Nitrogen adsorption is physical method that use in Isotherm Brunauer, Emmett and Teller (BET) method to determine total surface area and pore structure of a solid [6]. At figure 2, Nitrogen adsorption isotherm all of ZSM-5 sample show a similar pattern in which there is a rapid rise at a relatively low pressure ($P/P_0$), than increase slowly in the middle and again rapidly as $P/P_0$ approaches one. The gas absorption pattern at figure 2 clarifies that impregnation Ni metal effect to the catalyst characteristic result. Heating and stirring at impregnation process will caused expansion of space between sheets (space between basalts) in ZSM-5 catalyst and formation of a good pore system. Introduction nikel metal to the pore catalyst caused specific surface area Ni/ZSM-5 decrease with increasing nikel loaded. From BET result specific surface area ZSM-5 is 353 m$^2$/g and compare with microcrystalline synthesis ZSM-5 (MZ) result from sodium silikat, alumunium nitrat, and tetrapropil ammonium hidroksida at Saxena and Vismanadham [7] experiment that has surface area 342.4 m$^2$/g. Surface area Ni/ZSM-5 decrease to 295 m$^2$/g at 3% Ni metal impregnation. This result according with Chen et al. [8] experiment that ZSM-5 catalyst have surface area between 300-310 m$^2$/g and after loaded nikel metal surface area decrease to 230-250 m$^2$/g. The BET analyzed result from the catalysts is presented in table 1.

Table 1. ZSM-5 catalyst characteristic and Ni/ZSM-5 impregnation result.

| Catalyst Characteristic | ZSM-5 | 3%Ni/ZSM-5 |
|-------------------------|-------|------------|
| BET surface area (m$^2$/g) | 353   | 295.3      |
| Total pore volume (cm$^3$/g) | 0.0408 | 0.0357    |
| Pore diameter (nm) | 3.0598 | 3.0246    |
| Average diameter (nm) | 2.4488 | 2.4388    |
Reduction in specific surface area is proportional to the decrease pore volume. The largest pore volume 0.0408 cm$^3$/g was obtained on the initial catalyst before nickel metal impregnation. The pore volume decreased with the increase of % Ni metal to 0.0357 in the addition of 3% Ni metal.

In order to determine the effectiveness of the Ni metal loading process in the ZSM-5 catalyst, an AAS (Atomic Absorption Spectrophotometry) analysis was performed. From the results of AAS analysis, it is known that the Ni metal content in the catalyst is 2.88 wt. %.

3.1.2. XRD characteristic catalyst. From the XRD analysis result which presented in figure 3, it can be seen that the ZSM-5 catalyst has an orthorombic crystallinity. For comparison, figure 3 (c) is the XRD results of the ZSM-5 simulation conducted by Treacy and Higgins [9]. The main peaks of the ZSM-5 are expressed in $2\theta$ at 7.9; 8.8; 23.1; 23.9; and 24.4° which corresponds to the characteristics of ZSM-5 with specific peaks of $2\theta = 7.9^\circ$ and $23-25^\circ$. The results were similar to the XRD HZSM-5 catalyst synthesized by Vichaphund et al. [10] from Sodium metasilicate pentahydrate, Sodium aluminate, and Tetrapropilammonium. In the synthesis of ZSM-5 catalyst by Chen et al. [8] obtained XRD patterns with a specific peak of $2\theta$ in the range of 6-9° and 22.5-25.0°.

In an experiment conducted by Emori et al. [11], the XRD analysis results of the ZSM-5 catalyst showed the MFI structure with the characteristics of $2\theta = 8.04; 8.89; 23.19; 23.32$; and 23.78°. The results are similar to the experiments conducted by Zhao et al. [12] where the XRD analysis results of ZSM-5 showed the diffraction peak characteristics of the MFI structure at $2\theta = 8.04; 8.89; 23.19; 23.32$; and 23.78°.

![Figure 3. XRD pattern results (a)ZSM-5; (b)3%Ni/ZSM-5; and (c) ZSM-5 simulation [9].](image)

The diffraction intensity of the ZSM-5 support was seen decrease with the increase in the amount of nickel charged, the peak of the diffraction was very clear showing that the crystallographic structure did not change much after the nickel loading and calcination process. This shows that the addition of Ni metal does not change the structure of ZSM-5. In the calculation of the relative crystallinity calculated based on the number of peak intensities of $2\theta$, the Ni/ZSM-5 catalyst shows a decrease in crystallinity. This is due to the nickel metal dispersion on the surface of the ZSM-5 support causes a decrease in the degree of crystallinity (%). The crystallinity of the ZSM-5 catalyst from the experiments of Chen et al. [8] showed almost the same results 40.2%. The decrease in the crystallinity of ZSM-5 in Ni impregnation was due to metal dispersion on the surface of the catalyst.

3.2. Effect of reaction temperature on syngas yield

In syngas production process there are several parameters that affect the product, on of them is the reaction temperature. The effect of reaction temperature can be seen in figure 4.
Figure 4. Correlation between reaction temperature and syngas yield.

In the figure 4, it can be seen that the higher the temperature increase syngas yield. This is due to the glycerol decomposition reaction is an endothermic reaction. In theory, glycerol decomposition is an endothermic reaction that requires heat during the reaction [13]. So that the high temperature used will increase the glycerol decomposition reaction and produce greater syngas products.

3.3. Effect of % catalyst on syngas yield

The number of catalyst used can affect the product of the syngas production process. The effect of % catalyst can be seen in Table 2.

Table 2. Effect of % catalyst on syngas yield.

| Temperature (ºC) | % catalyst | Hydrogen yield (%) |
|------------------|------------|--------------------|
| 500              | 0          | 9.07               |
| 500              | 3          | 20.94              |
| 500              | 4          | 17.44              |
| 500              | 5          | 12.84              |

Table 2 shows that more catalysts used in the glycerol conversion process, can increase hydrogen yield product and the highest hydrogen yield produced with a catalyst of 3%. This is in accordance with the theory that the use of a catalyst can expand the catalyst contact surface, causing collisions between molecules increase so that the reaction rate increases as well and the resulting product is even greater [14]. The use of a catalyst will reduce the activation energy and speed up the reaction rate by providing an alternative pathway that is easier to produce product.

4. Conclusion

From the experiments that have been carried out can be concluded that glycerol has potentially to be converted to a syngas through a catalyzed cracking reaction process using modified zeolite formed Ni/ZSM-5 with the experiment results as follow:

- The temperature of the catalytic cracking reaction affects the syngas yield (%) where the higher the temperature, the syngas yield tends to increase.
- The ratio of catalyst to glycerol as a raw material has an effect on syngas yield. However, it did not produce a linear trend, where at the ratio of 3% syngas yield tend to increase but with the addition of 4 and 5% there was a decrease in yield.
- The highest yield was obtained at a process temperature of 500ºC with catalyst ratio of 3% which produced 49.45% of Syngas with the hydrogen selectivity of 20.94%.
Acknowledgments
The authors would like to acknowledge The Ministry of Research Technology and Higher Education of the Republic of Indonesia for financial support of this work through “Penelitian DIPA Swadana Inovatif 2020” from Politeknik Negeri Malang.

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