Preparation and Characterization of Ni/Al$_2$O$_3$ Catalyst and Its Utilization for Catalytic Cracking of Glycerol

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Abstract : The objective of this research was to prepare Ni-Al$_2$O$_3$ catalyst for catalytic cracking application. The catalyst was prepared by varying Ni concentration in the range of 2-10% and it was tested in catalytic cracking of glycerol with microwave as external energy. The result of showed that the peak of Ni impregnated in Al$_2$O$_3$ appeared at $2\theta= 62.9^0$ and crystallinity of catalyst increased from 35 to 40%. Furthermore, SEM analysis showed that during impregnation process Ni filled the active sites of Al catalyst. The highest yield was achieved at 84.67% with Ni- Al$_2$O$_3$ 6% catalyst.

1. Introduction

Biodiesel or Free Fatty Methyl Ester (FAME) is a fuel for diesel engines consisting of alkyl esters of fatty acids. FAME was synthezed from oil and methanol through esterification reaction. It can also be synthezed from triglyceride with methanol with transesterification reaction andglycerol as by product[1-3]. Glycerol is an alcohol with three hydroxyl groups which consist of two primary hydroxyl group and one secondary hydroxyl groups. Glycerol is a viscous liquid that has a sweet taste, colorless and odorless. Glycerol has both hydrophilic and hygroscopic and has a melting point and boiling point at18.17°C and 290°C, respectively[4].

Commonly, glycerol was used as an additive in the cosmetics manufactures, pharmaceutical formulations and food. As by product, glycerol has a purity of 70-80%, and therefore it needs an additional purification steps through electro dialysis and nanofiltration processes. Glycerol can be converted into products by using oxidation, hydrogenolysis, esterification, reforming to syn-gas and fermentation and etherification processes[5]. Some products derived from glycerol are glycerol trihepthanoate[6], glycerol triacetate[7] tribenzoin, and glycerol ether TTBG (tri-tert-butyl ether glycerol)[8,10]. Glycerol was also converted with hydrogenolysis to 1,2-propanediol (1,2-PDO) and 1,3-PDO[9]. Various noble metals (Pt, Ru, Pd, Rh, Ir and Re) and non-noble metals (Cu, Ni, Zn, Al, Fe, Mg, Si and Co) catalysts have been used for this reaction. Noble metal catalysts propagate the cleavage of both C−C and C−O bonds of glycerol leading to formation of degradation products[10-11]. Nickel is mostly selected for its low price and it is widely used in hydrogen production and also hydrogenolysis[10]. Meryemoglu *et al*.[12] compared aqueous phase reforming (APR) of glycerol by using Raney Ni and Pt based catalysts, and showing a higher conversion rate and hydrogen selectivity when Pt based catalyst was used. Utilization of $\square$-Al$_2$O$_3$ as support in preparation of catalyst was done by many researchers[12-16]. Copeland *et al*.[13] were studied at the effect of Pt/γ-Al$_2$O$_3$ catalyst with different metal contents on APR. Özgür *et al*.[14] investigated optimum reaction condition of APR process of glycerol in both autoclave and fixed-bed reactor using Pt/γ-Al$_2$O$_3$. Their optimized reaction condition for APR process of glycerol over Pt/Al$_2$O$_3$ catalyst

was achieevd at 230˚C, feed flow rate of 0.73 h−1 and WHSV with less than 45 wt% of glycerol concentration. Nickel also was used as active side in catalyst for reforming of glycerol[15-16]. The objective of this research was to prepare Ni/Al_2O_3 catalyst and to test the catalyst for glycerol catalytic cracking.

2. Methods

2.1. Material

Ni(NO$_3$)$_2$.6H$_2$O (>99%, Merck Indonesia) were used as precursors and Al2O3 /Alumina obtained from PT INALUM Indonesia was used as catalyst support . The standard chemical such as glycerol (>99%, Merck Indonesia) was used in High Performance Liquid chromatography (HPLC). Glycerol and methanol with industrial grade were used in catalytic cracking testing. Aquadest was produced by using reverse osmosis from Center of Research and Service Unit Diponegoro University (CORES-DU). The ultra high pure hydrogen (99.99%) and nitrogen (99.99%) supplied by Samator Gas PT was used directly without any further purification.

2.2. Catalyst preparation

Nickel was loaded on Alumina with variable (w/w) of 2%, 4%, 6%, 8% and 10%. It was synthesized by wetness impregnation method. Ni(NO$_3$)$_2$.6H$_2$O was dissolved into 25 ml of distilled water and Al$_2$O$_3$ support was added to this metal precursor solution under a fixed stirring. The slurry obtained was aged for 2 h at 85°C temperature then dried in an oven for 1.5 h at 120 °C, and subsequently calcined at 500 °C in the air for 2 h.

2.3. Catalyst characteristic

The catalyst product was characterized for its morphology and crystallinity. The analysis of crystallinity used X-ray diffractometer, XRD-7000S model Shimadzu brand with X-ray tube target Cu, voltage 30 kV, current 30 mA, and Kα radiation. XRD data was analyzed with PCXRD software. Morphology of catalyst was analyzed with JEOL PC Scanning Electron Microscope (PCSEM) model JSM-6510LA with magnification of x5000. The analysis process was conducted in Center of Research and Service Diponegoro University (CORES DU).

2.4. Catalytic testing of Ni/Al_2O_3

Catalytic activity test was carried out by the degradation of glycerol using a microwave. 50 ml methanol and 50 ml glycerol were added in reactor Followed by 2.5 gram of 2-Ni/Al$_2$O$_3$ catalyst. Catalytic cracking was carried in microwave with 400 watts powerA mixture was heated for 30 minutesand the same treatment was applied to the variable weight percent of the catalyst to the weight of the reactants of 1%, 3%, 4%, 5% and 6%.

3. Result and discussions

3.1. Characterization of Ni/Al_2O_3catalysts

The results SEM analysis was presented in Figure 1 . Figure 1.a. shows a morphology of alumina as support catalyst and the surface is still in amorphous phase.. Figure 1.b-f is morphology of Ni/Al$_2$O$_3$ catalyst that prepared by variation of Ni weight. The crystal morphology was different with γ-Al$_2$O$_3$ catalyst[17]. This difference may due to the different treatment and type of raw materials. Pudi et.al (2015) has also used γ-Al$_2$O$_3$ and calcination time longer than the current study. The longer of calcination time, the better of formation of Ni grains granules. Figure 1b-f also show that the nickel impregnation, the active space on the alumina filled by nickel [16].

The crystal morphology was similar to agglomerated alumina (Figure 1a-f). Particle agglomeration is caused by sintering of particles during heat treatments. EDX elemental mapping is used to determine the distribution of Cu, Ni metal on the surface of γ- and the elemental compositions are listed in Table 1.

Table 1. Metal composition of catalysts with SEM EDX analysis

Catalyst type	Atomic composition (mass %)					
	C	O	Cu	Na	Al	Ni
Al_2O_3	6.68	52.14	0.78	-	40.40	-
2% Ni/ Al_2O_3	-	54.72	-	-	44.24	1.04
4% Ni/ Al_2O_3	7.28	52.18	-	0.29	36.77	3.48
6% Ni/ Al_2O_3	6.04	52.26	-	-	35.75	5.95
8% Ni/ Al_2O_3	8.12	48.49	-	0.31	33.95	9.13
10% Ni/ Al_2O_3	6.42	48.47	-	-	35.75	9.37

Table 1 depicts that the amount of nickel attached to the surface of the alumina is not in accordance with the amount of impregnated nickel. This may occur because of the extent of the carrier is small so the nickel does not fill properly. Alumina as carrier has a function to provide more surface area as a place for Nickel to attach on the active surface so that the surface of the contacts can be wider.

Figure 1

The XRD patterns were recorded in order to identify the crystalline phase and crystal structure of catalysts. Figure 2 showed XRD patterns of γ-Al_2O_3 and Al_2O_3 as raw material. Al_2O_3 pattern was different with □- Al_2O_3 pattern. Al_2O_3 has peaks in 2 theta = 18, 26, 34, 36, 42 and 58. Al_2O_3 contained some amount of cuprum and carbon (Table 1). Difference pattern of Al_2O_3 and □ -Al_2O_3 because of difference impurities in Al_2O_3.

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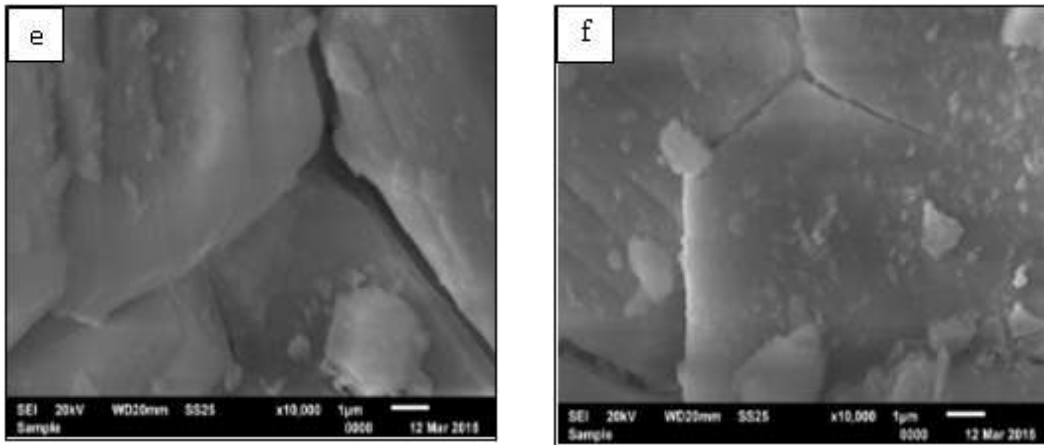
933
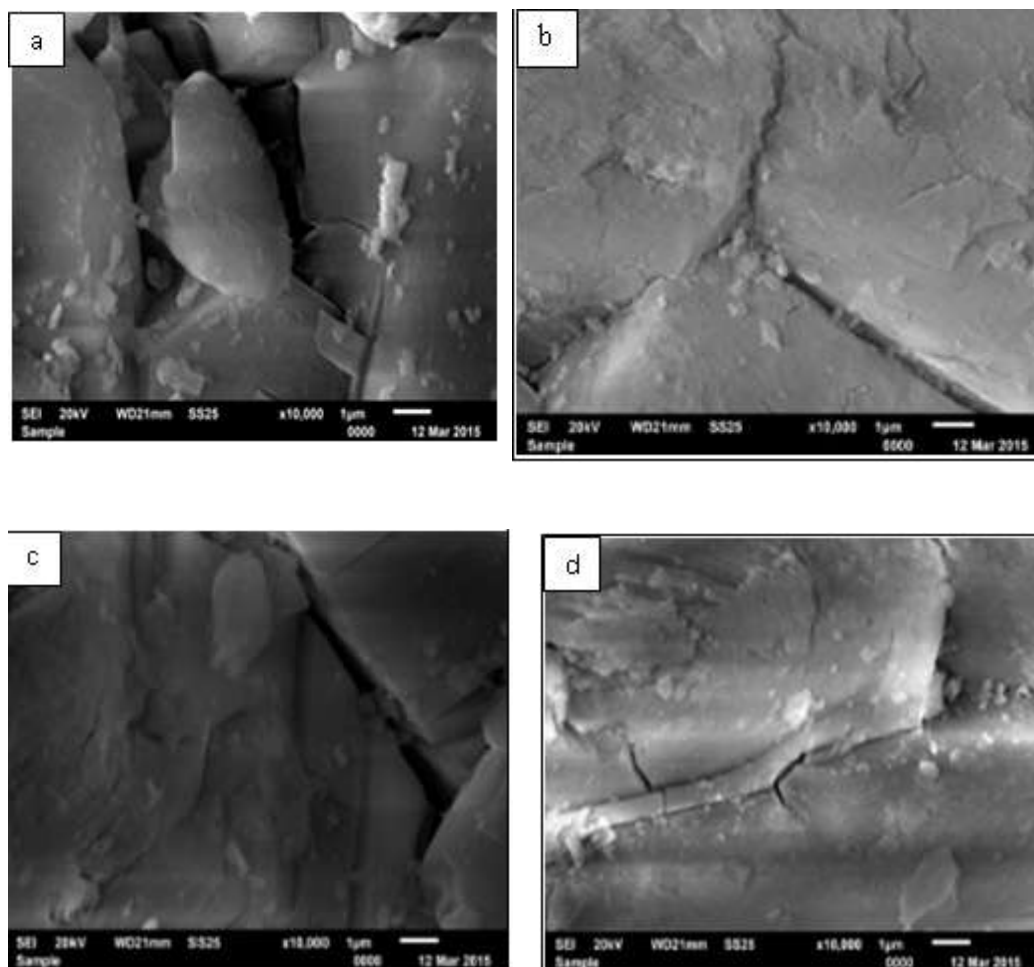
Figure 1. Photographs of catalyst with SEM-EDX analysis (a.Al$_2$O$_3$; b. 2% Ni/ Al$_2$O$_3$; c. 4% Ni /Al$_2$O$_3$; d. 6% Ni /Al$_2$O$_3$; e. 8% Ni/ Al$_2$O$_3$ and f. 10% Ni/ Al$_2$O$_3$)
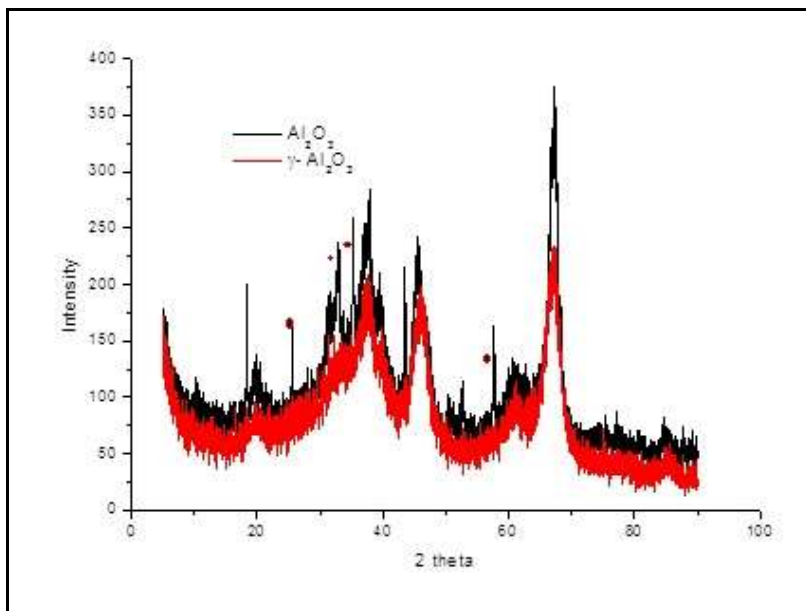

Figure 2. XRD pattern of Al$_2$O$_3$ with ☐☐ Al$_2$O$_3$

Figure 3 shows the XRD diffraction pattern of Ni/Al$_2$O$_3$ catalyst that has been synthesized. By comparing the results of the XRD analysis with XRD diffraction patterns in the literature. In the literature data, the peak of Ni impregnated on Al$_2$O$_3$ is at 2θ = 37.5°, 43.2°, and 62.9°, while the results of the analysis by XRD peak Ni impregnated on Al$_2$O$_3$ is at 2θ = 62.9°. While the peaks of Al$_2$O$_3$ is at 2θ = 32.6°, 37.5°, 46° and 67°. By comparing to the literature, the diffraction pattern of Ni/Al$_2$O$_3$ catalyst similar to the literature data, it indicates that nickel dispersed on Al$_2$O$_3$[15-16]. Figure 3 also shows the difference in height between the diffractogram patterns of Al$_2$O$_3$ which has not been impregnated with Ni metal with Al$_2$O$_3$ which has been impregnated with Ni metal. The difference indicates that there is an increase in the crystallinity of Al$_2$O$_3$ after impregnation of nickel on Al$_2$O$_3$. From the analysis, it was noted that the crystallinity Al$_2$O$_3$ increased from 35% to 40% .
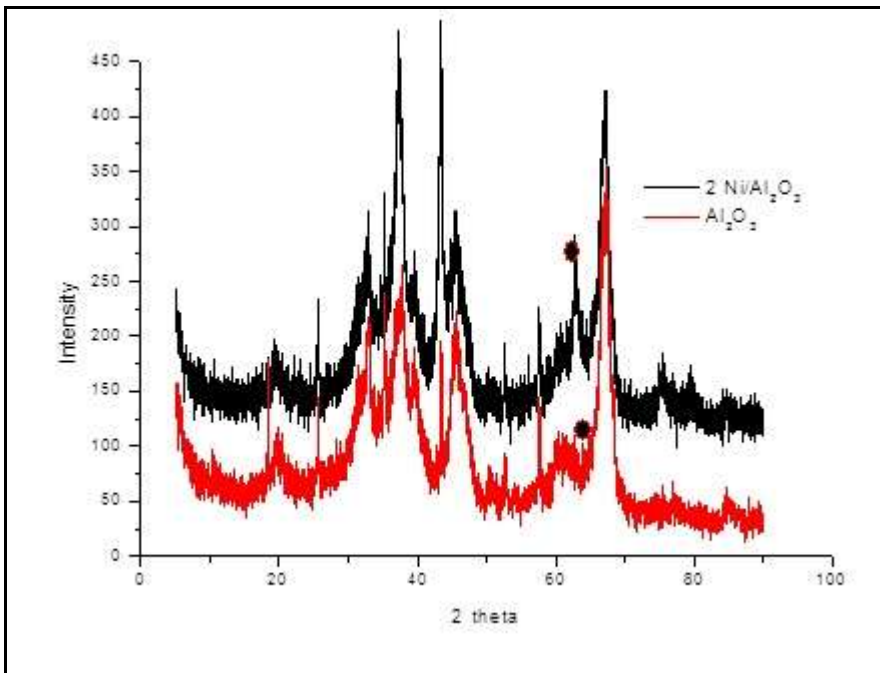
Figure 3. XRD pattern of Al₂O₃ with ☐☐i☐☐ Al₂O₃

3.2. Catalytic testing of Ni/Al₂O₃

Product from catalytic testing was analyzed by using Gas Chromatography Mass Spectrophotometry (GCMS) and the result was shown in figure 4. Ethanol was detected in retention time (RT) of 1.512 and 1.585 minute with searching index of 88 and 93%. Other typical of product during glycerol conversion were presented in table 2. Ethanol is the greatest content in the product. Ethanol was formed by decomposition of glycerol to ethylene glycol by releasing carbon monoxide and water.. Ethanol also can be formed from glycerol decomposition to propylene glycol and followed by decay to ethanol.. Ethanol forming from glycerol catalytic cracking was presented in figure 5.
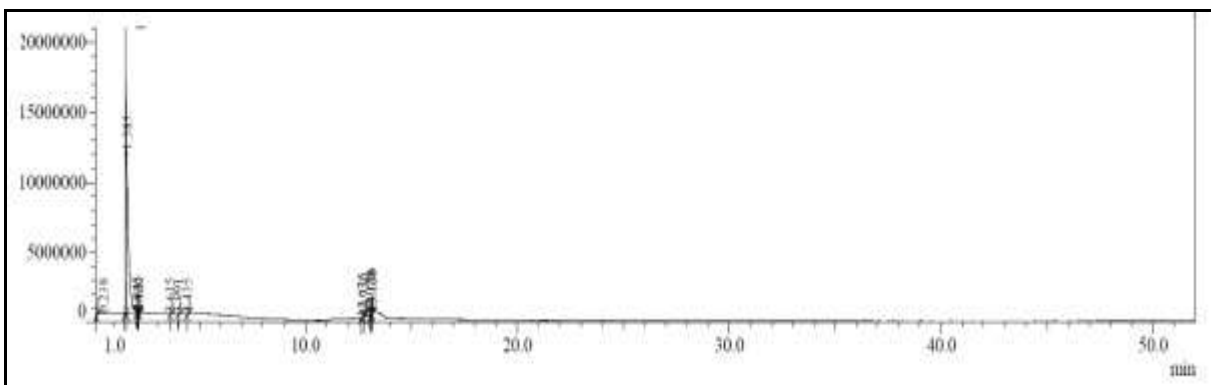

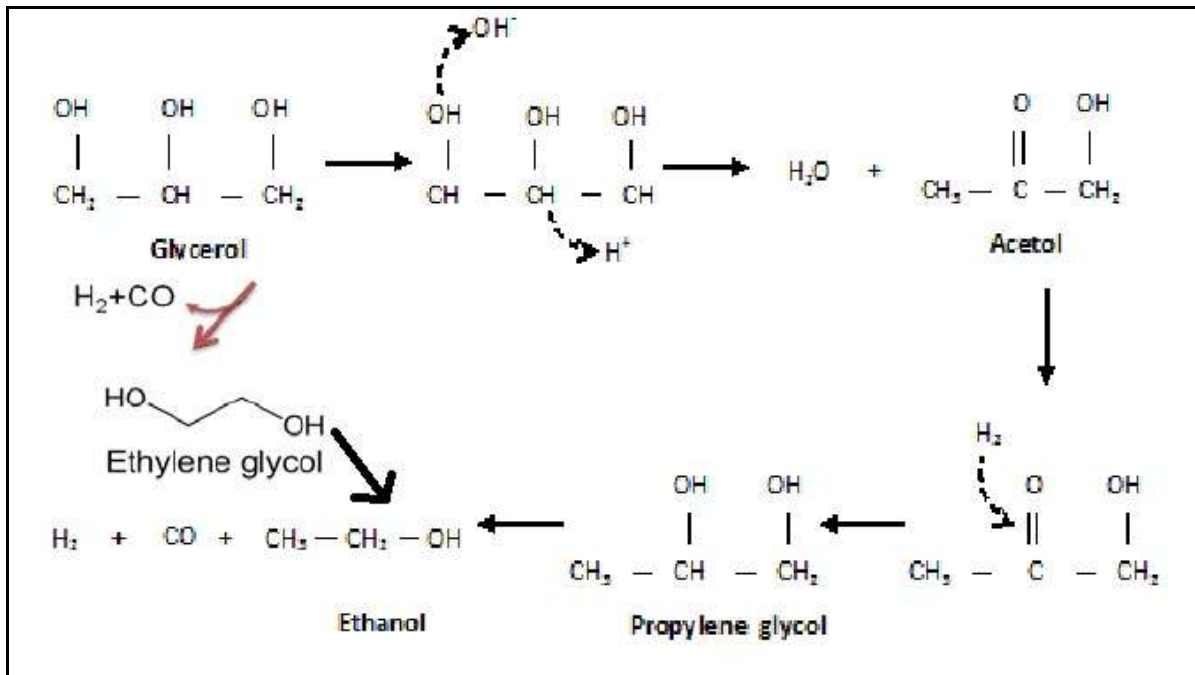**Figure 4. Chromatograph of biodiesel product**

Figure 5. Mechanisme of ethanol forming from glycerol

Table 2. Types of FAME in biodiesel product

Retention time (minute)	Compound	SI (Searching Index)	Composition (%)
0.238	1-Propyne	92	0.21
1.512	Ethanol	88	46.58
1.585	Ethanol	93	52.70
2.045	1,1 Dimehyldiborane	75	0.00
2.120	1,2,2-trimethylcyclopropylamine	82	0.01
2.160	11 bibicyclo (2.2.2) octyl-4-carboxylic acid	86	0.07
3.615	Cyclopropene	86	0.05
12.675	1,2,3-propanetriol	89	0.31

Nickel content in the catalyst will greatly affect the performance of the catalyst. This is caused by the presence of nickel in the catalyst which has a role as the active site of the catalyst. Figure 6 shows the effect of nickel content in the glycerol conversion process using microwave heating at a power of 400 W for 30 minutes. It shows that the glycerol conversion tends to increase by increasing %Ni in the catalyst. The use of nickel as the active site in the catalyst Ni/Al_2O_3 causes the bonds formed between Ni reactants is relatively weak, so that the reaction product can be easily detached from the surface of the catalyst. Thus the reaction process is faster even though the product has a long carbon chain[16-17].

The greatest conversion is obtained when using variable 6% Ni with glycerol conversion reached 82.04%. While the lowest conversion was obtained when using variable 2% Ni with glycerol conversion amounted to 23.53%. Other results showed the conversion of glycerol in variable 4% Ni, 8% Ni and 10% Ni were 75.79%, 51.53% and 56.9%, respectively.
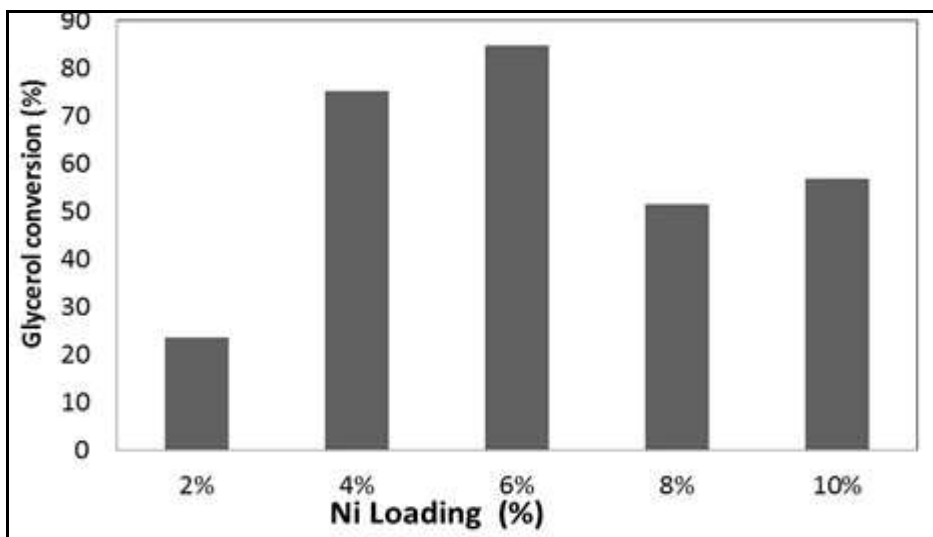
Figure 6. Effect of nickel content on the conversion of glycerol (reaction time 30 minutes; the weight of the catalyst 2.5%)

In the variable 8% Ni, glycerol conversion decreased, it is most likely because the agglomeration of Ni metal which impact on the sintering of the catalyst in accordance with Ni catalyst role as an active site in the catalyst Ni/Al$_2$O$_3$. It results in lower active surface area of the catalyst, resulting the decrease of catalyst activity. Highest glycerol conversion can be obtained in this study was 82.04% on a 6% Ni, this shows that the degradation reactions of glycerol run well in these conditions, where many glycerol reacts to form the product on the surface of the catalyst.

4. Conclusions

Ni/Al$_2$O$_3$ was prepared from alumina that obtained from PT INALUM. The characteristic of morphology was not different. The impregnation of nickel into Al$_2$O$_3$ causes the crystallinity of alumina increased from 35% to 40%. The highest glycerol conversion was obtained in 6 Ni /Al$_2$O$_3$ amounted to 82.04%, while the lowest conversion of glycerol obtained in the variable 2% Ni amounted to 23.53%. The qualitative analysis using GC-MS showed that glycerol has been converted into ethanol.

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