



ACETYLATION OF GLYCEROL FOR TRIACETIN PRODUCTION USING Zr-NATURAL ZEOLITE CATALYST

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ABSTRACT

Biodiesel is one of the key products to avoid the world energy crisis in the future. As by product of biodiesel production, glycerol should be utilized effectively to enhance the competitiveness of overall biodiesel production. In this study, the development of solid catalyst based on the abundant natural resources, zeolite was investigated. The performance testing of catalyst product in the glycerol acetylation were also evaluated at different temperature and compared with other commercial catalyst. Natural zeolite was activated with strong acid (H_2SO_4) and impregnated with $ZrOCl_2 \cdot 8H_2O$ at 80 °C. Based on XRD analysis, the crystalline structure of zeolite was not damaged during the process and the impurities were decreased. The BET surface area of zeolite catalyst increased during activation process from 54.318 m^2/g to 172.45 m^2/g . The Zr-Zeolite catalyst has been tested on the glycerol acetylation with acetic acids for triacetin production. The calculation of triacetin selectivity and glycerol conversion was done based on Gas Chromatography analysis. The results of triacetin selectivity and glycerol conversion are 26% and 94.3%, respectively for reaction temperature 110 °C and 30 minute. By comparison to other commercial catalyst such as Amberlyst-15 and K-10, the catalyst offered higher selectivity and product.

Keywords: glycerol acetylation, zeolite catalyst, triacetin.

INTRODUCTION

Nowadays, the world energy source is highly dependent of fossil fuels such as coal, oil and natural gas which is around 81.7% of the total energy [1]. It is well known that these energy sources are non-renewable and decreasing continuously over the world, therefore several actions are needed in order to avoid world energy crisis such as finding renewable energy resource, increasing power plant efficiency, etc. Among these renewable energy resources, biodiesel appears as one of the most potential and feasible due to the technology and production enhancement since 2004. Biodiesel is produced by trans-esterification reaction between vegetable oils and methanol with alkali-based catalysts. During the production, approximately 10% glycerol has been produced as byproduct [2]. The increasing of biodiesel production will cause also glycerol accumulation in the market. As economic rule, the glycerol price has been declined due to huge accumulation of glycerol in the market and limited area of utilization. In the holistic case, this condition also can influence the overall economics evaluation of biodiesel production. Therefore, the research which related to glycerol application is strongly required to enhance the competitiveness of biodiesel.

Glycerol can be applied as raw material for valuable chemical preparation, cosmetic and fuel additives as reported in recent review [2,3,4]. Acetylation of glycerol using acid catalyst is one of the great choices that produce monoacetin, diacetin and triacetin. The product of triacetin can be used as valuable transportation fuel additives for increasing octane number. Using this scheme, transportation fuel will be more environmental friendly and free from tetraethyl lead (TEL) and methyl tertiary

butyl ether (MTBE) which are employed as fuel additives [5, 6, 7].

The triacetin systematic is a complex reaction between glycerol and acetic acid as a reactant over acid catalyst following the mechanism in the Figure-1.

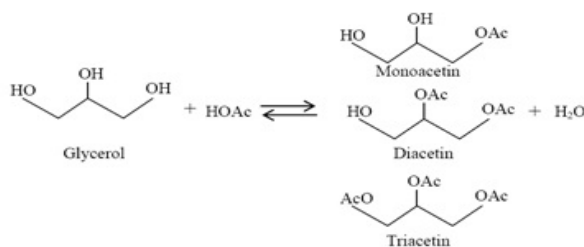


Figure-1. Glycerol acetylation with acetic acids schemes

The reaction above has been carried out over strong acid catalysts e.g. sulphuric acids which will lead the difficulty for separation and purification of the product. In addition, acid liquids catalysts also cause environment damage. The solid catalysts are tried to apply in the reaction to increase the triacetin product, simple and inexpensive purification process such as Amberlyst-15, K-10, montmorillonite, and niobic. Beside high cost for catalyst preparation, the selectivity of triacetin product in this system are still below the expectation. The production of other solid catalyst which is manufactured from abundant natural resource is highly required to decline the production cost and increase the selectivity of triacetin product.

Natural zeolites are a large group of natural aluminum silicates which usage widely use as ion-



exchange agents, catalysts, and molecular filters in a range of industrial processes. This material can be used as catalyst directly or as support for metal impregnation. Zeolite supported Pt-Ni can be used as catalyst agent for n-hexane isomerization [8]. Due to the impurities, natural zeolite must be prepared and activated for better performance of catalysis. The objective of this study was to develop the method for preparation of natural zeolites as catalyst in the triacetin production. The performance testing of catalyst product in the glycerol acetylation were evaluated at different temperature. In addition, the testing process was also done for comparison with other commercial catalyst.

EXPERIMENT

Catalyst preparation and characterization

Natural zeolite was obtained from Klaten, Jawa Tengah, Indonesia. The material was activated using sulphuric acid 0.5M at 80 °C for 4 hours stirred. After neutralization process using barium hydroxide Ba(OH)₂, the material was overnight heated overnight in the temperature of 130 °C. The product, activated zeolite was impregnated by ZrOCl₂·8H₂O (2.5 %wtZr) at 80°C and stirred during 3 hours. The impregnated catalyst sample was dried overnight at 110 °C and was subsequently calcined in N₂ flow at 450 °C over 4 hours in order to remove impurities and carbonaceous component which might have been formed and deposited in the catalyst pores. The last step was oxidation of the catalyst in O₂ flow at 250 °C over 3 hours.

The Brunauer-Emmett-Teller (BET) method was used to determine the total surface area of prepared catalyst by N₂ adsorption/desorption. A gas sorption analyzer (Quantachrome NOVA 1200 series) was used to calculate N₂ adsorption isotherm. Digestion process was done at the temperature 300 °C over 3 hours in order to eliminate the impurities. The structure of catalyst crystalline was identified using powder X-ray diffraction (XRD) (Shimadzu) at the voltage 40 kV and the current 30 mA. The scanning of the material is done at the scan range 3.02 – 65.00 deg and the continuous scanning speed 5 C/min

Catalyst performances

In order to evaluate the performance of catalyst product, the acetylation of glycerol with acetic acid was investigated using Zr-zeolite catalysts. The experiment was performed in three-neck flask equipped with heating mantle, cooling system, stirrer, thermometer and sampling equipment. Reaction experiments were performed at 10 %wt mole ratio of catalyst to glycerol. The different temperatures (95 °C, 105 °C, 115 °C) were tested to examine the temperature effect on the triacetin production.

Glycerol 93% (P&G chemicals), acetic acid 98% (Petrochemical Chang Cun) and the catalyst were mixed in the three-neck flask for reaction process over 30 minutes. The samples were taken and analyzed using gas chromatography (GC) and GC-MS to determine the

amount of glycerol, acetic acid, monoacetin, diacetin and triacetin (Morrisette and Link, 1964). The instrumentation that used was the GC Agilent 6890N MSD 5975B, HP-5ms column 5% Phenyl methyl siloxane, Model Number: Agilent 19091S-433, the injector temperature 275 °C, the temperature at the detector: MS Quad 150 °C, injection volume of 1 micro liter, injector pressure of 3.27 psi. Based on the data, the triacetin selectivity and glycerol conversion are calculated using the following equations.

$$\text{Glycerol conversion} = \frac{\text{No. of glycerol reacted}}{\text{Total no. of glycerol taken}} \times 100\% \quad (1)$$

$$\text{Selectivity} = \frac{\text{No. of desired product}}{\text{Total no. of all products}} \times 100\% \quad (2)$$

RESULT AND DISCUSSION

Catalyst characterization

Powder X-ray diffraction (XRD) patterns

Typical XRD patterns of fresh natural zeolite and impregnated Zr-supported zeolite catalyst were illustrated in the Figure-2. It could be seen that almost all the peaks of the XRD are similar. These indicated that activation and impregnation process did not destroy any crystalline structure of zeolite. The natural zeolite had the 3 strongest peaks at $2\theta = 25.77, 26.49, 22.43$. There was a high similarity with the 3 strongest peaks of impregnated zeolite at $2\theta = 25.3, 22.39, 27.83$. It can be seen that XRD patterns of the natural zeolite obviously were not different with that of impregnated zeolite catalysts.

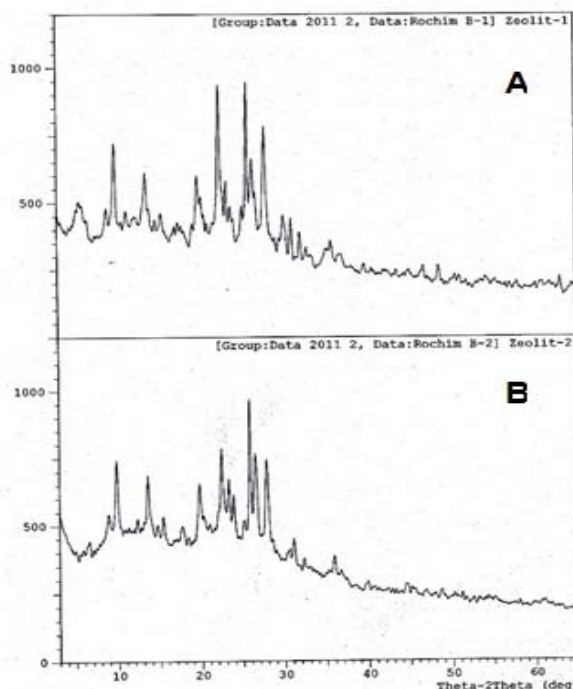


Figure-2. X-ray Diffraction (XRD) patterns of fresh natural zeolite (A) and Zr-zeolite catalyst (B).



BET Surface Area

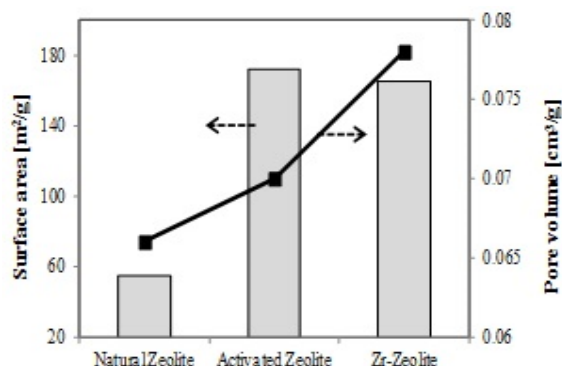


Figure-3. BET surface area and pore volume in each step of catalyst production.

The purpose of the activation step was to get more surface area in the porous catalyst where metal precursor would be impregnated. Figure-3 shows that the surface area and pore volume increased after the activation process. Using strong acid and heating process, the catalyst pore would be opened and also cleaned from several impurities without any destruction of the catalyst structure. Pore volume of the activated zeolite was higher than

that of natural zeolite, it indicated that more material as precursors or reactants could be accommodated.

The Figure-3 shows also that impregnation metal Zr into pore of the catalyst decreased the surface area and porous volume. The decreasing of this parameter was due to metal Zr as precursor which covered the active surface of the catalyst. A similar result was also obtained by Ferreira et.al. [9]

Catalyst performances

Table-1 shows the performance of several catalysts, both solid and liquid ones. It could be seen that Zr-zeolite provides the highest triacetin selectivity among all catalyst tested and the glycerol conversion almost similar with resin Amberlyst-15. After 30 minute of reaction time, the glycerol conversion was 94.56%, and the selectivity of 7% to monoacetin, 68% to diacetin, 26% to triacetin. The result of synthesis zeolite and Zr-zeolite was very different. The synthesis zeolite presented very low glycerol conversion and also no triacetin product. By assuming that the material of synthesis zeolite and natural zeolite was almost similar, metal Zr offered great effect to glycerol conversion and selectivity.

Table-1. Conversion and selectivity of glycerol acetylation reaction at the temperature 110 °C for different catalysts.

Catalysts	Glycerol conversion (%)	Selectivity (%)			Remarks
		Monoacetin	Diacetin	Triacetin	
Synthesis Zeolite (HUSY)*)	14	79	14	-	a
Zr-Zeolite	94.56	7	68	26	-
Resin Amberlyst-15*)	97	31	54	13	a
Sulphuric acid**)	86.7	2	54	44	-

a) the remaining percentage of selectivity belongs to hydroxy acetone

*) adapted from Valter et al [10]

**) adapted from Zahrul et al [11]

Liquid catalyst like sulphuric acid only presents 86.7 % glycerol conversion after 30 minute reaction. Based on the same reaction time, solid catalyst of Zr-zeolite has high activity of the reaction. Related to the triacetin selectivity, sulphuric acid provides higher selectivity than Zr-zeolite but there was more difficulty in purification of the products.

Effect of reaction temperature

Several factors could influence the conversion and selectivity in the glycerol acetylation, such as reaction time, temperature, molar ratio of glycerol to acetic acid and catalyst weight. Figure-4 shows the effect of reaction temperature on the conversion and selectivity during the glycerol acetylation over proposed catalyst, Zr-zeolite.

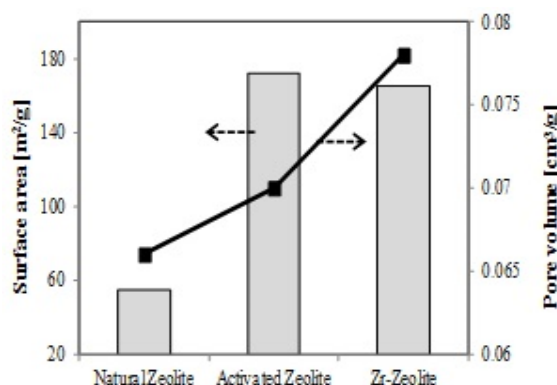


Figure-4. Effect of temperature on the conversion and selectivity during glycerol acetylation over Zr-Zeolite catalyst.



Glycerol conversion decreased at elevated temperature as showed in the Figure-4. Glycerol acetylation was categorized as exothermic reactions, so that the increasing reaction temperature would lead the chemical reaction equilibrium to shift towards reactants formation. Glycerol as a reactant would be formed and hence glycerol conversion would be reduced. When the reaction temperature increased from 95 to 110 °C, the glycerol conversion only decreased from 96.87% to 94.56%. It means that glycerol conversion was not sensitive with the changing of reaction temperature. Formation of the diacetin was predominant to monoacetin and triacetin over the whole range of reaction temperature. As a useful product, triacetin selectivity decreased with the increasing of reaction temperature. These results suggested that the triacetin production was more effective in the lower temperature.

CONCLUSIONS

The synthesis of solid catalyst from natural zeolite for glycerol acetylation was studied. Activation and impregnation could get better solid catalyst characteristic such as surface area, porous volume and active area. Crystalline structure of zeolite was not damaged during the process. Testing of Zr-zeolite catalyst for glycerol acetylation with acetic acid also offered better results for triacetin production.

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