

Glycerol acetylation using magnesium fluoride catalyst to produced DAG and TAG

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ABSTRACT

Glycerol acetylation with acetic acid using magnesium fluoride catalyst have been investigated. Magnesium fluoride catalyst was prepared by sol-gel method with ethanol as gelating agent. The glycerol acetylation produced monoacetyl glyceride (MAG), diacetyl glyceride (DAG) and triacetyl glyceride (TAG). The catalytic reaction carried out by thermal methods reflux under ambient conditions. The influence of reaction conditions such as the reaction time on the product distribution was investigated. The optimum of glycerol conversion was achieved at 5 hours of reaction time by 78.34% with selectivity of 30, 62 and 8% for MAG, DAG and TAG respectively. The reaction route over magnesium fluorides was observed by product as reactants, gradually. The results showed that the acetylation reaction of glycerol occurs via a parallel route to the first, followed by the consecutive route to produce DAG and TAG.

Keywords - MgF₂, acetylation glycerol, DAG, TAG

I. INTRODUCTION

Glycerol is widely used as a raw material that can be converted into a high value product such as additives for food, drugs, cosmetics and biodiesel [1], [2]. Glycerol can be obtained through the production process of biodiesel from vegetable oils and methanol as a byproduct of the transesterification reaction which amounted to about 10 wt% by weight of the total product [3]. Increased production of biodiesel in the next few years will lead to accumulation of large amounts of glycerol. This situation has prompted the search range of new applications of glycerol. The possible applications of glycerol are as feedstock additives to improve the quality of the properties of biodiesel itself such as viscosity and antiknocking [4]. Glycerol can be transformed into value added products of mono-, di- and triacetyl glycerol (namely MAG, DAG and TAG, respectively), which have found benefits in industrial applications [5]. DAG dan TAG compounds have applications in energy sector as additives biodiesel. They can be obtained through the acetylation of glycerol with acetic acid and/or acetic anhydride and/or acetyl chloride [6]. Recently, the acetylation of glycerol with acetic acid has been introduced as an alternative pathway for the synthesis of acetyl glycerol [7]. Acetic acid with its low boiling point of 56.9°C and environmentally friendly [8] can effectively lead to the new strategy for the synthesis of acetyl glycerol (especially DAG and TAG) involving an acid catalyst. The acid side of the catalyst will interact with the acetyl group to form intermediates form acylium ion to react with the alcohol group on glycerol to formed products [9].

The authors studied the reaction using magnesium fluoride catalyst. Catalyst preparation by sol-gel method. In the sol-gel process presence of specific gelating agent can be control the porosity and the nature of the catalyst acidity. Gelating agent suitable for sol-gel synthesis is alcohol or ether compound [10]. Most of the ether compound has a lower boiling point than the alcohol. The low boiling point lead gelating agent evaporates quickly at room temperature, whereas the presence of gelating agent necessary for the reaction for the polymerization process. Ethanol as gelating agent in the sol-gel synthesis can produce mesopore material wick have appropriate for acylation reactions [11], [12].

II. EXPERIMENTAL SECTION

2.1 Catalysts preparation and characterization

The materials used in this study are chemicals that have pro analysis purity includes magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$, 40% fluoride acid, ethanol. Magnesium fluoride synthesized by reacting stoichiometric of solution between $Mg(NO_3)_2$ in gelating agent and HF accompanied with stirring until the gel is formed and the gel aging carried out at room temperature. The gel was separated from the filtrate by decantation and then washed with distilled water. Gels were dried and calcined at $400^\circ C$.

Solid catalyst characterization by XRD have been applied to study the structure of the bulk material. FTIR pyridine adsorption spectra and nitrogen adsorption–desorption isotherms have been carried out to investigate the surface properties. The porosity characteristics of samples were determined by acquiring adsorption–desorption isotherms of nitrogen at 77.35 K in a vacuum. The Quantachrome ASiQwin Automated Gas Sorption Data version 2.0 was used for calculations based on the BJH model.

2.2 Catalytic test

Catalyst which have been synthesized were tested on glycerol acetylation. The procedure is performed through a thermal method reflux. Glycerol acetylation reaction was observed at temperature of $120^\circ C$ with a molar ratio of glycerol to acetic acid 1:9 in free solvent conditions, in a glass vial equipped with a magnetic stirrer. To this mixture were added 5 wt% of catalyst of glycerol used [13]–[15]. After that, the vial was closed, immersed in an oil bath and the charged mixture was stirred for 1; 3; 5; and 7 hours. Then the mixture is separated from the catalyst via centrifugation. The filtrate obtained was analyzed qualitatively and quantitatively by gas chromatography (GC) to search for the remaining concentrations of glycerol and products. The reaction route over magnesium fluorides was observed by product as reactants, gradually [16] at the optimum reaction time.

III. Results and Discussions

3.1. Catalysts properties and surface acidity

MgF_2 -et catalyst synthesized via sol-gel method with ethanol as gelating agent. The sol-gel method was chosen because many are known to produce a homogeneous product and takes place at low temperature [16], [17]. In addition, the porosity of the catalyst can be controlled through the use gelating agent [18]. Precursor in this synthesis is magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) as a source of Mg^{2+} cations, hydrofluoric acid (HF) as a source of anions F^- , ethanol as a gelating agent and the source alkoxy. The synthesis process of MgF_2 by sol-gel method, there are two stages through [19], [20]. The first stage is the formation of metal alkoxides of metal precursors with gelating agent. The second phase, ie when the reaction fluorolysis gel tissue begins to form and grow fluoride catalyst of the gel through postfluorination.

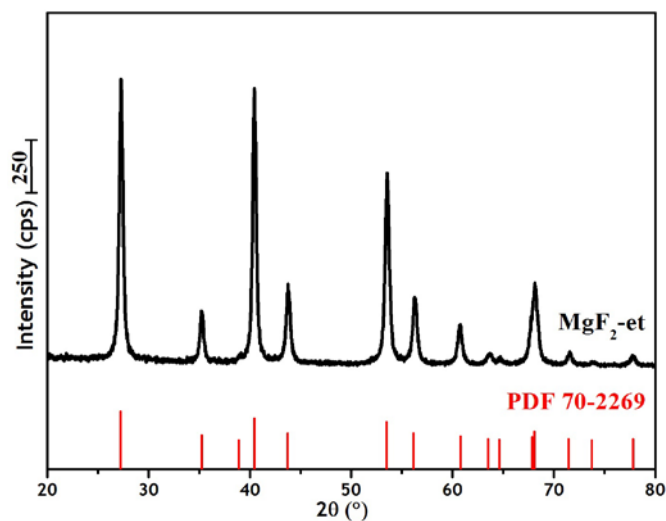


Figure 1 Diffractogram MgF_2 -et.

The solid catalyst were characterized its structure by X-ray diffraction (XRD) and obtained diffractogram presented in Figure 1. Diffractogram matched with a database JCPDS-International Center of Diffraction Data 2001 with PCPDFWIN program. After search and match data 2θ and intensity, the result was showed concordance with database PDF No. 70-2269 which indicates that the solid is MgF_2 with tetragonal structure. In addition to the database are matched with the target product (MgF_2), diffractogram also matched to the database precursor ie $\text{Mg}(\text{NO}_3)_2$ and substances that may have formed when Mg reacts with air, namely MgO . Matching results showed the absence of peaks corresponding to $\text{Mg}(\text{NO}_3)_2$ (PDF No. 19-0765) and MgO (PDF No. 87-0653). Based on the analysis, it can be concluded that the solids are synthesized MgF_2 with single-phase structure.

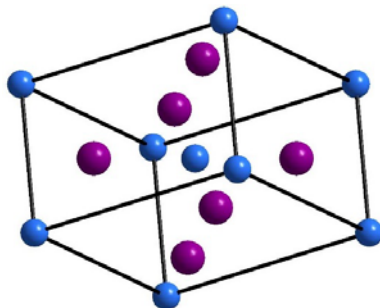


Figure 2 Crystal Structure MgF_2 -et with MAUD program (●) Atom Mg and (●) Atom F.

Diffractogram characterization results are then analyzed further by MAUD program. The program MAUD also used refinement to match the data with the standard and matching with ICSD code 9164 which was completed with a value of R_{wp} 12.78%. Structure 3D of MgF_2 -et crystal was presented in Figure 2. Crystal lattice length of MgF_2 -et was $a=b=4.625\text{\AA}$ and $c=3.052\text{\AA}$ at an angle $\alpha=\beta=\gamma=90^\circ$.

Determination of acidity of catalyst MgF_2 -et was done by pyridine adsorption method and characterized by Fourier Transform Infrared spectroscopy (FTIR). This method which used pyridine as probe molecule. Pyridine has a lone pair of electrons that can be used to detect the presence of either side of Lewis and Brønsted acids. Lewis acid can be detected for their coordination bonds between the lone pair on the nitrogen atom of the molecule pyridine with an empty orbital catalyst. While the Brønsted acid can be detected for their pyridinium ion derived from pyridine molecule which protonated by the proton on the surface of the catalyst. The solid catalyst was activation previously at temperature of 100°C for the desorption process of water molecules adsorbed on the surface of the catalyst. In this study, carried out to observations of the vibrational spectra at wavenumber $1900\text{--}1300\text{ cm}^{-1}$. Results of pyridine adsorption-FTIR spectra of catalyst is shown in Figure 3.

Figure 3 shows that the MgF_2 -et have Lewis and Brønsted acids. Side of Lewis acid characterized by peaks at wavenumber 1424 cm^{-1} , while the Brønsted acid is characterized by the presence of peaks at wave number 1659 cm^{-1} . The peak at 1524 cm^{-1} was the culmination of a combination of Lewis and Brønsted acids that appear squeezed [21]. Therefore, the amount of the Lewis acid, Brønsted acid and a combination of both should be determined semi-quantitatively through integration area under the peak of the FTIR spectra with the same catalyst mass. The results of the determination of the amount of the second acid catalyst is shown in Table 1.

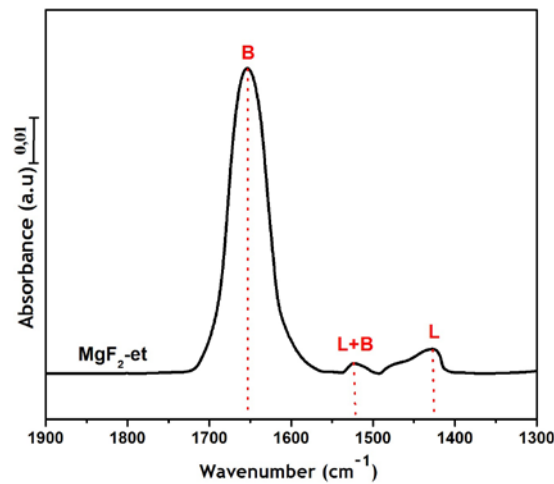


Figure 3 Adsorption Pyridin-FTIR Spectra of MgF₂-et.

Table 1 The results of the determination of the amount of the second acid catalyst

Catalyst	Acid side (size unit)		
	Lewis	Lewis Brønsted	& Brønsted
MgF ₂ -et	0,257	0,054	3,881

The surface area and porosity are two key points in the design of catalysts and heterogeneous catalysis. Measurement of surface area (S_{BET}) and porosity of the catalyst (BJH method) analyzed by adsorption-desorption of nitrogen isotherms. The surface area (S_{BET}) of MgF₂-et is 14.93 m²/g. The Isotherm curve of MgF₂ catalyst is presented in Fig. 4. According to the IUPAC definition was showed by type IV isotherm is typical for dominant mesoporous materials. This marked adsorbate uptake starting at p/p_0 higher than 0.3. The increase adsorbed volume at $p/p_0 > 0.3$ due to mesoporous adsorption. The opposite, if nitrogen volume increase at low p/p_0 region that indicates the presence of micropore. In Fig. 4 shows the hysteresis loops that reinforce the exhibits mesopores, hysteresis loops of the catalysts occur including H1 type for cylindrical pores.

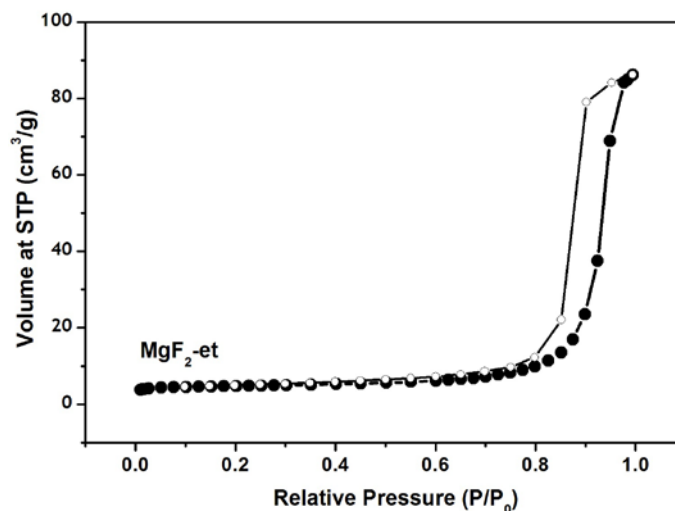


Figure 4 Adsorption-desorption isotherms curve of MgF₂-et.

3.2. Product analysis

The MgF_2 -et catalyst tested its performance in glycerol acetylation reaction. Molar ratio of glycerol to acetic acid is 1:9. The excess acetic acid amount was required to shift forward the equilibrium of the acetylation reaction, thus its fast transformation to higher acetyl glycerol (DAG and TAG) is a necessity.

The influence of reaction time on glycerol conversion and product selectivity was investigated and the results revealed that there was steady increase in glycerol conversion with the reaction duration. The study was performed at varying reaction time in 1;3;5 and 7 hours. According to the presented results in Fig. 5, it was found that reaction time of 5 hours is sufficient for the majority of glycerol to convert to acetyl glycerol. It was also observed that increasing reaction time beyond 5 h resulted in slightly increase the conversion of glycerol. The improve of conversions glycerol occur big enough at reaction time 1 to 5 hours, which is 46% with glycerol conversion changes from 32.54 into 78.34%, whereas the increase in the conversion of 5 to 7 hours only 1% to the value of 78.34 to 79.96%. So it can be said that the optimum reaction at the time of 5 hours with yield of DAG+TAG is 54.73%.

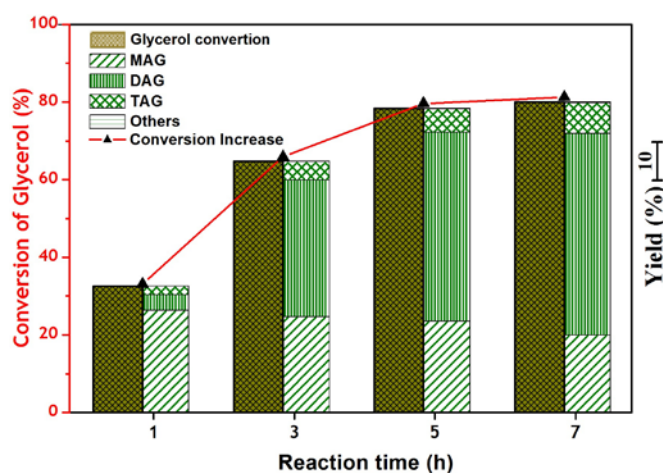


Figure 5 Effect of reaction time on glycerol acetylation.

In this study also carried out the reaction without catalyst in the reaction time at 5 hours as a test control catalytic reaction. Reaction without catalyst showed conversion of glycerol amounted to 29.06% with product distribution MAG, DAG and TAG respectively 24.58; 2.68 and 1.60%. The glycerol acetylation reaction has the ability to catalyze itself [22], but the distribution of the products will only be dominant in MAG despite having a high value of glycerol conversion. If this result is compared with the use of catalysts MgF_2 -et when the same reaction, then it looks very difference about the conversion of glycerol (more high) and the distribution of products, so it can be said that the catalyst MgF_2 -et active in the glycerol acetylation reactions and glycerol conversion can increase the average threefold compared to the reaction without a catalyst.

Trends of products was obtained by variation of the reaction time can be seen in Fig. 6 that the dominant product depends on the reaction time. MAG reaction result was observed predominantly at shorter reaction times, while DAG and TAG emerged as the dominant product on a longer reaction time. This is in accordance with the literature statement [23] that the product in the early stages of the glycerol acetylation reaction with liquid phase will produce a dominant product MAG then it will decrease with increase time duration accompanied by DAG and TAG formation.

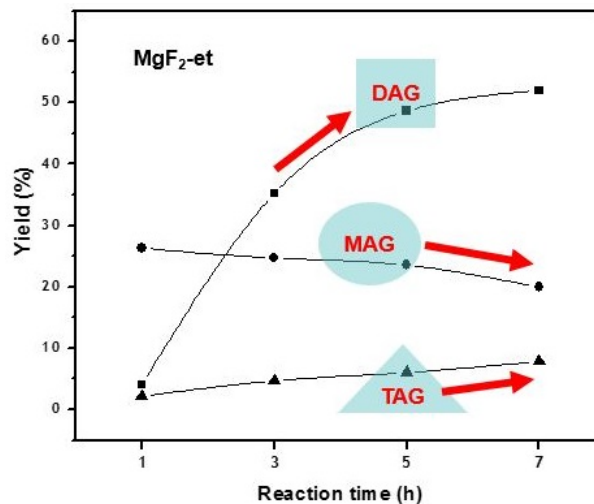


Figure 6 Trends of product on glycerol acetylation.

In addition to glycerol conversion and product yield, in this study also calculated the percentage of selectivity. From the selectivity point of view, the acetylation reaction was strongly time dependent. Variation of the reaction time can be seen in Fig. 7 that the dominant product depends on the reaction time. MAG reaction result was observed predominantly at shorter reaction times, while the longer of reaction duration, the higher value of DAG dan TAG.

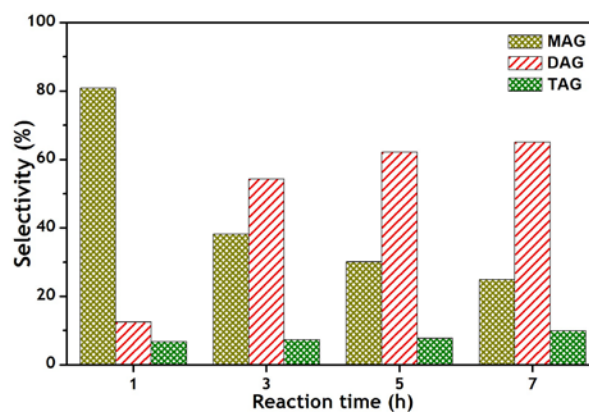


Figure 7 Selectivity product on glycerol acetylation.

3.3 Reaction route

The reaction route over magnesium fluorides was observed by product as reactants, gradually. This route needs to be observed to be used as the basis for the design of a suitable catalyst in the acetylation reaction. The reactants used in this observation is glycerol, MAG and DAG. MAG and DAG compound selected because the compound is a product formed in the acetylation reaction of glycerol so that further reaction of these products can be observed for the determination of these reactions. In catalytic reaction, any reaction has a typical route in the formation of the product.

The reactions are divided into three route, namely consecutive reactions, parallel reactions and equilibrium reaction^[24]. If the reaction is assumed to follow the consecutive reaction, the observations focused on the concentration of TAG formed from each reactant is glycerol, MAG and DAG.

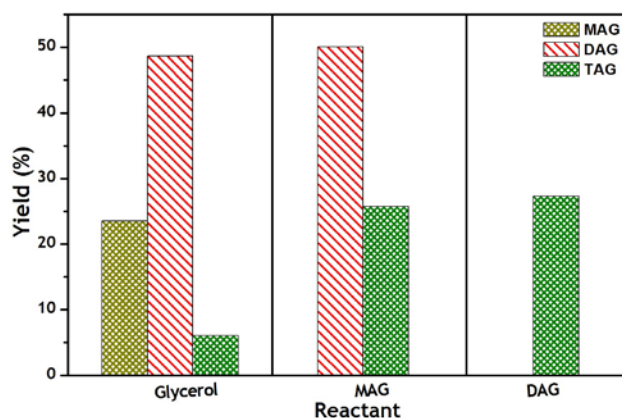


Figure 8 yield of product on observation reaction rate.

The yield of product is shown in Fig. 8. Products from all three experiments under the same conditions with a catalyst MgF_2 -et obtained TAG from reactant of glycerol; MAG and DAG respectively is 6.06; 25.72 and 27.33%. In the consecutive reaction, the minimum limit of the reaction products TAG from MAG and TAG from DAG should have a number with the reaction product of DAG from glycerol and DAG from MAG. The reaction product of DAG from glycerol is 48.66% and DAG from MAG is 50.08%. So, the mole ratio of DAG to TAG is 1:1.83 from reactants glycerol:MAG, as well as 1:1.89 from reactants MAG:DAG.

MAG reactants when reacted further with MgF_2 -et catalyst will turn into DAG product, so did the DAG reactants when reacted more will turn into a TAG product but the reaction of the reactants glycerol can also generate DAG and TAG numbers are not much different from the use of products as reactants so the results showed the reaction mechanism followed by the catalyst MgF_2 -et occurs via a parallel route to the first, and followed by the consecutive route to produce DAG and TAG. Based on this analysis, these schemes can be proposed with the following structure shown in Fig. 9

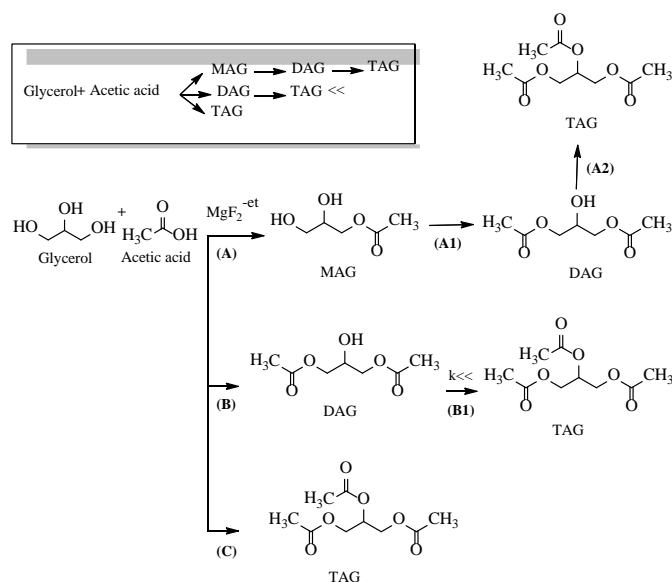


Figure 9 Schemes of glycerol acetylation reaction with MgF_2 -et.

At the initial stage of the reaction, catalytic performance of MgF_2 -et on glycerol acetylation to form MAG, DAG and TAG simultaneously as in Fig. 9.(A);(B);(C). Then, at a further stage, MAG will form TAG through the formation of DAG consecutively (Fig. 9.(A1);(A2)), while the product DAG formed in the early

stages will acetylated to form TAG with a slow rate (Figure 9.(B1)). Therefore, yield of TAG acquired only slightly.

IV. Conclusion

Magnesium fluoride catalysts synthesized by sol-gel method with ethanol as gelating agent, have a tetragonal structure, The surface acidity of MgF₂-et have Lewis and Brønsted acids. The surface area (S_{BET}) of MgF₂-et is 14.93 m²/g. Pore size is dominated by meso pores, although it has a bit of micro pores.

The optimum of glycerol conversion was achieved at 5 hours of reaction time by 78.34% with selectivity of 30; 62; and 8% for MAG, DAG and TAG respectively. The acetylation reaction of glycerol with MgF₂-et catalyst occurs via a parallel route to the first, afterwards followed by the consecutive route to produce DAG and TAG.

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