Selective Etherification of Glycerol over Heterogeneous Mixed Oxide Catalyst: Optimization of Reaction Parameters

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Abstract Glycerol etherification catalyzed by heterogeneous mixed oxide catalyst ($Ca_{1.6}La_{0.4}Al_{0.6}O_3$) was studied in a batch reactor and effects of different parameters on the reaction and distribution of the products during the etherification reaction were also studied. The catalyst showed the high selectivity to (di- + tri-) glycerol (88%) at 96.3% conversion, at 250°C, 8h of reaction time and 2 wt.% of catalyst loading. The variations of diglycerol isomers ($\alpha\alpha'$, $\alpha\beta$, and $\beta\beta'$) versus reaction time were studied for these catalyst and $\alpha\alpha'$ dimer was the favored diglycerol isomer, indicated that the reaction mainly occurred on the external surface of the catalyst. Reaction parameters were optimized based on this catalyst and the relationships between reaction parameters were investigated. The statistical optimal values of variables were obtained where the CCRD and the response at the different points yielded maximum diglycerol yield and a quadratic polynomial equation was developed.

Keywords: *glycerol, etherification, mixed oxide, diglycerol isomers, optimization*

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1. Introduction

The catalytic transformation of glycerol into various chemicals by hydrogenolysis [1], polymerization [2], etherification [3,4], oxidation [5], dehydration [6], acetylation [7], and transesterification [8] has been reported. Of these processes, etherification is the most promising option because it can directly yield compounds that can be used as fuel additives. Moreover, they can also be used as intermediates in the pharmaceutical industry, agrochemicals, and non-ionic surfactants [9]. Previous studies have used different types of homogeneous and heterogeneous catalysts for the etherification of glycerol and achieved promising results [3,4,9-15]. Some of the basic mesoporous catalysts used include a series of metal oxides (alkaline earth oxides) [11,13], impregnated alkaline metal oxide on mesoporous supports, modified zeolites, and others [15,16]. Impregnated mesoporous materials, such as MCM-41, have been studied for the etherification of glycerol [17,18,19,20]. Heterogeneous catalysts can be designed to provide higher activity and selectivity, eliminate corrosion problems, and improve thermal stability Heterogeneous catalysts also have low diffusion resistance (for highly porous materials) and generally longer lifetime [21,22]. The preparation of new catalysts with large pores is a challenging task because of the difficulty in controlling the resulting pore sizes and structures. Large-pore catalyst materials would enhance mass transfer and overcome diffusion resistance [23]. Metal oxide catalysts [10] have been used for etherification. The use of an alkaline binary metal oxide catalyst produces large amount of linear polyglycerols. Barrault et al. [2] studied the catalytic behavior of zeolitic and mesoporous catalysts with alkaline metals in glycerol etherification. In addition, glycerol etherification over mesoporous materials, such as MCM-41 impregnated with metals, was studied. Ruppert et al. (2008) investigated the use of CaO-based catalysts as heterogeneous catalysts in glycerol etherification to diglycerol (DG) and triglycerol (TG) [11]. In addition, in the absence of a solvent, MgAl has been used in the formation of polyglycerols from glycerol [24].

In our previous study [25], glycerol etherification over the $Ca_{1+x}Al_{1-x}La_xO_3$ ($0.1 \le$ x ≤ 0.9) heterogeneous catalyst in a solvent free system was investigated and it was found that 2 wt.% of $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst showed the highest activity at 250°C and 8h of reaction time. The independent structures and properties of these catalysts have been investigated. These catalysts have been selected for this study because of their various points of interest in a large field of applications and their desirable properties, such as basicity, catalytic properties, surface area, and good porosity. The current study investigated the optimization of etherification reaction over $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst to obtain a suitable reaction condition for the selective synthesis of diglycerol. The purpose of this study is to determine the relationship between reaction parameters including reaction

temperature, reaction time, and amount of catalyst used in the reaction.

2. Materials and Methods

2.1. Materials

Lanthanum nitrate hexahydrate (99.9%) was supplied by Sigma Sdn. Bhd., Malaysia. Potassium hydroxide (85%), aluminum nitrate nonahydrate (>98.5%), calcium nitrate tetrahydrate (>99%) and glycerol (99%) were obtained from Sigma–Aldrich, Malaysia. Diglycerol (>90%) from Solvay Chemicals and triglycerol (>90%) from Sigma–Aldrich were used as gas chromatography (GC) standards. High-purity anhydrous glycerol (>99%) was purchased from R&M Chemicals, Ltd., Malaysia. These reagents were used without further purification for catalyst synthesis and activity study.

2.2. Catalyst Preparation

The $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst was synthesized based on our previous study [20]. Heterogeneous catalysts $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ were synthesized using a co-precipitation method from the nitrate compounds of calcium, aluminum, and lanthanum. Based on 10 g of salt, 50 mL of mixed salt solution containing 3.07 M of $Ca(NO_3)_2$, 1.14 M of $Al(NO_3)_3$, and 0.33 M of $La(NO_3)_3$ were prepared. The solution was then precipitated with a controlled pH of 10 using 2 M KOH to obtain a mixed hydroxide solution. During the precipitation step, the mixture was continuously stirred at 600 rpm for 6 h on a magnetic hot plate-stirrer. The mixture was then aged at 80°C under stirring until the solution was homogenized. The resulting mixture was subsequently filtered, dried, and then thermally treated at 560°C for 6 h to obtain the composite mixed metal oxide catalyst. The as-synthesized catalyst was subsequently used in the etherification reaction.
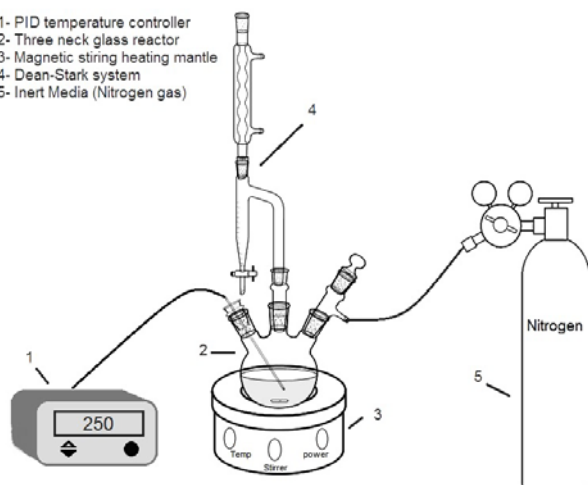
2.3. Reaction Procedure

Figure 1. Schematic diagram of the reactor setup

Glycerol etherification process was performed in a three-necked glass reactor vessel (250 mL) at atmospheric pressure using the synthesized catalysts. The reactor was first placed on a stirring-heating mantle equipped with a temperature controller. The reaction was conducted at different temperatures ranged between 200°C to 260°C for 8 h under continuous nitrogen gas flow to avoid glycerol oxidation. Water formed from the reaction was collected using a Dean–Stark system. In a typical experimental run, 50 g of anhydrous glycerol and 2 wt. % of the catalyst were added into the reactor. The reaction vessel was then heated to the desired reaction temperature under continuous stirring. A schematic diagram of the experimental setup is shown in Figure 1.

2.4. Analytical Methods

The samples obtained from the etherification of glycerol using the synthesized catalysts were collected at specific intervals during the reaction and were qualitatively analyzed using the GC analysis. Analysis was performed using the GCD 7890A System (Agilent Technologies, USA) with flame ionization detectors. The system was equipped with a capillary polyethylene glycol column (Agilent technologies) with the following dimensions: 30 m length, 0.32 mm i.d., and 0.25 μm film thickness. The temperature limit was from −60°C to 325°C. Nitrogen was used as the carrier gas. The injector temperature was set at 100°C, and the detector temperature was maintained at 250°C. The column temperature was kept constant at 100°C. The products were analyzed with GC after silylation.

3. Result and Discussion

3.1. Performance of Catalyst in Etherification Reaction

The chemical reaction rate is strongly affected by the reaction temperature. Therefore, the effect of reaction temperature on glycerol etherification was investigated as shown in Figure 2(a-c).

Figure 2(a) shows the effect of temperature on glycerol conversion while the reaction temperature varied between 200°C to 250°C in the presence of 2 wt. % of $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst. A significant increase in conversion from 28.1% to 96.3% occurred with increased reaction temperature from 220°C to 250°C. However, the conversion of glycerol at 260°C shows slightly higher values compared with that of at 250°C, but does not mean that the glycerol was converted to a desirable product (diglycerol). Thus, the yield of desirable products was considered. Figure 2(b,c) shows the yield of the products during the reaction at different temperatures. The high yield to diglycerol of more than 30% was observed at 250°C after 8 h of reaction, and decreased with increased temperature and reaction time. These results suggest that the reaction temperatures above 250°C may have accelerated the conversion of the remaining glycerol to enhance the subsequent etherification of diglycerol to higher glycerol oligomers, which resulted in decreased diglycerol selectivity. Furthermore, discoloration and polyglycerol odor generation can occur at such high temperatures. Meanwhile, the glycerol conversion decreased at reaction temperatures below 200°C. These observations are in good agreement with previously reported results [2,18,20].

Glycerol conversion generally increased with increased reaction time. Diglycerol yield reached about 17.8% after 4 h of reaction, and then increased gradually to 51% after 8 h, whereas reaction time was 250°C and 2 wt. % of catalyst was used in the reaction. When the reaction was prolonged, more glycerol molecules underwent dehydration or other forms of side reaction, which increased the glycerol conversion. The conversion of glycerol molecules may not exactly result in polyglycerol in the reactions; instead, the double dehydration of glycerol can convert it to other forms of undesired by-products, such as acrolein, which produces inauspicious products [19].
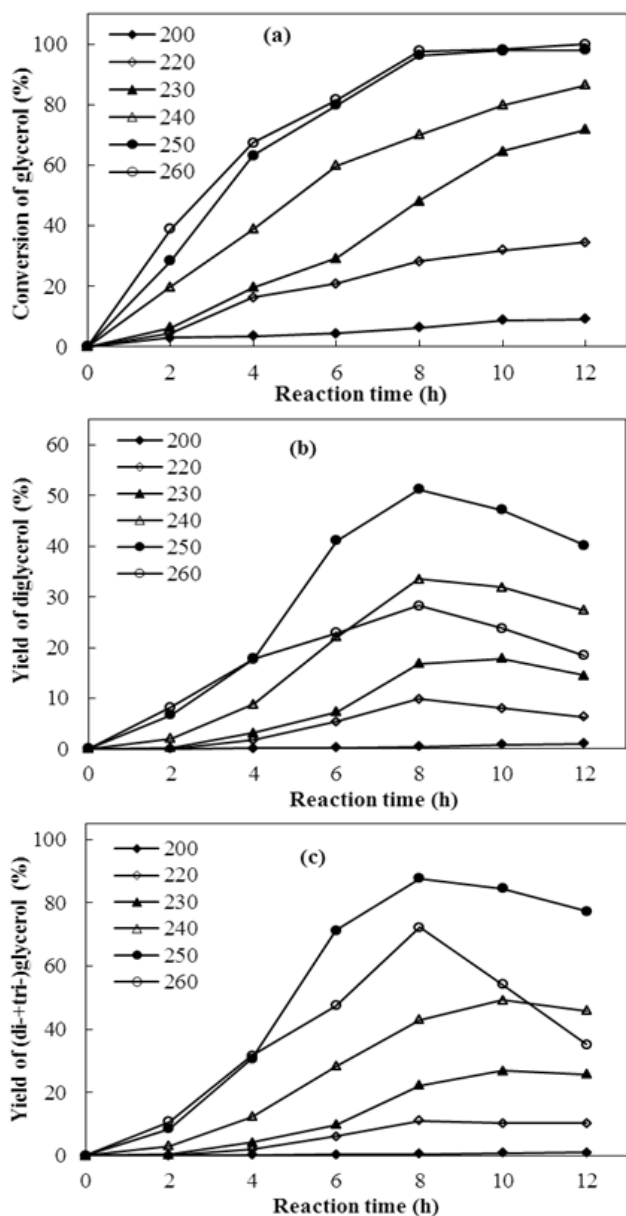

Figure 2. Product distribution (a) glycerol conversion (b) yield of diglycerol (c) yield of (di-+tri-) glycerol, catalyst loading, 2 wt. %

Furthermore, the results showed that no significant changes occurred in the conversion and when the reaction time was increased up to 10 h. By increasing the reaction time from 8 h to 12 h, glycerol conversion increased approximately by 0.4%, however 21.5% and 11.8% decrease were observed for diglycerol yield and (di- + tri-) glycerol, respectively. Thus, 8 h was considered as reaction time in this study.

3.2. Distribution of Diglycerol Isomer

The favorite product of the etherification reaction in this study was diglycerol, and the production of higher oligomers was ignored during this study. Diglycerol is represented by three peaks that indicate the primary–primary (αα'), primary–secondary (αβ), and secondary–secondary (ββ') dimers. Shape-selective reaction occurs and is influenced by the porosity of the catalyst used. Shape selectivity in the conversion of glycerol can be explained in two circumstances. First, the formation of undesired cyclic oligomers should be avoided, and second, the formation of polyglycerol should be restricted. Etherification of glycerol leading to dimers, trimmers, higher oligomers, and some cyclic compounds often result in different product distributions regardless of the reaction conditions and catalyst system used. Three probable dimers (αα', αβ, ββ') are available according to the position of the oxygen of the OH groups in the interacting glycerol molecule [26], following dimerization through either two terminal OH groups, one terminal and one middle OH group, or two middle OH groups, respectively.

The variations of diglycerol isomers (αα', αβ and ββ') versus reaction time at 250°C for heterogeneous $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst are shown in Figure 3. The αα' dimer is the favored diglycerol isomer after 10 h of reaction time. The αα' isomer with 71% was the preferred dimer after 2 h of reaction, but was decreased steadily to 63% after 10 h. Instead, the percentages of the ββ' and αβ dimers showed an increase by increasing the reaction time throughout the reaction, up to 10 h. However, after 10 h of reaction, the percentage of ββ' and αβ isomers was lower than that of αα' isomer. The ββ' dimer stayed almost constant at low level of 2% to 5%, and the αβ isomer increased from 25% to 32% with increased reaction time from 2 h to 10 h. Figure 3 also shows that the diglycerol isomer distributing behavior. The value of the αα' dimer over $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ was higher than that of the αβ isomer at 250°C for 10 h of reaction time. The reaction took place mainly on the external surface of the catalyst instead of internal pores, which may result to large molecular sizes of diglycerol or higher oligomer molecules. Therefore, the reaction of glycerol oligomerization occurs on the external surface area, whereas the internal surface was not fully employed.
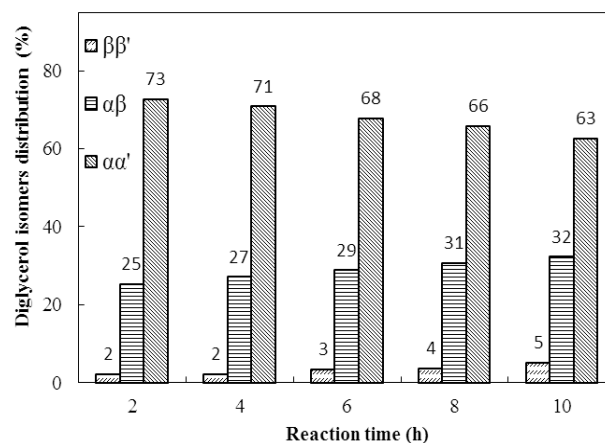

Figure 3. Distribution of linear αα', αβ and ββ' isomers of diglycerols as a function of reaction time at 250°C and 2 wt. % of $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst

The obtained results indicates that, in the etherification process over heterogeneous catalysts ($Ca_{1.6}La_{0.4}Al_{0.6}O_3$), the reaction between the primary −OH group of the first glycerol molecule at the first position of the second glycerol molecule, i.e., primary–primary dimer (αα'), is significant. The formation of αα' diglycerol isomer was enhanced during the catalytic etherification of glycerol over heterogeneous catalyst. The lower value of ββ' and αβ isomers than that of the αα' isomer may be due to the interaction that occurred between the activated glycerol molecule and proton provided by $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst. First, the linear form of diglycerol is created as the kinetic product, and then partially equilibrated into branched diglycerol, which is thermodynamically desired.

In addition, the formed linear diglycerol reacts faster than the branched isomers to produce higher oligomers of glycerol. The obtained results are in good agreement with the previous results reported by other researchers. Ruppert et al. (2008) studied the variations of diglycerol isomers with reaction time over calcium-based materials in the etherification reaction of glycerol [11]. They observed that linear diglycerol was created as the major product at the beginning of etherification reaction, whereas the branched form started to dominate at higher glycerol conversion. The observed result in the present study also showed that the synthesis of selective diglycerol steadily increased in the presence of active heterogeneous basic $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst with increased reaction time.

3.3. Optimization of Diglycerol Production Using Design if Experiment

An earlier study has revealed that the mixed-metal oxide $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst was active for the selective solventless etherification of glycerol to diglycerol. Thus, reaction parameters were optimized based on this catalyst. The reaction parameters were chosen by considering the operating limits of the experimental apparatus and the properties of the reactants. The lower and upper values of the diglycerol yield were 0% and 60%, respectively, as determined by experiments at different experimental conditions. The experimental design matrix table (Table 1) exposes corresponding levels for the reaction parameters, the interaction of the factors, and the responses. A series of 20 experimental runs obtained from the DOE software was conducted to illustrate the performance of the $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst in the etherification reaction. In this table, depending on the experimental condition, the diglycerol yield varied from 4% to 53%. Obtained results were better and comparable to the results obtained in previous studies using different catalysts [11,26].

3.3.1. Model Analysis

According to the experimental design with three independent variables (reaction temperature, reaction time, and amount of catalyst), the RSM design yielded a total of 20 runs as given in Table 1. The results were fitted to the response for various models (linear, 2FI, and quadratic and cubic polynomials). Obtained results show that the quadratic model was statistically significant to represent the results because it could simultaneously satisfy the three variables shown in Table 2. The quadratic model obtained for the result was utilized for the dependent

response (diglycerol yield) to determine the specific optimum reaction conditions.

The quadratic model was assumed based on the design program that was used to analyse the result. The central composite design of the software could also function as an optimal design for the desired response of the system based on the model obtained and the input criteria. The results of ANOVA as presented in Table 3 represent the parameters investigated for catalyst optimization and its activity during conversion of glycerol to diglycerol, and obtained results verified the adequacy of the model. Moreover, results from ANOVA were very important to the regression model as suggested by the high F-value.

From the results of Table 3, the Model F-value of 10.24 implies that the model is significant. The probability that a "Model F-Value" this large could occur because of noise is only 0.06%. The "Prob. >F" value indicates the probability of the proportion of the area under the curve of the F distribution that lies beyond the observed F-value. Values of "Prob > F" <0.0500 indicate that model terms significantly affected the diglycerol yield.

Table 1. Experimental design matrix and corresponding diglycerol yield

Run No.	Factor A: Reaction time (h)	Factor B: Reaction temperature (°C)	Factor C: Catalyst amount (wt. %)	Response 1: Diglycerol Yield (%)
1	6.00	210.00	2.00	1.8
2	2.00	220.00	3.00	5.3
3	2.00	260.00	3.00	15.1
4	8.00	250.00	2.00	52.3
5	10.00	220.00	1.00	12.1
6	6.00	240.00	2.00	29.6
7	6.00	280.00	2.00	3.1
8	2.00	260.00	1.00	11.2
9	8.00	260.00	2.00	38.7
10	10.00	260.00	3.00	34.8
11	14.00	240.00	2.00	29.1
12	2.00	220.00	1.00	1.9
13	6.00	240.00	4.00	28.2
14	10.00	260.00	1.00	26.7
15	6.00	240.00	0.00	1.7
16	8.00	240.00	2.00	37.1
17	10.00	220.00	3.00	20.4
18	2.00	250.00	2.00	10.7
19	6.00	250.00	2.00	47
20	10.00	250.00	2.00	46.8

Table 2. Sequential Model Sum of Squares

Source	Sum of Squares	df	Mean Square	F value	Prob > F	Remarks
Mean	10287	1	10287			
Linear	2238	3	746	3.98	0.0271	
2FI	103	3	34	0.15	0.9249	
Quadratic	2386	3	795	15.51	0.0004	Suggested
Cubic	482	8	60	4.01	0.2150	Aliased
Residual	30	2	15			
Total	15528	20	776			

In this case, A and C^2 are significant model terms. Values >0.1000 indicate that the model terms are not significant. The presence of numerous nonsignificant model terms (excluding those required to support hierarchy) indicates that model reduction may improve the model. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. According to the F-

values in Table 3, three factor parameters (A, B, and C) and respective quadratic terms (A^2, B^2, and C^2) had the largest effect on diglycerol yield during etherification.

Table 3. Analysis of variance of the response surface quadratic model

Source	Sum of Squares	df	Mean Square	F-value	Prob > F	Comments
Model	4728	9	525	10.24	0.0006	significant
A	1036	1	1036	20.22	0.0011	
B	608	1	608	11.87	0.0063	
C	367	1	367	7.17	0.0232	
A^2	567	1	567	11.07	0.0077	
B^2	1934	1	1934	37.72	0.0001	
C^2	753	1	753	14.69	0.0033	
AB	53	1	53	1.05	0.3300	
AC	10	1	10	0.20	0.6628	
BC	0.011	1	0.011	2.194E-004	0.9885	
Residual	512	10	51			
Cor Total	5241	19				

As shown in Table 4, the R-squared value of the model for the diglycerol yield was found to be 0.9022, which indicates that 90% of the total variations in the results could be attributed to the investigated independent variables. The R-squared value is a criterion for evaluating the suitability of the model, and values closer to unity shows that the predicted values are closer to the actual values. The significance of each term at a specified level of confidence was determined by examining its respective P- and F-values. Thus, the smaller value is the more significant coefficient [27]. Moreover, for the obtained model, the "Pred-R-squared" of 0.6802 is in reasonable agreement with the "Adj-R-squared" of 0.8292. Furthermore, "Adeq Precision" measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 5.815 for the obtained model indicates an adequate signal. This model can be used to navigate the design space [28].

Table 4. Statistics of the model to fit for diglycerol yield

R-Squared	0.9022
Adjusted (Adj) R-Squared	0.8141
Predicted (Pred) R-Squared	0.6470
Adeq Precision	8.930
Std. Dev.	7.16
Mean	22.68
Coefficient of Variance (C.V.)	31.57
Prediction Error Sum of Square (PRESS)	1849.88

The results from ANOVA indicate that the model actually represents the actual relationships of the parameters considered, which are well within the selected range. The final response model equation based on coded factor values for diglycerol yield (Y) was estimated and found to fit into the quadratic model equation expressed by equation 1.

$$Y = 38.72 + 9.48 \times A + 6.42 \times B + 4.79 \times C$$
$$-6.87 \times A^2 - 11.49 \times B^2 - 5.64 \times C^2 \qquad (1)$$
$$+2.50 \times A \times B + 1.14 \times A \times C + 0.0037 \times B \times C$$

where A is the reaction time, B is the reaction temperature and C is the amount of catalyst.

The second-order response function gives Y as the response for the diglycerol yield for the solventless etherification of glycerol over mixed-metal oxide $C_{a1.6}La_{0.4}Al_{0.6}O_3$ catalyst. The positive sign in front of the term indicates the synergetic effect to increase the diglycerol yield, whereas a negative sign indicates antagonistic effect [29]. Figure 4 shows the comparison between the actual response values that resulted from the experimental runs and the predicted response values based on the obtained quadratic model equation.

The predicted values reasonably matched the observed values with R-squared value of 0.9091 for the reaction conditions (i.e., reaction time, reaction temperature, and amount of catalyst) to employ in the solventless etherification of glycerol. These results imply the reliability of the quadratic equation model in representing the reaction condition to obtain the highest diglycerol yield in solventless etherification of glycerol. As a result, the above model equation indicated that the positive coefficients of A, B, and C were linear functions with diglycerol yield.
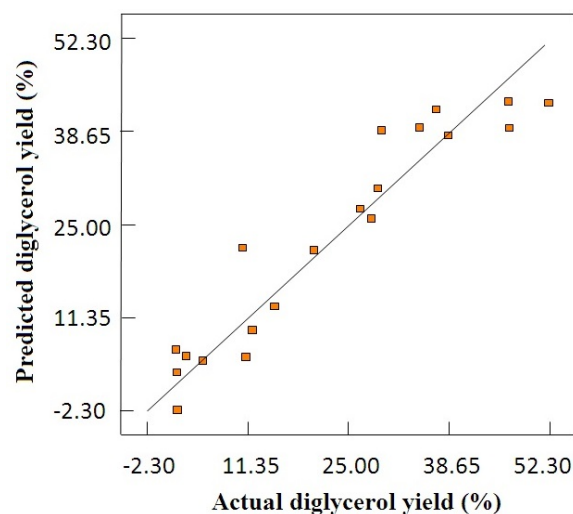

Figure 4. Relation between experimental and predicted diglycerol yield

3.3.2. Interaction between Factors during Activity Tests

In this study, the effect of individual based on response surface one factor plot, and the interaction between parameters is shown in the form of 3-D response surface. Figure 5(a-c) show the individual effects of A, B and C towards diglycerol yield for the solventless etherification of glycerol. The positive effect of these parameters on diglycerol yield was observed, as shown in equation 1. Higher F value of the parameters indicates its significant effect. As shown in Table 3, the parameters that positively influence the etherification reaction are reaction time (A), reaction temperature (B), and amount of catalyst (C), respectively.

These results indicate that in this reaction, increasing the reaction temperature, reaction time and catalyst amount would increase diglycerol yield. Generally, slow mass transfer is one drawback of the heterogeneous catalysts which is due to the little contact between the liquid mixture of reactant and the catalyst, resulting in lower diglycerol yield at shorter reaction time (Figure 5(a)). Consequently, the etherification of glycerol in the absence of solvent needs a longer time till the reactants diffuse into the pores of catalyst. Diglycerol yield decreased at longer reaction time (above 8 h), which might have been caused by the formation of higher oligomers, such as tri- and tetra- glycerol, reducing the selectivity of desired product.

Moreover, Figure 5(b) shows that diglycerol yield increased gradually when the temperature increased up to 250°C. Further increase in temperature led to decreased yield. Diglycerol yield increased with increasing amount of catalyst up to 2 wt.%. Amounts exceeding 2 wt.% did not significantly increase yield, but even slightly decreased diglycerol yield. Thus, increasing the amount of catalyst increased the available active sites on the catalyst, which leads to an increase in diglycerol yield.
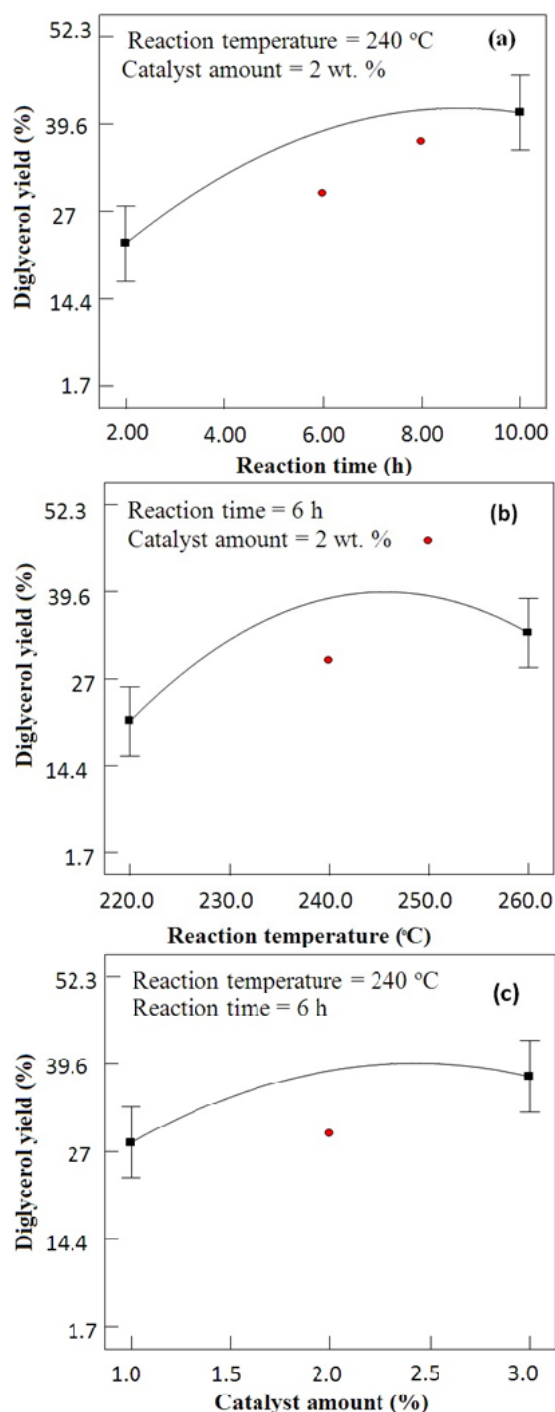

Figure 5. Individual effects of reaction parameters toward diglycerol in solventless etherification of glycerol: (a) reaction time, (b) reaction temperature, (c) amount of catalyst

The obtained results from individual effect of reaction parameters reveal that the highest diglycerol yield might be achieved at maximum values of reaction parameters. The interaction effects between these reaction parameters

should be considered because of their impacts on diglycerol yield. As shown in Table 3 ANOVA results of the response surface revealed that the interaction between reaction parameters slightly influenced the diglycerol yield.

The 3-D response surface plots of diglycerol yield with reaction condition parameters (i.e., reaction temperature, reaction time, and catalyst weight) were generated as shown in Figure 6 and Figure 7.
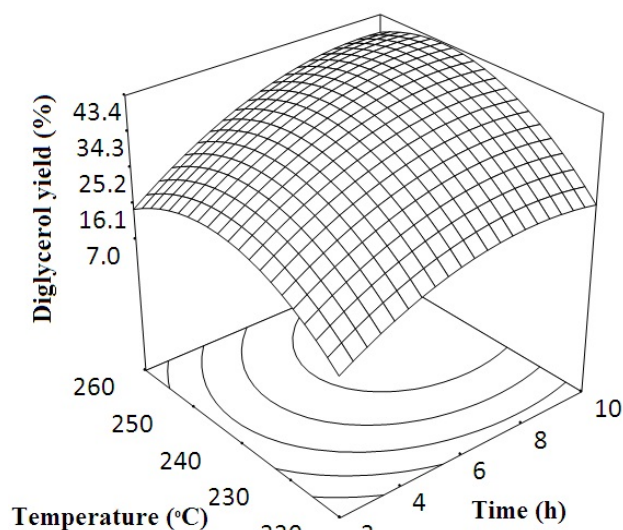

Figure 6. Three dimensional plots for the effect of reaction temperature and time on the yield of diglycerol

Etherification reaction at a low temperature of 220°C exhibited very low conversion and approximately 12% yield of glycerol after 10 h reaction. Increasing the reaction temperature up to 250°C resulted in higher diglycerol yield (52%), but further increase over 250°C reduced the diglycerol yield. This trend was altered by varying the reaction time from 2 h to 10 h. Increasing the reaction time from 2 h to 8 h, increased the yield, which was similar to the trend observed for the reaction temperature. However, the yield was reduced by increasing the reaction time above 8 h. As shown in the Figure 6, the optimum temperature was 250°C. The high reaction temperature caused by the formation of higher oligomers decreased diglycerol selectivity towards, consequently reducing diglycerol yield. Meanwhile, diglycerol yield increased with increasing reaction time. This result is consistent with the theory of the production of polyglycerols by the formation of active radicals of glycerol from the neutral glycerol molecule during etherification. From equation 1, the reaction time (A) with the highest coefficient (10.45) was the major parameter that affected the reaction, and this parameter had significant interaction with reaction time. The regression coefficient of the amount of catalyst is 4.60 for individual effect.

Figure 7 shows that the diglycerol yield increased when the temperature increased to 250°C. The same trend was observed for the amount of catalyst, which showed a positive influence on the diglycerol yield when this parameter was increased to 2% diglycerol. At higher catalyst loading, diglycerol yield decreased when the reaction time increased to 250°C. This phenomenon is correctly reflected by the positive value of regression

coefficient for AB (+2.50) in equation 1. The comparative studies in Figure 5, Figure 6 and Figure 7 reveal that the diglycerol yield increased when the reaction temperature and amount of catalyst were increased at 8 h reaction time. Shorter reaction times resulted in low diglycerol yield, and longer reaction time was required to complete glycerol conversion in the etherification reaction. However, a longer reaction time because of the conversion of the produced molecules of diglycerol to higher oligomers resulted in reduced diglycerol yield.
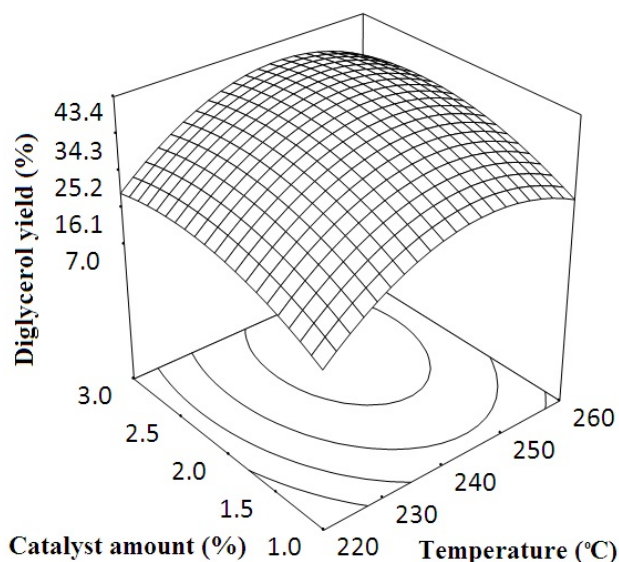

Figure 7. Three dimensional plots for the effect of reaction temperature and amount of catalyst on the yield of diglycerol

In a previous study on the etherification of glycerol using solid basic catalyst [13], the maximum diglycerol selectivity (94%) was achieved at 260°C at 8 h reaction time with 2 wt.% of catalyst. However, the diglycerol yield was still low (15%) because of the low glycerol conversion (16%) at this reaction. In the present study, glycerol conversion of 98% with 53% diglycerol selectivity was achieved at 2 wt.% of mixed-metal oxide ($Ca_{1.6}La_{0.4}Al_{0.6}O_3$) catalyst at 250°C and 8 h reaction time. The pore size of the catalyst plays an important role in the catalytic activity, whereas larger pore size of the mixed oxide catalyst leads to higher diglycerol selectivity by facilitating the diffusion of glycerol molecules into its mesopores for the reaction to occur.

3.3.3. Optimization of Reaction Parameters

Various reaction parameters (i.e., reaction temperature, reaction time, and amount of catalyst) in the etherification reaction of glycerol and their influences in the reaction were analyzed in the previous sections, and the interaction between different parameters was also considered. Using the Design Expert Stat Ease 6.0.6, numerical optimization method was employed to determine the optimum reaction conditions for diglycerol production. The statistical optimal values of variables were obtained where the CCRD and the response at the different points yielded maximum diglycerol yield. This phenomenon shows that the goals were set at which the glycerol conversion and diglycerol selectivity are expected to provide the maximum values. Other factors are in their desired range as presented in Table 5.

Table 5. Constrictions used in the etherification reaction of glycerol to diglycerol

Name	Goal	Lower Limit	Upper Limit
A: Reaction time (h)	is in range	2	10
B: Reaction temperature (°C)	is target = 250	-	-
C: Catalyst amount (wt. %)	is in range	1	3
Diglycerol yield (%)	maximize	0	60

Solutions were generated by the software for the optimum condition according to suitability, and the obtained optimized values are presented in Table 6. In this particular case, the software predicted that optimized conditions for the diglycerol yield were obtained when the reaction temperature, reaction time, and amount of catalyst were 8.29 h, 250°C, and 2.51 wt.%, respectively. The diglycerol yield at obtained optimum conditions was 44.7%, whereas diglycerol yield obtained from repeating the experiments at the obtained optimized conditions was 47.8%. Obtained results reveal that the experimental values with the mean error of 6.5% were reasonably close to the calculated values obtained from DOE. This result indicates that the generated model showed a good agreement with the experimental finding for the diglycerol yield in the etherification reaction.

Table 6. Optimized conditions for etherification reaction conditions obtained from DOE

Parameters	Value
Reaction time (h)	8.29
Reaction temperature (°C)	250
Catalyst amount (wt. %)	2.51
Predicted Diglycerol yield (%)	44.7
Experimental Diglycerol yield (%)	47.8
Error (%) Diglycerol yield	6.5

4. Conclusion

The etherification of glycerol catalyzed by heterogeneous mixed oxide catalyst ($Ca_{1.6}La_{0.4}Al_{0.6}O_3$) was studied in a batch reactor and effects of different parameters on the reaction and distribution of the products during the etherification reaction were also studied. The $Ca_{1.6}La_{0.4}Al_{0.6}O_3$ catalyst showed the high selectivity to (di- + tri-) glycerol at 96.3% conversion, at 250°C, 8h of reaction time and 2 wt.% of catalyst loading. The variations of diglycerol isomers (αα', αβ, and ββ') versus reaction time were studied for these catalyst and αα' dimer with 66% after 8 h of reaction was the favored diglycerol isomer compare to αβ, and ββ' isomers with 31% and 4%,respectively. Higher value of αα' during the reaction indicated that the reaction mainly occurred on the external surface of the catalyst. Glycerol was believed to be adsorbed on the active sites of the catalyst, and the surface reactions were deemed as the rate-determining step. The statistical optimal values of variables (i.e. reaction time, reaction temperature and catalyst loading) were obtained where the CCRD and the response at the different points yielded maximum diglycerol yield and a quadratic polynomial equation was developed. The comparison

between the actual response values resulted from the experimental runs and the predicted response values based on the obtained quadratic model equation was studied and results indicate the reliability of the developed quadratic model in representing the reaction condition to obtain the highest diglycerol yield in solventless etherification of glycerol.

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