

Kinetics Modeling of Glycerol Carbonate Synthesis from Glycerol and Urea over Amberlyst-15 Catalyst

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Abstract: Synthesize of glycerol carbonate from glycerol and urea is an attractive path as glycerol carbonate has a large potential as a green solvent. The aim of the present study was to develop a kinetic model of glycerol carbonate synthesis with amberlyst-15 resins as a catalyst. The investigation was carried out at various temperatures from 353 to 383 K and catalyst loading from 0.25 to 1 wt.% of glycerol. The experimental results indicated that both temperature and catalyst loading have an important effect on the glycerol conversion. According to the experimental result, the highest glycerol conversion was found 36.90% which was obtained using a molar ratio of urea to glycerol 1:3, catalyst loading of 1 wt.%, stirrer speed of 700 rpm, the temperature of 383 K and reaction time of 5 h. A kinetic model was developed based on elementary steps that take place over the catalyst. The model estimated that the pre-exponential factor was $2.89 \cdot 10^4 \text{ mol.g}^{-1} \cdot \text{min}^{-1}$ and the activation energy was 50.5 kJ.mol^{-1} . By comparing the simulation and experimental data, it could be inferred that the model could predict the trend of experimental data well over the range of temperature and catalyst loading investigated in the present study.

Keywords: amberlyst-15; glycerolysis; glycerol carbonate; kinetic modeling

■ INTRODUCTION

The government of Indonesia committed to increasing the portion of biodiesel in the present energy mix of transportation fuel. According to *Peraturan Presiden* No. 22 2017 and No. 66 2018, the amount of biodiesel should increase from 2.5 million kiloliters (KL) of B20 in 2016 to 6.9 million KL of B30 in 2025 [1-2]. Biodiesel is considered as an attractive alternative to diesel fuels especially for Indonesia as the largest palm oil producer in the world. Biodiesel is renewable, biodegradable, non-toxic and has similar properties with diesel fuels. It is predicted that biodiesel production will increase significantly in Indonesia. Glycerol is the byproduct of the biodiesel industry. Every 10 kg of biodiesel produced, 1 kg of glycerol will also be produced by the biodiesel plant as a side product. Without proper treatment, glycerol may cause an environmental problem. As a result, glycerol utilization is important to minimize the environmental problem that may be caused by glycerol [3-4].

One of the promising utilization of low-value glycerol is to convert it to glycerol carbonate. Glycerol carbonate is known as a green solvent. It has specific properties such as biodegradability, low toxicity, non-flammable and high boiling point [3-4]. Glycerol carbonate has various applications in several areas such as paints, coating, detergents, membranes, polyurethane foams, and solvents [3-4].

Glycerol carbonate could be synthesized via two different routes using heterogeneous catalysts: transesterification of glycerol with ethylene carbonate and carbonylation of glycerol with urea. Glycerolysis of urea to form glycerol carbonate is an attractive path as urea is widely available in the market. For this purpose, a number of the catalyst has been reported to promote glycerol conversion to glycerol carbonate [5-12]. Glycerolysis of urea using MgO as a catalyst is very attractive with minimal unit operation [5]. It was mentioned that conversion up to 71% in 6 h with 100% selectivity at 150 °C could be achieved with MgO catalyst [5]. In

addition, MgO, CaO, and mixed oxide as a catalyst have been reported to facilitate glycerolysis of urea at a lower temperature and lower catalyst loading [5,11]. As a result, high glycerol conversion as well as 98% selectivity to glycerol carbonate could be obtained. It has also been reported that Zn based catalyst showed promising activity [7,9-11]. Addition of lanthanum was reported to promote glycerol conversion [11]. Over zinc-based catalyst, ZnCl₂ showed the highest catalytic activity [10]. By using Zn-Al mixed oxide catalyst, it was found that a higher selectivity and yield of glycerol carbonate was obtained than that of ZnO catalyst [9]. This could be due to the formation of zinc glycerolate in the solid phase. In addition, the addition of Zr on Mg-Al-Zr mixed oxide catalyst showed a great effect on the structure and acid-base properties and found to be effective to enhance glycerol carbonate synthesis [12].

It is generally accepted that catalyst performance is highly affected by the catalyst preparation condition and catalyst support [7,9,11]. Surface area and porosity of the catalyst prepared by the precipitation method were higher than those prepared by combustion methods [11]. The influence of catalyst support also appears to be an important aspect. Kim et al. [7] prepared three different catalysts supported on polystyrene, silica, and chitosan. It was found that the rate constant for polystyrene was higher than chitosan and silica. In addition, consecutive conversion of glycerol to glycerol carbonate and glycidol has been reported by Endah et al. [13] over numerous zinc salts such as Zn(OAc)₂, ZnCl₂, ZnSO₄ and Zn(NO₃)₂. It was found that glycerol carbonate yield over 70% was obtained for all catalysts.

The temperature and pressure have been reported to influence glycerol conversion. Aresta et al. [3] found that the best operating temperature for glycerolysis of urea into glycerol carbonate using zirconium phosphate as the catalyst was 418 K with 3 h of reaction and catalyst loading of 0.6 to 1.5%. The glycerol conversion as high as 80% could be obtained. High temperature and low pressure are favorable to the reaction of glycerol and urea. The use of the microwave for glycerol carbonate synthesis has also

been reported in [14] by comparing the reaction under microwaves and by conventional heating. Microwave heating slightly increased conversion and greatly increased selectivity to glycerol carbonate. Lertlukkanasuk et al. [15] developed a new process for glycerolysis of urea by reactive distillation. Based on their simulation results using ASPEN Plus, it was found that glycerol conversion as high as 93.6% could be obtained with glycerol carbonate 100% purity in the final product.

Reaction mechanism of glycerol carbonate synthesis from glycerol and urea over gold catalyst has been reported by Hammond et al. [6]. They suggested that the formation of glycerol carbonate via formation of 2,3-dihydroxypropyl carbamate. An effort to study the kinetics of glycerol carbonate has been reported by Esteban et al. [16] who investigated the conversion of glycerol and dimethyl carbonate (DMC) as well as ethylene carbonate (EC) to glycerol carbonate over potassium methoxide catalyst. Here, a global kinetics model has been proposed which described the experimental data well with predicted *E_a* of 28.4 and 83 kJ/mol for DMC and EC, respectively. Unfortunately, the kinetic model which described the conversion of glycerol and urea to glycerol carbonate over an amberlyst catalyst, to our knowledge, has not been reported in the literature. In order to obtain a useful model especially for scale-up processes, the proposed kinetic model should not be too complicated, but it should accommodate possible routes to form glycerol carbonate.

The aim of the present study was to investigate the kinetics of glycerol carbonate formation from glycerol and urea over amberlyst-15 catalysts. The influence of temperature and catalyst loading were investigated [17]. In addition, we also aimed to develop a kinetic model based on elementary steps that possibly occurs in the catalyst. The model was then fitted to the experimental data with non-linear regression. It is expected that the model may elucidate the reaction mechanism and later on could be used to improve the catalyst design for glycerol carbonate synthesis.

■ EXPERIMENTAL SECTION

Materials

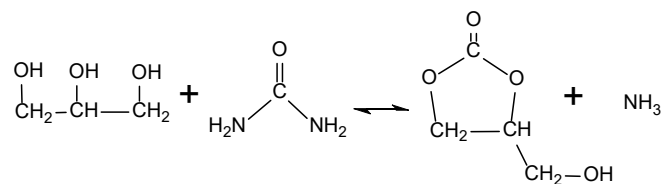
Glycerol technical grade (75.6%) was received from CV. General Labora. Urea commercial grade (98.57%) was received from PT Pupuk Sriwidjaja as fertilizer industry. Amberlyst-15 as a catalyst was purchased from Sigma Aldrich. Amberlyst-15 has a cation exchange capacity of 4.7 mmeq/mL, the surface area of 53 m²/g.

Procedure

The experiments were performed in a three necks flask batch reactor which is equipped with a heater, stirrer, and condenser system. Initially, 92 g of glycerol and 60 g of urea were added to the reactor with a low stirrer speed of 400 rpm to reach a homogenous mixture. The initial concentration of glycerol and urea used for the simulation were 6.1 and 8.1 M, respectively. This resulted in the ratio of urea to glycerol of 1.3. Subsequently, the temperature was raised to the targeted temperatures (353, 363, 373 or 383 K). At a certain time (denoted as $t = 0$), a certain amount of amberlyst-15 was added to the reactor which was followed by increasing the stirrer speed to 700 rpm. Sampling was then conducted at every 60 min for 300 min of the experiment. A similar procedure was repeated for various temperature and catalyst loading. The amount of glycerol was then analyzed using periodic acid based on the iodometric titration method according to AOCS Official Method Ca 14-56. Glycerol conversion was calculated by comparing the amount of free glycerol reacted to the initial amount of free glycerol content in the sample.

Modeling

The reaction rate mechanism for the synthesis of glycerol carbonate from glycerol and urea in the presence of amberlyst-15 as a catalyst has been studied as a heterogeneous catalytic reaction. Equation 1 shows the reversible reaction showing the reaction between glycerol and urea to form glycerol carbonate and ammonia. The selectivity of glycerol carbonate was assumed to be 100%. The elementary steps based on the Langmuir-Hinshelwood (LH) mechanism was proposed. The reaction steps of the LH model can be expressed as follows:



Adsorption of glycerol and urea into the catalyst surface active.



The reaction between the adsorbed glycerol and adsorbed urea on the active side of the catalyst surface.



Desorption of the adsorbed glycerol carbonate and adsorbed ammonia from the active catalyst surface.



Development of kinetic model from elementary steps

A heterogeneous catalyst model based on the Langmuir-Hinshelwood model was proposed with the surface reaction as the rate-limiting step. From site balance, we obtain:

$$C_{\text{tot}} = C_{As} + C_{Bs} + C_{Cs} + C_{DDs} + C_s \quad (7)$$

$$C_{\text{tot}} = K_A \cdot C_A \cdot C_s + K_B \cdot C_B \cdot C_s + K_C \cdot C_C \cdot C_s + K_D \cdot C_D^2 \cdot C_s + C_s \quad (8)$$

$$C_s = \frac{C_{\text{tot}}}{1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2} \quad (9)$$

Adsorption and desorption of A:



$$C_{As} = K_A \cdot C_A \cdot C_s \quad (11)$$

$$C_{As} = \frac{K_A \cdot C_A \cdot C_{\text{tot}}}{1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2} = \frac{K_{AI} \cdot C_A}{1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2} \quad (12)$$

Adsorption and desorption of B:



$$C_{Bs} = K_B \cdot C_B \cdot C_s \quad (14)$$

$$C_{Bs} = \frac{K_B \cdot C_B \cdot C_{\text{tot}}}{1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2} = \frac{K_{BI} \cdot C_B}{1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2} \quad (15)$$

Adsorption and desorption of C:



$$C_{Cs} = K_C \cdot C_C \cdot C_s \quad (17)$$

$$C_{Cs} = \frac{K_C \cdot C_C \cdot C_{tot}}{1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2} \quad (18)$$

$$= \frac{K_{Cl} \cdot C_C}{1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2}$$

Adsorption and desorption of D:



$$C_{DDs} = K_D \cdot C_D^2 \cdot C_s \quad (20)$$

$$C_{DDs} = \frac{K_D \cdot C_D^2 \cdot C_{tot}}{1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2} \quad (21)$$

$$= \frac{K_{Dl} \cdot C_D^2}{1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2}$$

Rate determining step was the surface reaction:



$$-r_A = k_1 \cdot C_{As} \cdot C_{Bs} - k_2 \cdot C_{Cs} \cdot C_{DDs} \quad (23)$$

$$-r_A = \frac{k \cdot (C_A \cdot C_B - \frac{C_C \cdot C_D^2}{K_{eq}})}{(1 + K_A \cdot C_A + K_B \cdot C_B + K_C \cdot C_C + K_D \cdot C_D^2)^2} \quad (24)$$

Assuming that K_C and K_D are ≈ 0 (desorption rate is much larger than adsorption rate), then we may obtain:

$$-r_A = \frac{k \cdot (C_A \cdot C_B - \frac{C_C \cdot C_D^2}{K_{eq}})}{(1 + K_A \cdot C_A + K_B \cdot C_B)^2} \quad (25)$$

$K_{eq} = 1.417$ which is extracted from reference [18]

$$-r_A = \frac{k \cdot (C_A \cdot C_B - \frac{C_C \cdot C_D^2}{1.417})}{(1 + K_A \cdot C_A + K_B \cdot C_B)^2} \quad \frac{\text{mol}}{\text{g} \cdot \text{min}} \quad (26)$$

Reactor model and stoichiometry

For simulation, the following batch reactor model for the heterogeneous catalytic reaction was proposed:

$$\frac{dX}{dt} = \frac{-r_A \cdot W}{C_{A0} \cdot V} \quad (27)$$

From stoichiometry, it can be derived:

$$C_A = C_{A0} \cdot (1 - X) \quad (28a)$$

$$C_B = C_{B0} - C_{A0} \cdot X \quad (28b)$$

$$C_C = C_{A0} \cdot X \quad (28c)$$

$$C_D = 2 \cdot C_{A0} \cdot X \quad (28d)$$

The reaction rate as in Eq. (26) and (27) are then incorporated with the batch reactor data. There are 3 kinetic

Table 1. The fitted parameters during non-linear regression and their relationship to the proposed kinetic model as presented in Eq. 26

Notations	Parameters	Unit
P1	ln kref	kref in $L^2 \cdot g^{-1} \cdot mol^{-1} \cdot min^{-1}$
P2	ln KA0	KA0 in $L \cdot mol^{-1}$
P3	ln KB0	KB0 in $L \cdot mol^{-1}$
P4	E_a	$kJ \cdot mol^{-1}$
P5	ΔH_{r1}	$kJ \cdot mol^{-1}$
P6	ΔH_{r2}	$kJ \cdot mol^{-1}$

Note:

$$k = \exp(\ln kref - \frac{E_a}{R} (\frac{1}{T_{ref}} - \frac{1}{T})) \rightarrow k = \exp(P1 - \frac{P4}{R} (\frac{1}{T_{ref}} - \frac{1}{T}))$$

$$K_A = \exp(\ln KA0 - \frac{\Delta H_{r1}}{R} (\frac{1}{T_{ref}} - \frac{1}{T})) \rightarrow K_A = \exp(P2 - \frac{P5}{R} (\frac{1}{T_{ref}} - \frac{1}{T}))$$

$$K_B = \exp(\ln KB0 - \frac{\Delta H_{r2}}{R} (\frac{1}{T_{ref}} - \frac{1}{T})) \rightarrow K_B = \exp(P3 - \frac{P6}{R} (\frac{1}{T_{ref}} - \frac{1}{T}))$$

parameters namely k , K_A and K_B which followed Arrhenius type of equations. As a result, there are 6 parameters to fit as shown in Table 1. All parameters were estimated to the experimental data from temperature and catalyst loading variation. Gradient search methods, as well as ODE solver in MATLAB, have been used for parameter fitting and simulation, respectively. A kinetic model that was proposed here was developed based on a realistic kinetic mechanism to elucidate the reaction mechanism of glycerol and urea to form glycerol carbonate over amberlyst-15 catalysts. As shown in Table 1, there are 6 parameters to fit from the experimental data based on the kinetic model as proposed in Eq. (26).

The objective of parameter estimation was to minimize the residuals of conversion from simulation and experimental data (X simulation-X data). The *lsqnonlin* function in Matlab was used during parameter estimation. The *lsqnonlin* algorithm is a gradient search optimization method based on Lavenberg-Marquardt algorithm. The 95% confidence interval of fitted parameters were estimated using *nlparci* function.

RESULTS AND DISCUSSION

In this study, the synthesis of glycerol carbonate was conducted by the reaction of glycerol and urea catalyzed by amberlyst -15. It was investigated by various

experimental conditions such as reaction temperatures and catalyst loading. The reaction was conducted at temperature of 353 K to 383 K, catalyst loading up to 1 wt.% of glycerol and a constant stirrer speed of 700 rpm, 5 h of reaction time and the constant ratio of urea to glycerol as 1.3.

The Influence of Reaction Temperature (353-383 K)

The influence of reaction temperature on glycerolysis with urea was investigated at 353, 363, 373 and 383 K. Fig. 1 shows that the glycerol conversion increased with increasing temperature from 353 to 383 K. As seen here, the highest conversion was obtained at the highest temperature of 383 K. As the temperature increased, the glycerol conversion increased to reach a maximum conversion of 36% at 383 K.

The performance of amberlyst-15 could also be compared with other catalysts such as purolite C100. It was found that purolite C100 maximum conversion of ca. 38% at 373 K with a catalyst loading of 12 wt.% [19]. By increasing the temperature to 383 K, the conversion of purolite decreased as the catalyst degraded and hence gave lower conversion than that of amberlyst-15 [19]. In addition, conversion of glycerol with amberlyst-15 was higher than Mg-Al-Zr catalyst which showed the negligible conversion of glycerol below 393 K [12]. However, Mg-Al-Zr showed a dramatic increase of glycerol conversion up to 96% as the temperature reached 413 K. The glycerol carbonate selectivity and yields also increased to 90.8 and 87.8% respectively. Further, by comparing amberlyst-15 with $ZnBr_2$ containing ionic liquid to catalyze the same reaction, it was found that glycerol conversion could reach 52 to 65% within the temperature range of 393–413 K with a catalyst loading of 0.5% [10]. Kondawar et al. [20] investigated the influence of temperature within a range of 393–433 K over Zn catalyst. It was found that glycerol conversion increased from 56 to 95%. However, a slight decrease in glycerol carbonate selectivity was observed along with the increase of temperature to 433 K. The maximum selectivity of 98% was achieved at 413 K. Urea glycerolysis using biosolid-based catalyst has been reported by Bartoli et al. [21] and they showed that the influence of temperature is the key

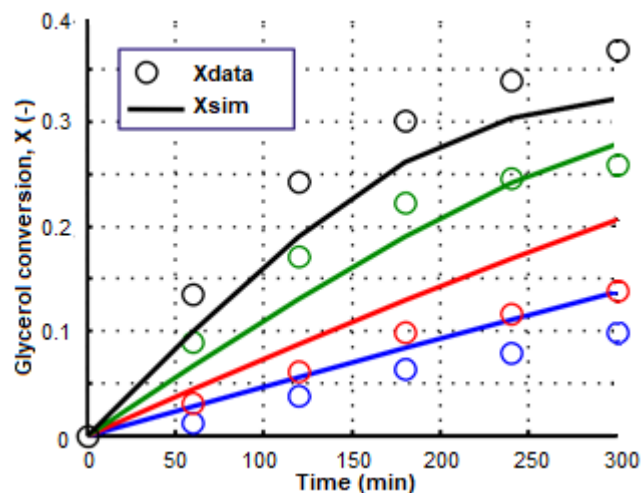


Fig 1. The effect of reaction temperature on glycerol conversion based on modeling and experimental results with 1 wt.% catalyst. Color notation: Blue (353 K), Red (363 K), Green (373 K) and Black (383 K)

parameter for glycerol conversion. The glycerol conversion reached as high as 44% at 373 K after 6 h. However, by increasing temperature to 433 K, glycerol conversion as high as 44% was obtained only after 1 h. Hence, it could be seen that increasing temperature may accelerate the glycerol conversion.

All by all, it could be inferred that amberlyst-15 is a promising catalyst for glycerol carbonate synthesis which has comparable performance to biosolid-based catalyst yet it is still lower than that of Zn and other metal oxide catalysts. Hence, it could be envisaged that further improvement might be improved by using the ionic liquid in order to improve the mass transfer between the bulk solutions with the catalyst as suggested by Kim et al. [7].

The Influence of Catalyst Weight (0.25–1 wt.%)

The influence of catalyst loading was investigated by varying the amount of amberlyst-15 between 0.25 to 1 wt.% with respect to glycerol. Fig. 2 expressed the influence of catalyst loading on glycerol conversion. As seen here, increasing the catalyst amount also caused an increase of glycerol conversion from 11.75 to 36.90% after 5 h reaction time. Here, one may observe that the magnitude of the increase due to the addition of a catalyst is nearly similar to the influence of temperature.

Hence, one may infer that the catalyst loading and temperature inhibited similar effect to the glycerol conversion over the range studied in the present work.

Our present results could also be compared to our previous work which showed that by increasing the catalyst loading from 4 to 12% of purolite C100 gave an increase of glycerol conversion from 28.94 to 38.63% after 5 h reaction time [19]. As a result, again, it could be concluded that amberlyst-15 was more active than purolite C100 as amberlyst-15 required a lower amount of catalyst than that of purolite C100 to reach the maximum conversion of ca. 36%. In addition, the glycerolysis of urea using mixed oxide of Mg-Al-Zr showed that the glycerol conversion was enhanced with the increase of catalyst loading. However, the glycerol carbonate selectivity and yield reach their peak at 0.2 g which was followed by the decrease of glycerol conversion with a further increase of catalyst loading [12]. The glycerol carbonate synthesis using MgO catalyst at the range of 0.015 to 0.045 found that the glycerol conversion could reach up to 71% with a selectivity of 100% at a temperature of 423 K [5]. In addition, urea glycerolysis using biosolids-based catalyst gave glycerol conversion of 70.8 % at 413 K after 6 h of reaction using 12 wt.% of catalyst loading [21].

The Result of Kinetic Modeling and Parameter Estimation

The modeling results were also presented in Fig. 1 and 2. From parameter estimation, the resulting parameters are presented in Table 2. The minimization process gave the final Sum Square of Residuals (SSE) of 0.0452.

As depicted in Fig. 1 and 2, in general, it can be observed that the model could predict the trend of experimental data well over the temperature range of 353–383 K and catalyst loading of 0.25–1 wt.%. However, the model gave a larger deviation at the lower temperature of 353 K which probably due to slightly higher activation energy that has been obtained in the present study. Similarly, comparing the model and experimental data for various catalyst loading (Fig. 2), the largest deviation was observed again at the lowest catalyst loading. The resulting parameters as presented in Table 2 could be used

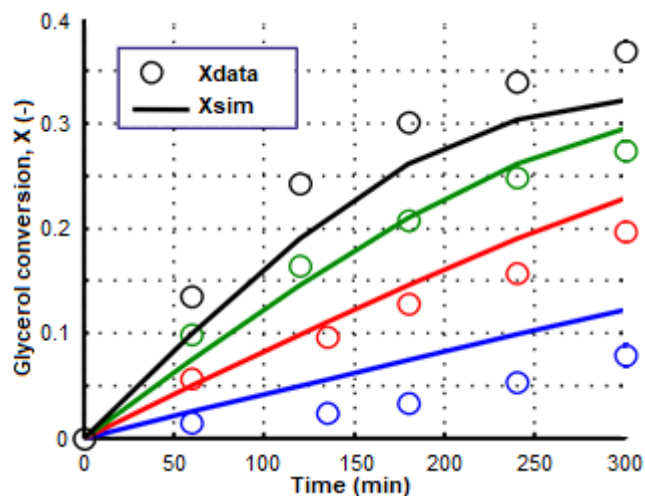


Fig 2. The effect of catalyst loading on glycerol conversion based on modeling and experimental results at 383 K. Color notation: Blue 0.25 wt.%, Red 0.5 wt.%, Green 0.75 wt.% and Black 1 wt.%

Table 2. The result of parameter estimation and their 95% confidence interval

Parameter	Value	Parameter	Value
P1	-10.10 ± 0.0035	P4	50.50 ± 0.0307
P2	0.10 ± 0.0005	P5	1.40 ± 0.0003
P3	0.09 ± 0.0003	P6	2.20 ± 0.0006

to estimate the pre-exponential factor by using parameter P1 and P4 to give a pre-exponential factor of $2.89 \times 10^4 \text{ mol.g}^{-1}.\text{min}^{-1}$. The activation energy (E_a) obtained from present work was 50.5 kJ.mol^{-1} . This value could be compared to Zn/MCM-41 catalyst which gave activation energy of $39.82 \text{ kJ.mol}^{-1}$ [20]. The value of E_a here was also lower than that of polystyrene, chitosan and commercial silica which gave 142.9, 163 and $166.7 \text{ kJ.mol}^{-1}$, respectively [7]. Again, by comparing the performance of amberlyst-15 with other inexpensive catalysts as presented in [7], it shows that amberlyst-15 is quite promising as it has lower E_a to facilitate glycerol carbonate formation.

CONCLUSION

The influence of temperature and catalyst loading of glycerol and urea reaction to form glycerol carbonate over amberlyst-15 catalyst has been investigated. The experimental results indicated that both temperature

and catalyst loading is important in order to improve the glycerol conversion within 353–383 K and 0.25–1 wt.% of catalyst loading. Based on our experimental result, the highest glycerol conversion was found 36.90% which was obtained by using a molar ratio of urea to glycerol 1.3, catalyst loading of 1 wt.%, stirrer speed of 700 rpm, a temperature of 383 K and reaction time of 5 h. A kinetic model was developed based on elementary steps that take place over the catalyst. The resulting kinetic model based on 6 parameters proposed here was:

$$-r_A = \frac{k \cdot (C_A \cdot C_B - \frac{C_C \cdot C_D^2}{1.417})}{(1 + K_A \cdot C_A + K_B \cdot C_B)^2}$$

Parameter k , K_A , and K_B followed the Arrhenius type equation which resulted in a total of 6 fitted parameters. Parameter fitting was conducted by implementing non-linear regression to minimize the SSE of glycerol conversion and followed by the significance test. The model estimated that the pre-exponential factor was $2.89 \times 10^4 \text{ mol.g}^{-1}.\text{min}^{-1}$ and the activation energy was 50.5 kJ.mol^{-1} . By comparing the simulation and experimental data, it could be inferred that the model could predict the trend of experimental data well over the range of temperature and catalyst loading investigated in the present study.

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