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Synthesis of Glycerol Carbonate and Kinetic Modeling Using $ZnBr_2$ Catalyst

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ABSTRACT

The rapid expansion of biodiesel production in Indonesia has resulted in a surplus of glycerol as the main by-product, which has significantly decreased its market value. To increase its economic potential, glycerol can be converted into one of its value-added derivatives such as glycerol carbonate. The purpose of this study was to obtain the best conditions for the reaction and to model the reaction kinetics. The reaction was carried out using the urea carbonylation method with glycerol to produce glycerol carbonate and ammonia. The resulting samples were analyzed using iodometric titration analysis. This study focuses on the kinetic modeling of the synthesis of glycerol carbonate from glycerol and urea using $ZnBr_2$ as a catalyst under optimal conditions. The highest glycerol conversion was achieved at a temperature of 130°C, the addition of 5% catalyst by weight, and a reaction time of 300 minutes, resulting in a conversion rate of 52.74%. Based on the kinetic model analysis, the first-order reversible nonelementary model can be selected as the best model to describe the overall reaction kinetics. This model provides the best balance between prediction accuracy (smallest SSE value), which is 4.42×10^{-7}, consistency with kinetic theory (k value increases with increasing temperature), which are 0.0028, 0.0038, and 0.0042 at each temperature, namely 110°C, 120°C, and 130°C, respectively. The realistic physical parameters of A and Ea values are 10.5909 s-1 and 26.1417 kJ/mol.

Keywords: $ZnBr_2$, glycerol, glycerol carbonate, conversion, kinetic modeling

1. INTRODUCTION

The biodiesel industry in Indonesia has witnessed rapid growth due to strong governmental policies aimed at increasing domestic production. As a result, glycerol, a by-product of biodiesel production, is generated in large quantities—approximately 1 kg of glycerol for every 10 kg of biodiesel produced [1]. If not properly utilized, this surplus glycerol could lead to environmental concerns. One promising derivative product is glycerol carbonate.

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is highly valued in the industry due to its favorable physical properties and chemical reactivity [2]. It finds a wide range of applications, including in the production of elastomers, surfactants, adhesives, inks, paints, lubricants, and electrolytes. As a solvent, it is compatible with both organic and inorganic compounds, making it suitable for use in cosmetics, coatings, batteries, and other formulations [3]. Glycerol carbonate is commonly synthesized through various methods, including the carboxylation of glycerol with urea, transcarbonation reactions using carbonate sources such as ethylene carbonate or dimethyl carbonate, and the supercritical reaction of glycerol with carbon dioxide [4].

Numerous studies have explored the synthesis of glycerol carbonate using different zinc-based catalysts. Glycerol carbonate (4-hydroxymethyl-1,3-dioxolane-2-one) has been effectively synthesized via the urea glycerolysis process, initiated by a $Zn(OBu)_2/Al(OBu)Cl_2$ catalyst system derived from $ZnCl_2$ and $Al(OBu)_3$. This zinc–aluminum complex was able to catalyze the reaction under solvent-free conditions at 150 °C and 1 atm N_2, achieving up to 85% yield and 97% selectivity with a 1:1 molar ratio of glycerol to urea over 4 hours. The reaction mechanism involved isocyanate as a key intermediate, and kinetic analysis indicated pseudo-first-order behavior with an estimated activation energy of 38 kJ/mol. Further, DFT calculations using the MN15-L functional suggested that the formation of glycerol carbonate is thermodynamically favorable, with a Gibbs free energy change of −28.41 kJ/mol [5].

Several studies have investigated the catalytic synthesis of glycerol carbonate (GC) from glycerol and urea using various zinc-based catalysts. One notable approach involves the use of deep eutectic solvents (DESs) composed of $ZnCl_2$ as the hydrogen bond acceptor and either monoethanolamine or acetamide as the donor. This system demonstrated high catalytic activity, with glycerol conversion reaching 93.85% and GC yield up to 90.77% under optimized conditions, without the need for additional organic solvents or co-catalysts. The enhanced performance was attributed to the strong hydrogen bonding network between $ZnCl_2$ and acetamide, as evidenced by FTIR analysis. While this study provided valuable insights into catalyst design and reaction optimization, it did not explicitly address the reaction kinetics or propose a kinetic model. In contrast, the use of $ZnBr_2$ as a conventional homogeneous catalyst has also shown promising results in GC synthesis. Therefore, a detailed kinetic investigation using $ZnBr_2$ is essential to better understand the reaction mechanism and to establish predictive models for process design and scale-up [6]. In another study, a single-atom Zn catalyst supported on N-doped porous carbon (Zn1/NC) was developed as a highly efficient and robust heterogeneous catalyst. Operando ReactIR analysis and DFT calculations confirmed that Zn^{2+} single-atom sites selectively activate urea and suppress the formation of inactive Zn–glycerol complexes. Although this research provided valuable mechanistic insights at the molecular level, it did not address reaction kinetics quantitatively. Compared to these systems, the use of $ZnBr_2$ as a homogeneous catalyst presents a simpler and well-defined environment for studying the intrinsic kinetics of glycerol carbonylation. Therefore, kinetic modeling using $ZnBr_2$ is crucial to deepen the mechanistic understanding and support future catalyst design and process optimization [7].

Reaction kinetics and mecanism for the synthesis of glycerol carbonat from glycerol and urea using $ZnSO_4$ catalyst has been reported by Wang and Ma [8]. They developed a kinetic model for the reaction of glycerol carbonate formation from glycerol and urea using $ZnSO_4$ as a catalyst. The operating conditions employed were a temperature of 140 °C, a reaction time of 4 hours, a catalyst concentration of 5%, and a molar ratio of urea to glycerol of 1.1:1. The activation energies obtained using the $ZnSO_4$ catalyst were E_{a1} = 143.39 kJ/mol and E_{a2} = 87.29 kJ/mol. Statistical analysis indicated that the developed kinetic model was accurate [8].

However, despite the promising catalytic performance of $ZnBr_2$, detailed kinetic modeling of the reaction between glycerol and urea using this catalyst has not yet been reported. Therefore, this study aims to develop a comprehensive kinetic model for synthesizing glycerol carbonate using $ZnBr_2$ and investigate the effects of temperature and reaction time on glycerol conversion.

2. MATERIALS AND METHODS

2.1 Materials

Technical-grade glycerol ($C_3H_5(OH)_3$, 85% purity) was obtained from CV. Rudang Jaya Abadi, Medan. Urea ($(NH_2)_2CO$, 99% purity) was sourced from PT. Petrokimia Gresik. The $ZnBr_2$ 98% LOBA CHEMIE catalyst was purchased from CV. Multichem, Depok.

2.2 Experimental procedure

The experimental setup used in this research is shown in Figure 1. Urea and a portion of glycerol were added to a three-neck flask and heated to the desired reaction temperature under continuous stirring. The catalyst, previously dissolved in the remaining glycerol, was introduced once the target temperature was reached. The reaction was conducted under constant temperature for various durations. Samples were taken every 60 minutes over 6 hours.

2.3 Methods of analysis

Iodometric titration was performed using standardized 0.01 N sodium thiosulfate ($Na_2S_2O_3$) solution by the Indonesian National Standard (SNI) [9]. Quantification of glycerol via iodometric titration in biodiesel, oils, and fats was conducted by the AOCS Ca 14-56 standard methods [10]. This method is based on the oxidation of glycerol by sodium periodate ($NaIO_4$), followed by a reaction with iodide ions from potassium iodide (KI) solution. The liberated iodine is then titrated with sodium thiosulfate using starch as an indicator. The amount of glycerol in the sample is calculated based on the difference in titrant volume between the sample and the blank. Glycerol conversion was determined by iodometric titration using sodium thiosulfate ($Na_2S_2O_3$). The conversion was calculated based on the difference between the initial and final free glycerol concentrations [11].

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} \times 100\% \qquad (1)$$

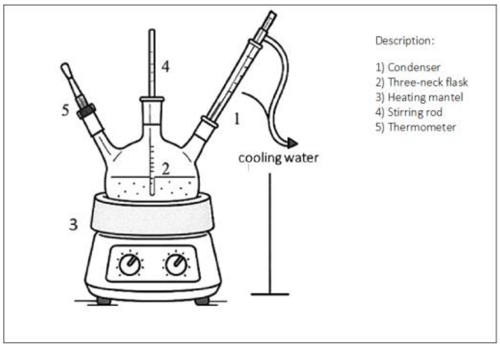


Figure 1. Experimental setup of glycerol carbonate production.

2.4 Kinetic model analysis

This study examined the effects of temperature, catalyst loading, and kinetic model selection based on the rate constant (k), and activation energy (Ea) in the homogeneous phase. The reaction between glycerol and urea yields glycerol carbonate and ammonia. Four kinetic models were evaluated: irreversible elementary reaction, irreversible non-elementary reaction, reversible elementary reaction, and reversible non-elementary reaction.

$$C_3H_8O_3 + NH_2CONH_2 \overset{k}{\leftrightarrow} C_4H_6O_4 + 2NH_3 \quad (2)$$

1. Elementary irreversible reaction model:

$$-r_A = kC_AC_B \quad (3)$$

2. Non-Elementary irreversible reaction model,

$$-r_A = kC_A^{\alpha}C_B^{\beta} \quad (4)$$

3. Elementary reversible reaction model

$$-r_A = k_1C_AC_B - k_2C_CC_D^2 \quad (5)$$

4. Non-Elementary reversible reaction model

$$-r_A = k_1C_A^{\alpha}C_B^{\beta} - k_2C_C^{\gamma}C_D^{\omega} \quad (6)$$

Kinetic parameters were estimated using MATLAB through multivariable optimization to minimize SSE between calculated and experimental values [12]

$$SSE = \sum\left(X_{A,\ hitung} - X_{A,\ data}\right)^2 \quad (7)$$

Activation energy (Ea) is the minimum energy required for a reaction to proceed. To determine Ea, the reaction temperature is varied, and the rate constant k is measured at each temperature. The relationship between the rate constant and temperature can be described by the Arrhenius equation [13].

$$k = A \exp\left(-\frac{Ea}{RT}\right) \quad (8)$$

where A is the frequency factor, Ea is the activation energy, R is the gas constant, and T is the temperature in Kelvin. To derive Ea and A, the Arrhenius equation is transformed into a linear form by taking the natural logarithm [14].

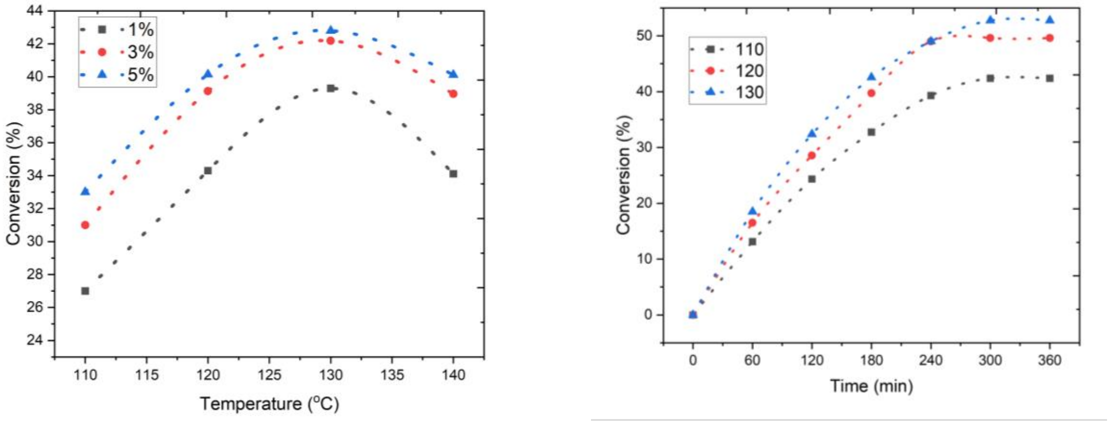
$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T} \quad (9)$$

This linear form resembles the equation of a straight line, y = mx + b, where ln k is plotted against 1/T. The slope (m) corresponds to $-\frac{E_a}{R}$ and the y-intercept of the graph gives ln A.

3. RESULTS AND DISCUSSION

This study was conducted by reacting glycerol with urea using $ZnBr_2$ as a catalyst. The independent variables used were the catalyst amount (1%, 3%, and 5%) and the reaction temperature (110°C, 120°C, 130°C, and 140°C). The effects of catalyst amount and reaction temperature on glycerol conversion are presented in the following graph.

Based on Figure 2(a), an increase in catalyst concentration from 1% to 5% consistently enhances glycerol conversion at all investigated temperatures. The higher catalyst amount increases the availability of active sites for the reaction, accelerating the reaction rate and improving conversion. The highest conversion was achieved at a catalyst concentration of 5%, reaching 42.80%. This indicates that the catalyst amount significantly influences the efficiency of the reaction. However, after reaching the optimal concentration, further addition of the catalyst does not provide a significant increase and may lead to resource waste as well as the potential formation of undesirable by-products, which can have a negative impact and decrease reaction efficiency [15]. In addition, temperature also affects the conversion results. The optimum temperature was found to be 130°C, at which the highest conversions were obtained across all catalyst concentrations. However, at 140°C, the conversion slightly decreased compared to 130°C, particularly at higher catalyst concentrations. This decline is likely due to product degradation or the formation of by-products caused by the excessively high temperature [16].



(a) (b)

Figure 2. (a) Effect of Temperature on Conversion at Various Catalyst Amounts
(b) Effect of Reaction Time on Conversion at Various Temperatures

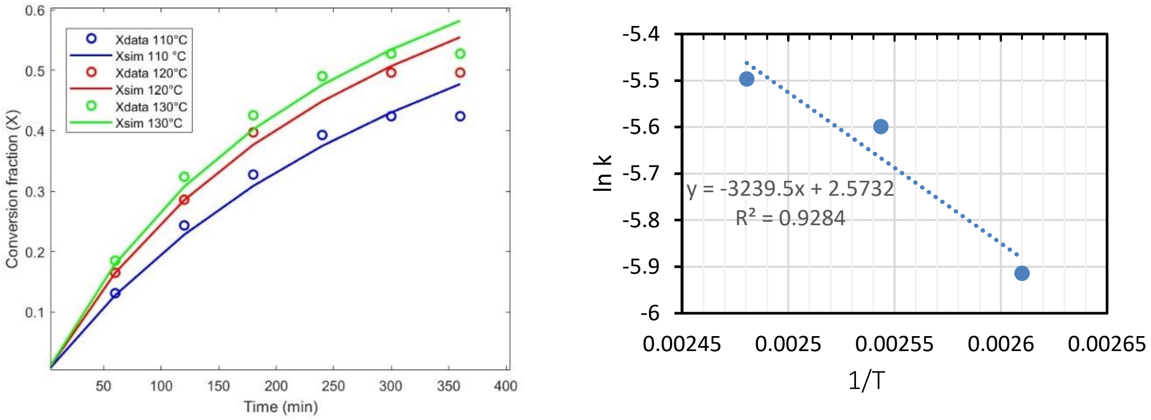
Meanwhile, based on Figure 2(b), the highest conversion was obtained at 300 minutes and a temperature of 130°C, reaching 52.74%. During the initial stage of the reaction (0–180 minutes), conversion increased sharply at all temperatures, indicating a high reaction rate in the early phase. After approximately 240 minutes, the rate of conversion began to slow down and tended to approach a plateau, suggesting that the system was reaching reaction equilibrium or that the remaining reactants were becoming limited. These findings indicate that a longer reaction time results in higher conversion, although the rate of increase diminishes over time. The reaction time is fundamentally associated with the reaction rate. At the early stage of the reaction, the rate is typically high due to the elevated concentrations of reactants, which provide a greater driving force for molecular collisions. As the reaction proceeds, the depletion of reactants leads to a reduced frequency of effective collisions, thereby causing a gradual decline in the reaction rate [17].

3.1. Reaction Kinetics Modeling

Kinetic modeling is essential to understanding the reaction mechanism, as it provides insights into the rate-determining steps and the influence of various parameters on reaction rate. This approach, known as chemical dynamics, builds on the foundational work of Arrhenius, who first established the relationship between reaction rate and the energy associated with reactant molecules [18]. The optimized parameter values for each proposed model are presented in the following graph.

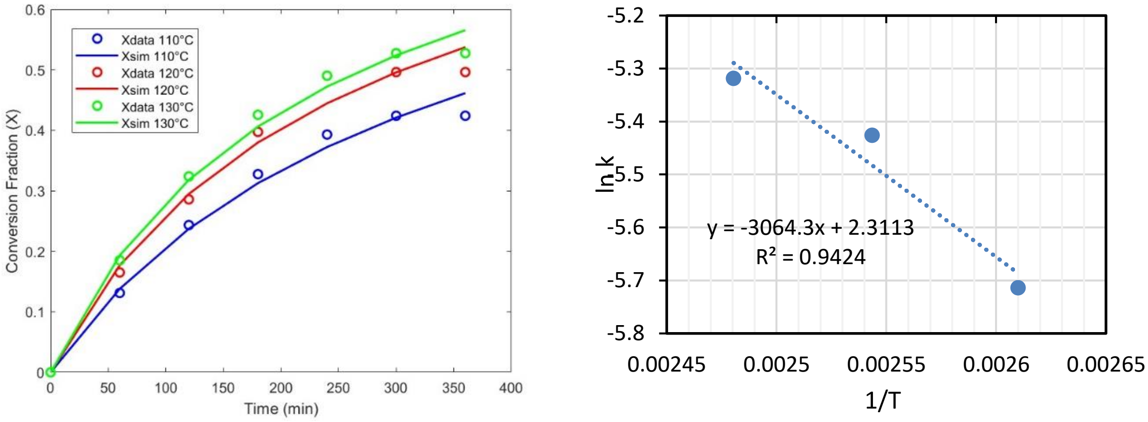
3.2. Analysis of SSE (Sum of Squared Errors)

The Sum of Squared Errors (SSE) quantifies the total deviation of data points from their respective cluster centroids [19]. In this study, a lower SSE value suggests that the data within each cluster are more tightly grouped, indicating a higher degree of intra-cluster similarity and thus more effective clustering performance. Based on the parameter estimation results, the reversible nonelementary model shows the smallest SSE value of 4.42×10^{-7}, indicating that this model provides the best prediction accuracy compared to the experimental data. In contrast, the irreversible and reversible elementary models show much larger SSE values, at 3.95×10^{-5} and 2.48×10^{-5}, respectively, indicating that these models are less suitable in representing the overall reaction kinetics.



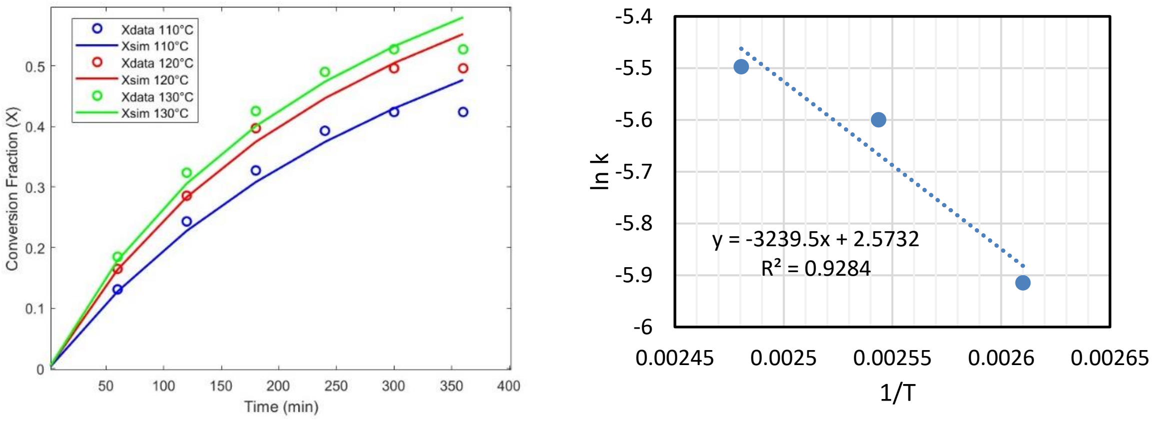
(a) (b)

Figure 3. (a) Graph of the Effect of Reaction Temperature on Conversion Based on the Irreversible Elementary Model; (b) Plot of ln k versus 1/T



(a) (b)

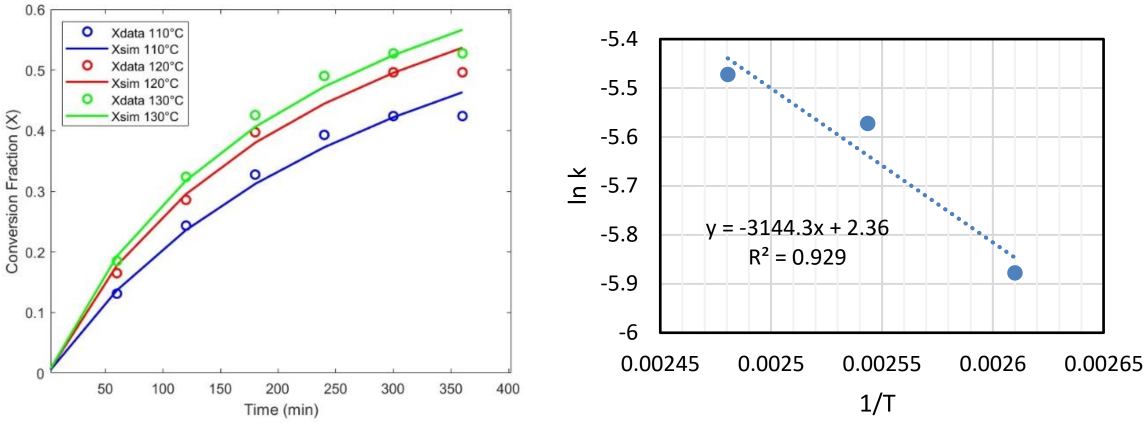
Figure 4. (a) Graph of the Effect of Reaction Temperature on Conversion Based on the Irreversible Nonelementary Model; (b) Plot of ln k versus 1/T



(a) (b)

Figure 5. (a) Graph of the Effect of Reaction Temperature on Conversion Based on the Reversible Elementary

Model; (b) Plot of ln k versus 1/T



(a) (b)

Figure 6. (a) Graph of the Effect of Reaction Temperature on Conversion Based on the Reversible Nonelementary Model; (b) Plot of ln k versus 1/T

Table 1. Parameter Values for Each Kinetic Model.

Model	T (K)	k_1	k_2	α	β	γ	ω	SSE	A (s^{-1})	Ea (kJ/mol)
Elementary *irreversible*	383,15	0,0027	-	-	-	-	-	3.95×10^{-5}	13,108	26,933
	393,15	0,0037	-	-	-	-	-			
	403,15	0,0041	-	-	-	-	-			
Non-elementary *irreversible*	383,15	0,0033	-	1,419	1,150	-	-	5.58×10^{-7}	10,088	25,477
	393,15	0,0044	-	1,305	1,163	-	-			
	403,15	0,0049	-	1,284	1,150	-	-			
Elementary *reversible*	383,15	0,0027	0	-	-	-	-	2.48×10^{-5}	13,108	26,933
	393,15	0,0037	0	-	-	-	-			
	403,15	0,0041	0	-	-	-	-			
Non-elementary *reversible*	383,15	0,0028	0	1,243	1,291	1,032	1,083	4.42×10^{-7}	10,591	26,142
	393,15	0,0038	0	1,241	1,282	0,987	1,067			
	403,15	0,0042	0	1,206	1,245	1,013	1,072			

3.3. Rate Constant Analysis

In general, all models show an increase in rate constant values with increasing temperature, which is consistent with the Arrhenius principle. The highest value was obtained at a temperature of 403.15 K, with a peak value of 0.0049 (for the reversible nonelementary model), indicating that the reaction rate increases significantly with temperature. However, this increase in value is not always accompanied by a decrease in SSE. Therefore, while understanding the reaction rate is important, its accuracy still needs to be supported by other evaluation parameters such as SSE.

3.4. Analysis of Activation Energy (Ea) and Pre-exponential Factor

Activation energy is the minimum energy required for a reaction to occur. The presence of a catalyst in the glycerol-urea reaction system plays a vital role in accelerating the reaction rate. It facilitates an alternative reaction mechanism with a lower activation energy (Ea) compared to the uncatalyzed pathway. This reduction in Ea increases the number of effective molecular collisions, thereby promoting the formation of glycerol carbonate [20]. The values across various models range from 25.4766 to 26.9332 kJ/mol. The model with the lowest value is the irreversible nonelementary model (25.4766 kJ/mol), indicating that the reaction occurs more easily under these conditions. However, when combined with the SSE value, the reversible nonelementary model, with a value of 26.1417 kJ/mol, proves to be superior, as it provides a balance between ease of reaction and kinetic prediction accuracy. Therefore, the evaluation should be aligned with the SSE and other parameters to obtain a comprehensive view of the kinetic model's performance.

The pre-exponential factor is related to the frequency and orientation of reactant molecule collisions that result in a reaction. The highest value, 13.1077 s^{-1}, was obtained from the elementary models, both irreversible and reversible. However, the high value in these models does not correspond with the low SSE value, making them less accurate in representing the actual kinetic data. In contrast, the reversible nonelementary model has a value of 10.5909 s^{-1}, which, although lower, remains within a realistic range and is accompanied by a very low SSE value. This indicates that an excessively high value does not necessarily imply a good model, and it needs to be evaluated alongside other parameters.

4. CONCLUSION

This study successfully addressed the identified research gap regarding the lack of detailed kinetic modeling for the reaction between glycerol and urea using $ZnBr_2$ as a catalyst. The objectives to develop a comprehensive kinetic model and investigate the effects of temperature and reaction time on glycerol conversion have been achieved.

Firstly, temperature and reaction time were found to significantly influence glycerol conversion. The optimal reaction temperature was determined to be 130°C; temperatures above this level led to urea evaporation and decomposition, thereby reducing reactant availability and overall efficiency. Reaction time positively affected conversion in the early stages but approached equilibrium after 300 minutes.

Secondly, this study developed and evaluated four kinetic models, with the reversible non-elementary model emerging as the most accurate and representative. This conclusion was supported by the model’s lowest SSE value (4.42×10^{-7}), consistent increase in the rate constant (k) with temperature, and physically reasonable kinetic parameters, including a pre-exponential factor ($A = 10.5909\ s^{-1}$) and activation energy ($E_a = 26.1417$ kJ/mol). Therefore, this model best describes the kinetics of glycerol carbonate synthesis using $ZnBr_2$ and contributes valuable insight to the existing body of knowledge.

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CONFLICT OF INTEREST

No potential conflict of interest was reported by the author(s).

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Agnes Febrianti: conceptualization, methodology, writing—original draft, resources, and editing.
Sonia Sembiring: investigation, data curation.
Heri Rustamaji: conceptualization, methodology, writing—original draft, resources, and editing, supervision.
Herti Utami: Conceptualization, writing- review editing.

REFERENCES

[1] H. Rahman, “Purifying Crude Glycerol From Biodiesel Production For Sustainable Energy Solutions,” *J Teknol*, vol. 11, no. 1, pp. 85–99, Nov. 2023, doi: 10.31479/jtek.v11i1.269.

[2] S. Nomanbhay, M. Y. Ong, K. W. Chew, P. L. Show, M. K. Lam, and W. H. Chen, “Organic Carbonate Production Utilizing Crude Glycerol Derived As By-Product Of Biodiesel Production: A Review,” 2020, MDPI AG. doi: 10.3390/en13061483.

[3] S. K. Karmee, “A Review On Preparation And Applications Of Glycerol Carbonate: Focus Biocatalysis,” 2024, Taylor and Francis Ltd. doi: 10.1080/10242422.2023.2232914.

[4] S. M. Gade, V. B. Saptal, and B. M. Bhanage, “Perception Of Glycerol Carbonate As Green Chemical: Synthesis And Applications,” Dec. 01, 2022, Elsevier B.V. doi: 10.1016/j.catcom.2022.106542.

[5] D. D. Andriyani, L. A. Kadir, N. P. Indriyani, and Y. Permana, “Glycerol Carbonate Synthesis Via Zn(Obu)2/Alcl2(Obu) Initiated-Glycerolysis Of Urea,” Chemistry of Inorganic Materials, vol. 2, p. 100040, 2024, doi: 10.1016/j.cinorg.2024.100040.

[6] H. Wang, J. Ma, Y. Li, and T. Wang, “The Synthesis Of Glycerol Carbonate From Glycerol

And Urea Using Deep Eutectic Solvent Zncl2:Acetamide As A Catalyst," *Applied Catalysis O: Open*, vol. 198, p. 207022, 2025, doi: 10.1016/j.apcato.2024.207022.

[7] J. Shi *et al.*, "N-Doped Porous Carbon-Anchored Zinc Single-Atom As An Efficient And Robust Heterogeneous Catalyst For Glycerol Carbonylation With Urea," *Chemical Engineering Journal*, vol. 466, p. 143317, 2023, doi: 10.1016/j.cej.2023.143317.

[8] H. Wang and J. Ma, "Reaction Kinetics and Mechanism for the Synthesis of Glycerol Carbonate from Glycerol and Urea Using ZnSO4 as a Catalyst," *Catalysts*, vol. 14, no. 1, Jan. 2024, doi: 10.3390/catal14010041.

[9] Badan Standarisasi Nasional, "SNI 7182-2015 : Biodiesel," 2015.

[10] L. O. Santos, S. F. L. S. Rocha, C. M. Barra, M. Tubino, and J. G. Rocha, "A Simple, Rapid, and Reliable Titrimetric Method for the Determination of Glycerol at Low Concentration," *J Braz Chem Soc*, vol. 33, no. 6, pp. 530–540, 2022, doi: 10.21577/0103-5053.20220004.

[11] H. Scott Fogler, *Elements of Chemical Reaction Engineering 3rd Ed. - H. Scott Fogler*, 3rd ed. Upper Saddle River, New Jersey: Prentice-Hall, Inc. (now Pearson Education, Inc.), 1999.

[12] H. Rustamaji, *Komputasi Teknik Kimia dengan MATLAB dan Simulink*. Bandarlampung: AURA (CV. Anugrah Utama Raharja) , 2017.

[13] Q. U. Putri, D. Augustin, and H. Hasanudin, "Kinetika Esterifikasi Asam Lemak Bebas dari Sludge Industri Crude Palm Oil (CPO) Menggunakan Katalis Komposit Montmorillonite/Karbon Tersulfonasi dari Tetes Tebu," *ALCHEMY Jurnal Penelitian Kimia*, vol. 18, no. 1, p. 48, Feb. 2022, doi: 10.20961/alchemy.18.1.50470.48-57.

[14] Octave. Levenspiel, *Chemical Reaction Engineering*, 3rd ed. New York: John Wiley & Sons, Inc, 1999.

[15] Z. Khan *et al.*, "Current Developments In Esterification Reaction: A Review On Process And Parameters," *Journal of Industrial and Engineering Chemistry*, vol. 103, pp. 80–101, Nov. 2021, doi: 10.1016/j.jiec.2021.07.018.

[16] C. Tempelman, B. el Arkoubi, J. Spaan, R. Slevani, and V. Degirmenci, "Decomposition of Heavy Diesel SCR Urea Fluid Adsorbed in Cu/HZSM-5 SCR Catalysts Studied by FTIR Spectroscopy at Ambient Conditions," *Reactions*, vol. 3, no. 4, pp. 576–588, Dec. 2022, doi: 10.3390/reactions3040038.

[17] N. D. Jespersen, J. E. Brady, and A. Hyslop, *Chemistry: The Molecular Nature of Matter, Sixth Edition*, 6th ed. United States of America: Wiley , 2012.

[18] S. Phimmavong, "Effect of Concentration on Reaction Speed," International Journal Papier, vol. 1, no. 1, pp. 21–29, Aug. 2020.

[19] L. Petra Refialy, H. Maitimu, and M. Soyano Pesulima, "Perbaikan Kinerja Clustering K-Means pada Data Ekonomi Nelayan dengan Perhitungan Sum of Square Error (SSE) dan Optimasi nilai K cluster," 2021.

[20] M. Singh and M. Review, "Catalysis: Accelerating Chemical Reactions for a Sustainable Future Keywords: Nanomaterial's • Catalysis research • Chemical engineering • Energy production 55 Singh M," Review Advanced Materials Science Research Adv. Mate. Sci. Res, vol. 6, no. 3, p. 6, 2023, doi: 10.37532/aaasmr.2023.6(3).54-56.