

Kinetic model of glycerol chlorination with hydrochloric acid

Jong Hun Lim*, Won Seob Song**, Sung Yul Woo**, and Dong Hyun Lee*,†

*Department of Chemical Engineering, Sungkyunkwan University, 300 Chunchun, Jangan, Suwon 440-746, Korea

**Production Technology Center, Samsung Fine Chemicals Co., Ltd., Korea

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Abstract—A new reaction model for dichloropropanol (DCP) synthesis from glycerol chlorination is proposed based on the models reported by Tesser et al. (2007) and Luo et al. (2009). Two reaction steps, glycerol to glycerol-1-acetate and α -MCP to 3-chloropropanediol-1-acetate, were defined as reversible reactions and other reaction steps were defined as irreversible processes. Using the experimental data reported by Luo et al. (2009), the values predicted in this study were compared with the previous model reported by Luo et al. (2009) using both the average absolute deviation (AAD) and root mean square deviation (RMSD). The AAD and RMSD of the new model were 31% and 33% lower than that of the existing one, respectively. Overall, the proposed model for glycerol chlorination is superior to the previous model.

Key words: Kinetic Model, Glycerol, Chlorination, Dichloropropanol, Hydrochloric Acid

INTRODUCTION

Dichloropropanol ($C_3H_6Cl_2O$, DCP) is widely used as an intermediate for epichlorohydrin (ECH, C_3H_5ClO), an intermediate for epoxy resin [1]. Recently, propylene and chlorine were reacted directly to produce allyl chloride (AC, C_3H_5Cl), which was then reacted with chlorine in the presence of excess industrial water to make DCP (called the propylene method). However, the economic efficiency has been decreased due to an increase in the price of propylene. A method of producing DCP by reacting glycerin and hydrogen chloride directly (called Glycerin method) is economically efficient and many relevant studies have been reported. Considerable glycerin (Glycerol, $C_3H_5(OH)_3$) is being created as a byproduct of biodiesel production [2].

DCP synthesis by glycerin, which was developed in Germany in 1906 [3-5], has been studied [6,7]. However, most studies provide only technological information in order to apply for patents [8-12] and to check the change in DCP yield depending on the choice of catalyst and reaction conditions [13-17].

To manage DCP synthesis efficiently, it is essential to predict the yield depending on both the reaction conditions and time, and then reaction rate equation needs to be derived. Regarding the glycerin-method for the DCP reaction mechanism and reaction rate, Tesser et al. [18] examined malonic acid as a catalyst, and Luo et al. [19, 20] reported the use of acetic acid under the conditions of excess water. However, there are only a few results on the reaction rate equation.

This paper proposes a new reaction mechanism based on those reported by Tesser et al. [18] and Luo et al. [20]. Using the experimental data reported by Luo et al. [20], the predicted values in this study were compared with the previous model reported by Luo et al. [20] using the average absolute deviation (AAD) and the root mean square deviation (RMSD).

THEORETICAL BACKGROUND

The DCP reaction from glycerin involves two steps. The first step is a reaction in which monochloropropanediol (MCP) is created after glycerin and hydrogen chloride react with each other. In the second step, MCP reacts with hydrogen chloride to produce DCP. At each step, 1 mole of either glycerin or MCP reacts with 1 mole of hydrogen, producing 1 mole of water. As 1 mole of DCP is created from 1 mole of glycerin, 2 moles of hydrogen chloride are ultimately spent, and 2 moles of water are created. MCP is divided into α -MCP and β -MCP according to the location where the -OH radical is substituted with chlorine, which creates 1,3-DCP and 2,3-DCP, respectively. According to Tesser et al. [18], the reaction of glycerin with α -MCP is a reversible reaction, whereas the reaction with β -MCP is irreversible. In addition, the creation of 1,3-DCP from α -MCP is a reversible reaction, whereas the production of 2,3-DCP from β -MCP is irreversible.

Luo et al. [19,20] divided the synthesis reaction of MCP from glycerin into two steps. The first step is where glycerol reacts with an acetic acid catalyst to produce glycerol-1-acetate and glycerol-2-acetate with water, respectively. In the second step the glycerol-1-acetate and glycerol-2-acetate react with hydrogen chloride to produce α -MCP and β -MCP, respectively, as well as water.

The main difference between the two reaction mechanisms is that the mechanism reported by Tesser et al. [18] involves a reversible reaction from glycerin to α -MCP and from α -MCP to 1,3-DCP, and Luo et al. [20] suggested that the esterification reaction to glycerol-1-acetate and glycerol-2-acetate is reversible.

Therefore, in this study, a new reaction mechanism was suggested based on the reaction mechanisms of Tesser et al. [18] and Luo et al. [20]. The new reaction mechanism is based on that of Tesser et al. [18] and considers the conversion reaction from glycerin to α -MCP and that from α -MCP to 1,3-DCP as being reversible reactions. According to Luo et al.'s [20] reaction mechanism for the esterification reaction and chlorination reaction, chlorination is irreversible. Fig. 1 shows the new reaction mechanism. The fol-

†To whom correspondence should be addressed.
E-mail: dhlee@skku.edu

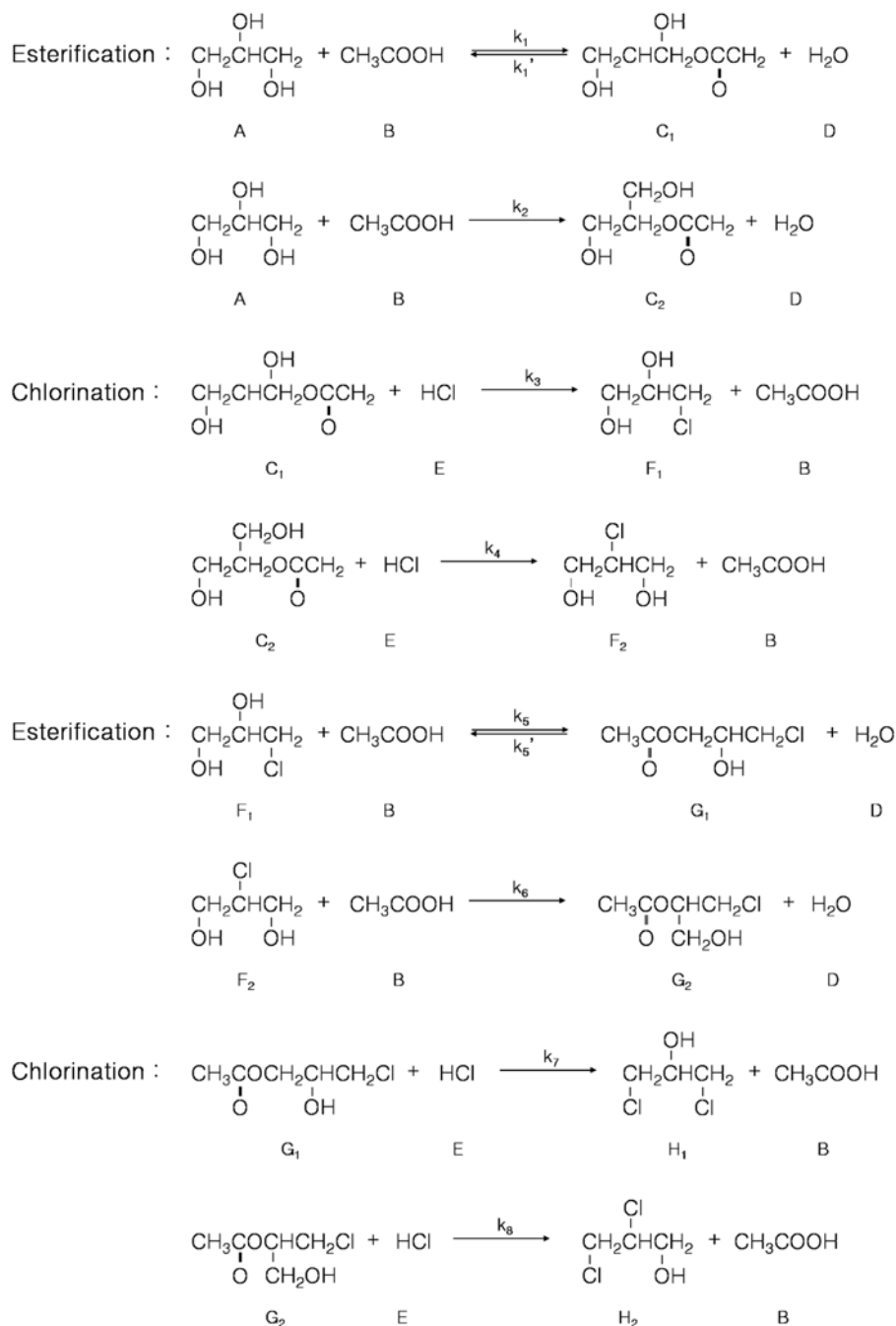


Fig. 1. New reaction scheme for DCP production.

lowing modeling assumptions were made [20]:

1. According to the concentration of the acetate intermediate, c_{C1} , c_{C2} , c_{G1} and c_{G2} produced during the esterification process, a quasi-stationary assumption is applied. Therefore, the concentration does not change with time. Also, the concentration of catalyst also does not change with time.

2. The HCl concentration is constant and can be obtained according to saturation in the organic phase due to its weak/difficult dissolution ability in the organic phase.

3. Since water is in excess, the water concentration does not change with time.

The following reaction rate equations are proposed based on the

abovementioned assumptions:

$$\frac{dc_A}{dt} = \left(-(k_1 + k_2) + \frac{k_1 k_1' c_D}{k_1 c_D + k_3 c_{E0}} \right) c_A c_{B0} \quad (1)$$

$$\frac{dc_{F1}}{dt} = -k_5 c_{F1} c_{B0} + \frac{k_1 k_3 c_A c_{B0} c_{E0}}{k_1 c_D + k_3 c_{E0}} + \frac{k_5 k_5' c_{F1} c_{B0} c_D}{k_5 c_D + k_7 c_{E0}} \quad (2)$$

$$\frac{dc_{F2}}{dt} = k_2 c_A c_{B0} - k_6 c_{F2} c_{B0} \quad (3)$$

$$\frac{dc_{H1}}{dt} = \frac{k_5 k_7 c_{F1} c_{B0} c_{E0}}{k_5 c_D + k_7 c_{E0}} \quad (4)$$

Table 1. Estimated reaction parameters in this study

T, [K]	K ₁ , [1/s]	K ₂ , [1/s]	K ₃ , [1/s]	K ₄ , [1/s]	K ₅ , [1/s]	K ₆ , [1/s]
363	-2.46E-04	2.68E-04	5.25E-05	3.75E-06	6.60E-07	1.25E-05
373	-3.06E-04	3.02E-04	4.83E-05	4.36E-06	1.53E-06	2.30E-05
383	-5.59E-04	4.73E-04	4.38E-05	6.97E-06	2.05E-06	3.21E-05
388	-6.64E-04	5.67E-04	4.89E-05	8.08E-06	2.48E-06	3.65E-05
393	-7.67E-04	6.30E-04	5.46E-05	8.80E-06	3.00E-06	4.34E-05

$$\frac{dc_{H2}}{dt} = k_6 c_{F2} c_{B0} \quad (5)$$

The reaction rates could be organized into five equations, and several reaction rate constants can be shown in a single parameter. The reaction rate parameters, K₁-K₆ were as follows:

$$K_1 = \left(-(k_1 + k_2) + \frac{k_1 k_1' c_D}{k_1' c_D + k_3 c_{E0}} \right) c_{B0} \quad (6)$$

$$K_2 = \frac{k_1 k_3 c_{B0} c_{E0}}{k_1' c_D + k_3 c_{E0}} \quad (7)$$

$$K_3 = k_5 c_{B0} - \frac{k_5 k_5' c_{B0} c_D}{k_5 c_D + k_7 c_{E0}} \quad (8)$$

$$K_4 = k_2 c_{B0} \quad (9)$$

$$K_5 = k_6 c_{B0} \quad (10)$$

$$K_6 = \frac{k_5 k_7 c_{B0} c_{E0}}{k_5 c_D + k_7 c_{E0}} \quad (11)$$

When parameters, K₁-K₆, are substituted into the reaction rate equation and the differential equation solved, the concentration of glycerin, α -MCP, β -MCP, 1,3-DCP and 2,3-DCP at each time can be arranged as follows:

$$c_A = c_{A0} e^{K_1 t} \quad (12)$$

$$c_{F1} = \frac{K_2 c_{A0}}{K_1 + K_3} (e^{K_1 t} - e^{-K_3 t}) \quad (13)$$

$$c_{F2} = \frac{K_4 c_{A0}}{K_1 + K_5} (e^{K_1 t} - e^{-K_5 t}) \quad (14)$$

$$c_{H1} = \frac{K_2 K_6 c_{A0}}{K_1 + K_3} \left(\frac{e^{K_1 t}}{K_1} + \frac{e^{-K_3 t}}{K_3} \right) - \frac{K_2 K_6}{K_1 K_3} c_{A0} \quad (15)$$

$$c_{H2} = \frac{K_4 K_5 c_{A0}}{K_1 + K_5} \left(\frac{e^{K_1 t}}{K_1} + \frac{e^{-K_5 t}}{K_5} \right) - \frac{K_4}{K_1} c_{A0} \quad (16)$$

The equations were solved using the method of least squares, and the reaction rate parameters, K₁-K₆, were optimized to follow the experimental data. The accuracy of the reaction model was tested by comparing the results with those obtained by the calculation using Luo et al.'s [20] experimental data and Luo et al.'s [20] suggested reaction mechanism and rate parameters. The methods used to calculate the error were the average absolute deviation (AAD, δ_1) and root mean square deviation (RMSD, δ_2), and the formulae are as follows:

$$\delta_1 = \frac{100}{N} \sum_{i=1}^N \left| \frac{\text{prediction} - \text{experimental}}{\text{experimental}} \right| \quad (17)$$

$$\delta_2 = 100 \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{\text{prediction} - \text{experimental}}{\text{experimental}} \right)^2} \quad (18)$$

The initial concentration of each material was 2.36 mol/L for glycerin, 0.79 mol/L for acetic acid catalyst, 32.53 mol/L for water and 9.42 mol/L for hydrogen chloride [20]. The reaction temperature was between 363 and 393 K.

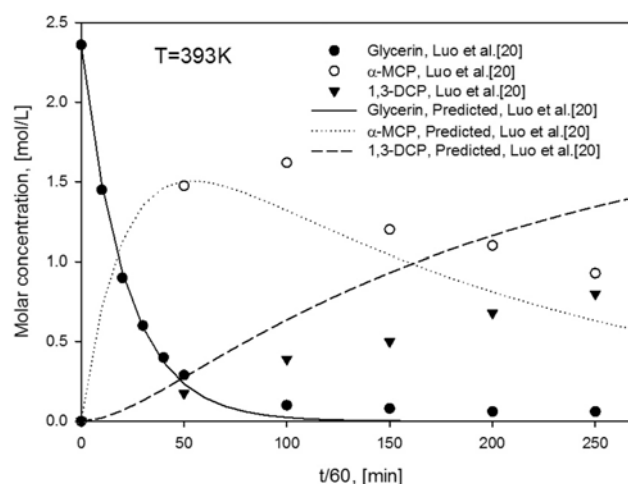


Fig. 2. The predicted values of Luo et al. [20] and experimental results reported by Luo et al. [20] for glycerin, α -MCP and 1,3-DCP.

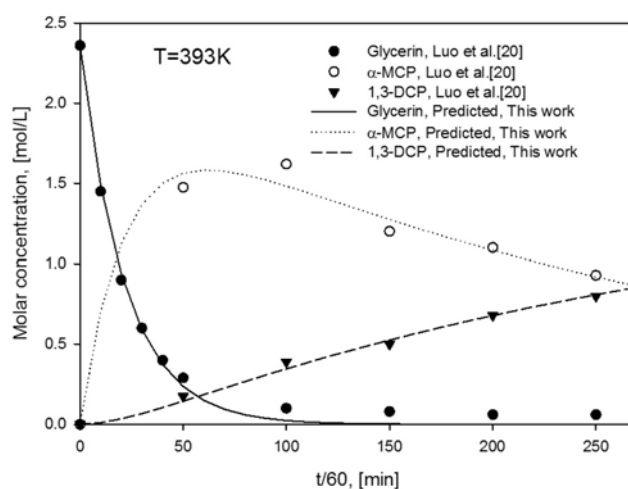


Fig. 3. The predicted values of this work and experimental results reported by Luo et al. [20] for glycerin, α -MCP and 1,3-DCP.

RESULTS AND DISCUSSION

Table 1 shows the reaction rate parameters gained by solving the reaction rate equations on the new reaction mechanism. Figs. 2 to 4 show the results calculated by Luo et al.'s [20] reaction model and the results predicted by the new mechanism. In Fig. 2, the results of glycerin, α -MCP, 1,3-DCP predicted by Luo et al. [20] and the experimental data reported by Luo et al. [20] were compared. Fig. 3 shows a comparison of the experimental values on glycerin, α -MCP, 1,3-DCP of Luo et al. [20] and the results predicted by the newly suggested model in this study. Fig. 4 shows a comparison of experiment values reported by Luo et al. [20] on β -MCP and 2,3-DCP, along with the results predicted by Luo et al. [20] and the values predicted in this study. From the experimental values, the glycerin concentration decreased with time. The α -MCP and β -MCP concentration increased initially until the glycerin concentration reached its lowest point, reaching a maximum followed by a gradual decrease thereafter. The 1,3-DCP and 2,3-DCP concentration increased gradually as the reaction progressed. In terms of MCP creation, when the α -MCP and β -MCP concentrations are compared, α -MCP has

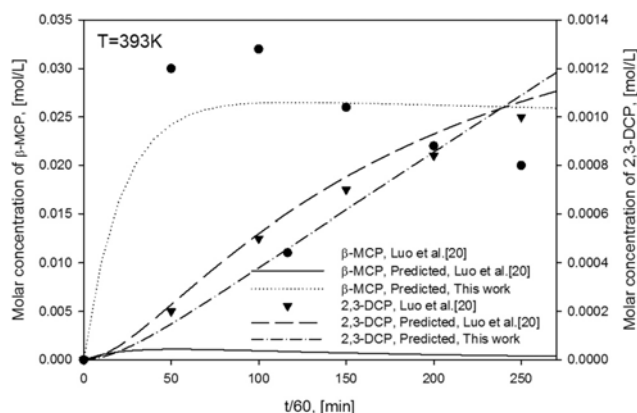


Fig. 4. Experimental data of β -MCP and 2,3-DCP reported by Luo et al. [20] and the data predicted by Luo et al. [20] and this model.

many more products than β -MCP. This was attributed to the more frequent occurrence of substitution reactions on the outermost car-

Table 2. Mole balances reported by Luo et al. [20]

T, [K]	Time, [min]	Glycerin, [mol/L]	α -MCP, [mol/L]	β -MCP, [mol/L]	1,3-DCP, [mol/L]	2,3-DCP, [mol/L]	Total, [mol/L]	Balance, [mol/L]
363	0	2.36	0	0	0	0	2.36	0
	50	1	1.26	0.025	0.025	4.00E-05	2.31	0.05
	100	0.6	1.625	0.033	0.08	8.00E-05	2.34	0.02
	150	0.45	1.6	0.032	0.15	1.50E-04	2.23	0.13
	200	0.4	1.56	0.031	0.22	2.00E-04	2.21	0.15
	250	0.37	1.48	0.03	0.25	2.40E-04	2.13	0.23
373	0	2.36	0	0	0	0	2.36	0.00
	50	0.90	1.21	0.02	0.05	6.00E-05	2.18	0.18
	100	0.46	1.73	0.04	0.16	2.00E-04	2.38	-0.02
	150	0.30	1.60	0.03	0.28	3.50E-04	2.21	0.15
	200	0.26	1.48	0.03	0.36	4.00E-04	2.13	0.23
	250	0.25	1.30	0.03	0.48	6.00E-04	2.06	0.30
383	0	2.36	0	0	0	0	2.36	0
	50	0.45	1.38	0.03	0.10	1.20E-04	1.96	0.40
	100	0.22	1.68	0.03	0.25	3.20E-04	2.18	0.18
	150	0.17	1.49	0.03	0.43	5.50E-04	2.12	0.24
	200	0.14	1.28	0.03	0.51	6.00E-04	1.96	0.40
	250	0.13	1.10	0.02	0.63	7.00E-04	1.88	0.48
388	0	2.36	0	0	0	0	2.36	0
	50	0.36	1.45	0.03	0.11	1.50E-04	1.95	0.41
	100	0.15	1.73	0.03	0.31	4.00E-04	2.22	0.14
	150	0.14	1.43	0.03	0.48	6.00E-04	2.07	0.29
	200	0.12	1.20	0.03	0.58	7.00E-04	1.93	0.43
	250	0.1	1.00	0.02	0.73	9.00E-04	1.85	0.51
393	0	2.36	0	0	0	0	2.36	0
	50	0.29	1.48	0.03	0.18	2.00E-04	1.97	0.39
	100	0.1	1.62	0.03	0.39	5.00E-04	2.14	0.22
	150	0.08	1.20	0.03	0.50	7.00E-04	1.81	0.55
	200	0.06	1.10	0.02	0.68	8.40E-04	1.86	0.50
	250	0.06	0.93	0.02	0.80	1.00E-03	1.81	0.55

Table 3. Average absolute deviation (AAD, δ_1) reported by Luo et al. [20] and this work

Luo et al. [20]						This work				
T, [K]	363	373	383	388	393	363	373	383	388	393
Glycerin	25.92	34.52	41.50	43.36	45.30	27.17	28.64	40.09	44.41	45.12
α -MCP	6.75	5.19	11.23	16.16	18.39	2.72	2.94	3.70	4.95	4.65
β -MCP	97.69	97.34	97.18	97.23	97.23	13.32	14.36	13.12	13.76	17.50
1,3-DCP	151.63	103.36	82.78	82.88	69.04	4.83	3.49	3.94	4.06	7.04
2,3-DCP	22.06	8.91	6.88	7.21	8.47	18.05	10.86	15.52	12.34	14.52
Total	49.33					17.91				

Table 4. Root mean square deviation (RMSD, δ_2) reported by Luo et al. [20] and this work

Luo et al. [20]						This work				
T, [K]	363	373	383	388	393	363	373	383	388	393
Glycerin	37.24	50.33	57.95	60.82	62.95	39.81	43.60	59.38	61.75	62.86
α -MCP	7.32	5.89	11.69	17.47	21.14	3.41	4.02	4.65	5.95	5.46
β -MCP	97.69	97.34	97.18	97.23	97.23	15.64	16.59	14.72	16.06	19.71
1,3-DCP	152.19	103.89	83.02	83.69	69.73	5.10	3.82	4.75	4.73	9.61
2,3-DCP	23.40	9.44	7.84	8.76	9.14	23.80	12.20	17.45	13.98	17.22
Total	66.65					32.05				

bon; a substitution reaction of α -location of the glycerin occurs more readily than that of the β -location [21]. For this reason, a larger amount of 1,3-DCP was produced from α -MCP than 2,3-DCP from β -MCP.

As shown in Fig. 2, when the change in concentration was examined in accordance with the calculation result of the reaction rate model reported by Luo et al. [20], the general tendency was well matched, but the experimental data at 100 minutes after the reaction did not correspond to the values predicted by the model. The experimental result at a reaction temperature of 393 K shows that the glycerin concentration converges to approximately 0.06 mol/L. However, the model's prediction converges at a zero concentration. Table 2 shows the mole balance in respect to the reaction time based on Luo et al.'s [20] experimental result. Since the initial amount of glycerin was 2.36 mol/L, the sum of the reactant and product concentration must maintain the same mole balance as the initial glycerin concentration. However, this was not the case, as shown in Table 2. As shown in Fig. 2, the value predicted by the model on α -MCP corresponds to the experimental value quite well. However, after 100 minutes, there were discrepancies between the experiment and prediction values. In Fig. 4, there was a tenfold difference in the order of calculation between the experiment and prediction. As shown in Figs. 2 and 4, there was a twofold difference between predicted value by Luo et al. [20] for 1,3-DCP and the experiment value at the end of reaction, and there was a huge gap between the predicted and experiment values for 2,3-DCP at 393 K. The discrepancy between the predicted and experiment value might be due to a possible miscalculation of the suggested reaction rate parameter and/or structural impossibility of the reaction rate model to follow the experiment result.

An analysis of Figs. 3 and 4 suggests good correspondence between the predicted value of this model and experimental results of 1,3-DCP and 2,3-DCP by Luo et al. [20]. As shown in Figs. 3 and 4 for α -MCP and β -MCP, respectively, the calculated values corre-

spond relatively well to the experimental result until 100 minutes, but diverge thereafter. As shown in Figs. 3 and 4, the 1,3-DCP and 2,3-DCP values predicted by this model followed the experiment results.

On the other hand, both the value predicted by Luo et al. [20] and the value predicted in this work did not follow the change in glycerin concentration accurately. Table 2 shows the mole balance with respect to the reaction time based on Luo et al.'s [20] experimental results. Since the initial amount of glycerin was 2.36 mol/L, the sum of the reactant and product concentration must maintain the same mole balance as the initial glycerin concentration. However, this was not the case, as shown in Table 2.

AAD, δ_1 and RMSD, δ_2 were calculated to compare the accuracy of the previous model and the new model suggested in this work. Tables 3 and 4 show the calculation results of δ_1 and δ_2 by each material and temperature. The predicted value of α -MCP shows less error in general. For β -MCP, the error is approximately 80% because Luo et al.'s [20] predicted value has a huge gap with the experimental results. For 1,3-DCP, the error was decreased significantly in this new model. This suggests that in predicting the yield of the final product of 1,3-DCP, the new model followed the experimental values. In the case of Luo et al. [20] the error was >60-100% for 1,3-DCP. However, the values predicted by this new model showed a lower error of <5%. The reaction rate model of this study showed 30% less error than the previous model reported by Luo et al. [20]. Based on the results, the reaction rate equation and reaction mechanism suggested in this study are superior to Luo et al. [20]'s model.

CONCLUSION

The reaction mechanism for the reaction that creates dichloropropanol from glycerin was examined, and a new reaction rate model

was established. The reaction rate model in this study was confirmed to be superior to the previous model. In the case of glycerin, α -MCP and β -MCPs did not follow the experiment results perfectly but showed a similar tendency. The predicted DCP concentration well matched the experimental data reported by Luo et al. [20] in general. When AAD, δ_1 and RMSD, δ_2 were compared with those of the previous results, the new model had less error than the previous model. Therefore, the new reaction model indicated a fair amount of advance. The reaction that produces DCP from glycerin also produces water. Anhydrous HCl should therefore be used in order for this reaction to be suitable for industry. Therefore, a reaction model to predict such experiments will be needed in the future.

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NOMENCLATURE

c_A	: concentration of glycerol in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{A0}	: initial concentration of glycerol in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_B	: concentration of acetic acid in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{B0}	: initial concentration of acetic acid in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{C1}	: concentration of glycerol-1-acetate in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{C2}	: concentration of glycerol-2-acetate in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_D	: concentration of H_2O in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{D0}	: initial concentration of H_2O in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_E	: concentration of HCl in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{E0}	: initial concentration of HCl in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{F1}	: concentration of α -MCP in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{F2}	: concentration of β -MCP in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{G1}	: concentration of 3-chloropropandiol-1-acetate in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{G2}	: concentration of 3-chloropropandiol-2-acetate in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{H1}	: concentration of 1,3-DCP in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
c_{H2}	: concentration of 2,3-DCP in the reaction system [$\text{mol}\cdot\text{L}^{-1}$]
E	: activation energies [$\text{kJ}\cdot\text{mol}^{-1}$]
$k_1, k'_1, k_2, k'_2, k_3, k'_3, k_4, k_5, k'_5, k_6, k_7$ and k_8	: reaction rate constants [$\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$]
k_0	: unit reaction rate constants [$\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$]
R	: ideal gas constant [$8.314\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$]
t	: reaction time [s]
T	: absolute temperature [K]

T_0	: unit temperature [K]
δ_1	: average absolute deviation [%]
δ_2	: root mean square deviation [%]

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