Thermodynamics and Kinetics Study of Diethyl Carbonate (DEC) Synthesis from CO₂, Ethanol, and Epoxides with Various Catalysts

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Abstract. Carbon dioxide (CO₂) has been the main contributor for global warming over the past decades. However, it can potentially be utilized as raw material of valuable products, such as organic carbonate compound namely diethyl carbonate (DEC). Formation of DEC via indirect route from CO₂ and ethanol is accompanied with epoxides as dehydrating agent. This work has been devoted to study thermodynamics and kinetics of indirect DEC synthesis using ethylene oxide (EO), propylene oxide (PO), and butylene oxide (BO) with various catalysts. Data from scientific journals and previous experiments conducted at Laboratory of Thermodynamics, ITS were analyzed in this study. Based on the value of (ΔG), it was found that indirect synthesis using EO is the most spontaneous reaction, followed by BO and PO, respectively. Simulation using Aspen HYSYS V8.8 also reveals that reactant and product system after 3 hours of reactions falls into vapor-liquid region and superheated region. Meanwhile, kinetics evaluation of experiment using PO and KI/EtONa catalyst showed that the aforementioned reactions are exothermic due to decreasing value of reaction constant upon reaching certain temperature. Based on Arrhenius equation while presuming that the reaction is elementary and non-elementary, activation energy was estimated as 55.62 kJ/mol and 54.80 kJ/mol, respectively. Furthermore, the use of KI/EtONa as catalyst resulted the highest yield among other catalysts namely KI, KI/CeO₂, and KI/Zeolite.

1. Introduction

Based on data from the Ministry of Environment and Forestry of the Republic of Indonesia, it was noted that in 2017 the emission of 558,890 tons of CO₂ equivalent was produced by the energy sector, corresponding to 48.6% of the total CO₂ emissions in Indonesia. This number is expected to keep increasing in the future, considering that domestic consumption of energy has increased by 2.4% in the 2014 – 2018. Greenhouse gas emissions such as CO₂ are dangerous because they trigger global warming. One way to reduce greenhouse gas emissions is by utilizing CO₂ from energy sector emissions as raw material for various chemical products, such as urea and organic carbonate compounds like dimethyl carbonate (DMC) and diethyl carbonate (DEC). Organic carbonates are classified as environmentally friendly and have the potential to replace many harmful chemicals for different applications, because of...
their properties such as low toxicity and higher biodegradability [1]. The utilization of CO₂ into DEC becomes the most potential for several reasons. First, domestic demand for urea has been fulfilled. Based on data from the Indonesian Fertilizer Producers Association (APPI), in 2019 urea production reached 7.7 million tons / year, an increase of 3.7 % from the previous year. Meanwhile, the domestic urea consumption in 2019 was only 3.7 million tons / year or decreased by 9.3 % from the previous year. Second, DEC is more suitable as a fuel additive compared to DMC. Table 1 shows the physical properties of DEC, DMC, and Diesel.

| Property                | DMC [2] | DEC [3] | Diesel [2] |
|-------------------------|---------|---------|------------|
| Molecular Formula       | C₃H₆O₃ | C₅H₁₀O₃ | C₁₀ – C₂₁   |
| Molecular Weight        | 90.1    | 118.1   | 190 – 220  |
| Density (kg/m³)         | 1079    | 975     | 830.7      |
| Calorific Value (MJ/kg) | 15.78   | 21.2    | 42.5       |
| Boiling Point (°C)      | 90.1    | 126     | 180 – 360  |
| Cetane Number           | 35 – 36 | 58      | 40 – 55    |

Based on Table 1, DEC has higher calorific value than DMC, it means that to achieve the same energy, DEC fuel consumption is lower than DMC. In addition, another parameter that needs to be considered is the cetane number. A higher cetane number indicates that the fuel ignites more readily when sprayed into hot compressed air. Compared to DMC, DEC has higher cetane number. It means that if DEC is mixed into diesel, it doesn’t reduce the quality of the fuel. The high oxygen content in DEC (40.6%) when compared to other additives such as ethanol (35%) and MTBE (18%) also one of the reasons why DEC is suitable to be used as a fuel additive. The gasoline/water distribution coefficient of DEC is better than ethanol and that of other carbonates such as DMC. DEC decomposes to benign CO₂ and ethanol when released into environment [1]. Based on the engine test, DEC has the expected effect of drastically diminishing smoke in the exhaust under all operating conditions of the diesel engine [4]. In addition, DEC increases RON value of blended light naphta [5]. Being an excellent solvent, DEC is widely used in pharmaceutical products, fertilizer, pesticide and manufacture of dyes. Presence of ethyl and carbonyl groups in DEC help in its conversion to important chemicals such as polycarbonates and carbamates.

Synthesis of DEC from CO₂ and ethanol over various epoxides and catalysts have been widely researched [8-10]. The thermodynamic and kinetic studies on the synthesis reaction of DEC from CO₂, ethanol, and butylene oxide over cerium (IV) oxide have been reported in the literature conducted by Leino et al. [6]. However, these two studies have not been carried out on the synthesis of DEC with ethylene oxide and propylene oxide as epoxides and various other catalysts such as KI, KI / CeO₂, KI / EtONa, and KI / Zeolite. Therefore, this research included thermodynamic studies and reaction kinetics on the synthesis of DEC with various epoxides and catalysts.

2. Experimental Section

2.1. Description of Materials

The reactants used in this experiment are shown in the Table 2. Catalyst of zeolite 0.3 nm was obtained from Merck, potassium iodide (KI) from Wuhan Fortuna Chemical Co, cerium oxide (CeO₂) and sodium ethoxide (EtONa) from Sigma Aldrich.
Table 2. The specifications of reactant used in the experiment

| Component        | CAS No. | Purity (%) | Molar mass (g/mol) | Source                                |
|------------------|---------|------------|--------------------|---------------------------------------|
| Carbon dioxide   | 124-38-9 | 99.5       | 44.01              | PT Samator, Indonesia                 |
| Ethanol          | 64-17-5 | 99.8       | 46.07              | Merck, Germany                        |
| Ethylene oxide   | 75-21-8 | 99.5       | 44.05              | PT Aneka Gas, Indonesia               |
| Propylene oxide  | 75-56-9 | 99.5       | 58.08              | Merck, Germany                        |
| Butylene oxide   | 109-99-9 | 99.5       | 72.11              | Sigma Aldrich                         |

Prior to use, the water content in ethanol is reduced by pre-treatment using a molecular sieve. Other chemicals are used directly without any purification.

2.2. Experimental Procedures

The experimental apparatus and typical procedures are described in our previous work [10]. At this work the epoxides used are ethylene oxide, butylene oxide and propylene oxide. Unlike the use of ethylene oxide, introducing liquid epoxides such as butylene oxide or propylene oxide into the reactor is carried out first, then the catalyst, ethanol and CO₂ are added sequentially according to the variables.

3. Results and Discussion

3.1 Thermodynamic Analysis

In analysis of DEC synthesis from carbon dioxide, ethanol, and dehydrating agent, such as ethylene oxide, propylene oxide and butylene oxide, calculating thermodynamic of reaction can provide better understanding about the type of occurring reaction. The thermodynamic data used in this analysis are shown in Table 3

| Component        | ΔH₂⁹⁸ (kJ/mol) | S₂⁹⁸ (kJ/mol.K) | Cp¹ (kJ/mol.K) |
|------------------|---------------|----------------|---------------|
| DEC              | -637.9        | 0.413          | 0.275         |
| CO₂              | -393.5        | 0.213          | 0.043         |
| Ethanol          | -235.1        | 0.283          | 0.208         |
| Butylene Oxide   | -168.9        | 0.230          | 0.235         |
| Butylene Carbonate | -487.6    | 0.423          | 0.256         |
| 1,2-Butanediol   | -523.6        | 0.223          | 0.281         |
| Ethylene Oxide   | -52.6         | 0.242          | 0.069         |
| Ethylene Carbonate | -571.5    | 0.175          | 0.205         |
| Ethylene Glycol  | -454.8        | 0.167          | 0.212         |
| Propylene Oxide  | -94.7         | 0.282          | 0.193         |
| Propylene Carbonate | -531.9   | 0.767          | 0.767         |
| Propylene Glycol | -421.3        | 0.288          | 0.256         |

¹ Heat capacity at temperature of 170 °C and pressure of 30 bar

The calculation of Gibbs energy in reaction conditions is carried out based on the method described by Leino et al. [6] using the equations (1) to equation (5). While the equilibrium constant (K) is calculated using the equation (6) and (7).

\[
\Delta_r H^\theta_T = \Delta_r H^\theta_{298K} + \Delta C_p(T - 298) \quad (1)
\]

\[
d\left(\frac{\Delta_r G^\theta}{T}\right) = \left(\frac{\Delta_r H^\theta}{T^2}\right) dT \quad (2)
\]
The two sides are integrated into the equation:

\[ \Delta r_G = T \Delta G^\circ - 164.44 \left( \frac{1}{T} - \frac{1}{298} \right) T + 0.04T \ln \left( \frac{T}{298} \right) \]  \hspace{1cm} (4)

\[ \Delta r_G = \Delta r_G^\circ - RT \ln \left( \frac{P}{P^\circ} \right) \]  \hspace{1cm} (5)

\[ K = e^{-\frac{\Delta r G}{RT}} \]  \hspace{1cm} (6)

The equilibrium constant for the reaction of CO₂, ethanol and ethylene oxide:

\[ K = \frac{x_{C_5H_{10}O_3} x_{C_2H_6O_2}}{x_{CO_2} x_{C_2H_4O} x_{C_2H_6O}} \]  \hspace{1cm} (7)

The equilibrium constant for the reaction with butylene oxide or propylene oxide is typical to equation (7)

| Epoxides          | Reactions                                      | \( \Delta r G \) (kJ/mol) | Equilibrium Constant, K | Equilibrium Conversion, X |
|-------------------|------------------------------------------------|---------------------------|--------------------------|---------------------------|
| Ethylene Oxide    | \( CO_2 + C_2H_5OH + 2C_2H_6OH \rightleftharpoons C_2H_4O_3 + C_3H_8O_2 \) | 0.75                      | 8.15 x 10⁻¹              | 1.19%                     |
| Propylene Oxide   | \( CO_2 + C_3H_6O + 2C_2H_5OH \rightleftharpoons C_3H_6O_3 + C_3H_8O_2 \) | 28.72                    | 4.10 x 10⁻⁴              | 0.05%                     |
| Butylene Oxide    | \( CO_2 + C_4H_6O + 2C_2H_5OH \rightleftharpoons C_5H_{10}O_3 + C_4H_{10}O_2 \) | 3.89                      | 3.48 x 10⁻¹              | 0.90%                     |

\( \Delta r G \) is calculated at reaction temperature of 170 °C and CO₂ initial pressure of 30 bar.

Gibbs energy is used to determine whether a reaction is spontaneous or non-spontaneous. Gibbs energy of DEC synthesis is obtained by subtracting Gibbs energy of products with Gibbs energy of reactant. Spontaneous reaction at specific temperature is denoted by negative value of Gibbs energy, meanwhile non-spontaneous reactions is marked by positive value of Gibbs energy. In Table 4, it is shown that DEC synthesis at 30 bar and temperature of 170 °C using ethylene oxide, propylene oxide, and butylene oxide resulted in positive value of Gibbs energy which means the reactions are non-spontaneous. However, reactions occurred through the help of catalyst which was capable to lower its activation energy. Out of the three epoxides, DEC synthesis using ethylene oxide yielded the lowest amount of Gibbs energy. Therefore, it was the most spontaneous reaction, followed by DEC synthesis with butylene oxide and propylene oxide, respectively.

3.2 Kinetics Analysis

3.2.1 Reaction Kinetics Calculation based on Leino et al. Data [6]

Leino et al. [6] has calculated the activation energy in the synthesis of DEC from CO₂, Ethanol and BO, which is 18.6 kJ / mol, but there is no information about the chemical reaction rate. In this study, chemical reaction rates and constants were calculated by referring to Leino et al. data [6]. It was assumed that the reactants which mainly took part in the reaction were ethanol and butylene oxide, while CO₂ was assumed to be in zero order due to its low conversion. Based on experimental data, results of
calculation for initial concentration and initial flow rate of each could be obtained and reactant conversion for butylene oxide and ethanol are presented in Table 5

| Compound    | Stoichiometric Coefficient | Conversion |
|-------------|----------------------------|------------|
|             |                            | T = 413 K  | T = 443 K  | T = 453 K  |
| Butylene Oxide | 1                          | 5.8%       | 8.4%       | 8.9%       |
| Ethanol     | 2                          | 0.7%       | 1.0%       | 1.1%       |

Because the reactor was equipped with mechanical stirrer, the reactor system was presumed to be a mixed flow reactor. This type of reactor with solid catalyst can be approached using equation (8)

\[
\frac{W}{F_{A0}} = \frac{X_A}{-r_A'}
\]

where \( W \) symbolizes weight of catalyst, \( F_{A0} \) is the initial flowrate of component \( A \), \( X_A \) represents conversion of component \( A \), and \(-r_A'\) signifies the reaction rate of component \( A \) in mol/kg.hour. Reaction rates with the basis of ethanol (component A) conversion and the ones using butylene oxide (component B) as basis of conversion are depicted in Table 6.

| T (K) | \( -r_A' \) (mol/kg.hour) | \( -r_B' \) (mol/kg.hour) |
|-------|---------------------------|---------------------------|
| 413   | 0.096                     | 0.556                     |
| 443   | 0.139                     | 0.808                     |
| 453   | 0.148                     | 0.859                     |

In the calculation of reaction constant, there are three assumptions: Case 1 represents elementary reaction in which its reaction orders are equal to the stoichiometric coefficients, reaction rate equation equals to \( kC_A^2C_B \). Case 2 represents non-elementary reaction in which its reaction orders are not equal to the stoichiometric coefficients, reaction rate equation equals to \( kC_A^2C_B^2 \). The backward reaction is assumed insignificant therefore it is not considered. Result of reaction constant calculation plotted based on Arrhenius Law, equation (9), is portrayed on Figure 1.

\[
\ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right)
\]
In addition, activation energy for each case and basis of conversion is provided in Table 7.

| Parameter     | Case 1 (Ethanol) | Case 1 (BO) | Case 2 (Ethanol) | Case 2 (BO) | Leino et al. [6] |
|---------------|------------------|-------------|------------------|-------------|------------------|
| Slope         | -2297.79         | -2297.79    | -2279.37         | -2279.37    | -2232.57         |
| Intercept     | -2.13            | -0.37       | 0.56             | 2.32        | -5.03            |
| A             | 0.12             | 0.69        | 1.75             | 10.19       | 0.01             |
| Ea (kJ/mol)   | 19.10            | 19.10       | 18.95            | 18.95       | 18.56            |
| Deviation of Ea | 3%              | 3%          | 2%               | 2%          | -                |

With the same calculation steps, it was obtained that activation energy for Case 1 and Case 2 are 19.10 kJ/mol and 18.95 kJ/mol, respectively. The amount of deviation from activation energy mentioned by Leino et al. [6] are 2 – 3%. In this analysis, it is apparent that CO₂ did not contribute much in rate of reaction because the amount of CO₂ reacted was small. Furthermore, the initial amount of CO₂ was much greater than ethanol and butylene oxide, hence it can be safely concluded that CO₂ is not the limiting reactant of DEC synthesis.

3.2.2 Kinetics Analysis in This Work

Reaction kinetics study in this work was applied to experimental data as shown in Table 8. Case 1 represents elementary reaction in which its reaction orders are equal to the stoichiometric coefficients, reaction rate equation equals to kCₐ²Cₐ. Case 2 indicates non-elementary reaction in which its reaction orders are not equal to the stoichiometric coefficients, reaction rate equation equals to kCₐ²Cₐ². Only forward reaction is considered while assuming that backward reaction is insignificant. Cₐ represents ethanol concentration and Cₐ signifies propylene oxide concentration.
Table 8. Experimental data in this work

| Temperature (K) | Initial Mole | Final Mole | Yield |
|-----------------|--------------|------------|-------|
|                 | Ethanol      | CO₂        | Propylene Oxide | DEC |        |
| 403             | 0.351        | 0.1064     | 0.035       | 0.0007 | 1.98%  |
| 423             | 0.351        | 0.1064     | 0.035       | 0.0015 | 4.39%  |
| 443             | 0.351        | 0.1064     | 0.035       | 0.0038 | 10.82% |
| 463             | 0.351        | 0.1064     | 0.035       | 0.0083 | 23.67% |
| 483             | 0.351        | 0.1064     | 0.035       | 0.0060 | 17.23% |

The yield of DEC is defined as the mole ratio of DEC formed to moles of epoxide. Result of reaction constant calculation and Arrhenius plot are displayed in Table 9 and Figure 2.

Table 9. Rate reaction constants in this work

| T (K) | Case 1, Ethanol | Case 1, PO | Case 2, Ethanol | Case 2, PO |
|-------|-----------------|------------|-----------------|------------|
|       | k               | ln k       | k               | ln k       | k           | ln k       |
| 403   | 0.001           | -7.26      | 0.004           | -5.59      | 0.011       | -4.52      | 0.058       | -2.85      |
| 423   | 0.002           | -6.43      | 0.009           | -4.75      | 0.025       | -3.70      | 0.132       | -2.02      |
| 443   | 0.004           | -5.43      | 0.023           | -3.76      | 0.066       | -2.71      | 0.354       | -1.04      |
| 463   | 0.012           | -4.44      | 0.063           | -2.77      | 0.174       | -1.75      | 0.928       | -0.08      |
| 483   | 0.008           | -4.87      | 0.041           | -3.19      | 0.115       | -2.16      | 0.615       | -0.49      |

Table 9 shows that at temperature of 403 – 463 K, reaction constant continuously rose which led to increasing yield of DEC as much as 23.67% at reaction condition of 463 K. On the other hand, at temperature of 483 K, reaction constant experienced a decrease, resulting in declining yield of DEC to 17.23%. This pattern further proves that DEC synthesis from carbon dioxide, ethanol and propylene oxide is an exothermic reaction. When temperature is increased beyond a certain point, reaction equilibrium will shift towards the reactant side, causing less formation of product.

Figure 2. Arrhenius plot in this work
As indicated on Table 10, activation energy for DEC synthesis is 55.62 kJ/mol if calculated based on the assumption of elementary reaction and 54.80 kJ/mol if assuming the reaction is non-elementary.

### Table 10. Activation energy of case 1 and case 2

| Parameter | Case 1 (Ethanol) | Case 1 (PO) | Case 2 (Ethanol) | Case 2 (PO) |
|-----------|----------------|-------------|----------------|-------------|
| Slope     | -6690.25       | -6690.25    | -6590.70       | -6590.70    |
| Intercept | 9.48           | 11.15       | 11.97          | 13.64       |
| A         | 13087.70       | 69860.88    | 157849.91      | 842587.33   |
| Ea (kJ/mol)| 55.62         | 55.62       | 54.80          | 54.80       |

### 3.3 Effect of Catalyst towards DEC Yield

The effect of binary catalyst towards DEC synthesis is shown on Table 11.

### Table 11. DEC Yield using various catalyst and epoxides

| Operating Conditions | Epoxides   | Catalyst | DEC Yield |
|----------------------|------------|----------|-----------|
| P initial CO$_2$ 30 bar, T 170°C; t = 3 hours; ethanol/epoxide = 1:5 | Ethylene oxide | KI | 1.31% |
|                      |            | KI/CeO$_2$ | 1.15%     |
| P initial CO$_2$ 30 bar, T 170°C; t = 3 hours ethanol/epoxide = 1:15 | Ethylene oxide | KI/EtONa | 5.18% |
|                      |            | KI/Zeolit | 3.61%     |
|                      |            | Butylene oxide | KI/EtONa | 21.01% |
|                      |            | KI/Zeolit | 21.00%    |
|                      |            | Propylene oxide | KI/EtONa | 19.29% |
|                      |            | KI/Zeolite | 7.15%     |

According to Table 11, on DEC synthesis using ethylene oxide as dehydrating agent, the use of KI as catalyst produced higher yield than binary catalyst KI/CeO$_2$. This result is in contrast with previous experiment conducted by Wang et al. [7]. DEC synthesis is a two-step reaction consists of cycloaddition followed by transesterification. Ionic salt such as KI in binary catalyst KI/CeO$_2$ is suitable to enhance cycloaddition process, while basic catalyst CeO$_2$ plays the role as co-catalyst to assist transesterification process. In the reaction of DEC synthesis using ethylene oxide and propylene oxide as dehydrating agent, binary catalyst KI/EtONa produced higher yield of DEC than KI/Zeolite. Meanwhile the difference of yield produced using KI/EtONa and KI/Zeolite appears to be trivial for butylene oxide. To gain better understanding of the kinetics of those reactions, calculation of reaction constant using the same method as Section 3.2 is performed with the result indicated on Table 12.

### Table 12. Comparison of reaction rate constant using KI/EtONa and KI/Zeolite

| Catalyst | Reaction rate constant (k) |
|----------|---------------------------|
|          | Case 1, Ethanol | Case 1, PO | Case 2, Ethanol | Case 2, PO |
| KI/EtONa | 0.008          | 0.061      | 0.120          | 0.946      |
| KI/Zeolite | 0.002        | 0.019      | 0.038          | 0.301      |
For both case 1 and case 1, DEC synthesis using KI/EtONa as catalyst led to greater value of reaction constant than KI/Zeolite. This calculation result is consistent with experimental yield of DEC which demonstrates higher yield in the presence of KI/EtONa catalyst compared to KI/Zeolite. Greater reaction constant indicates higher reaction rates which in turn generates higher yield of DEC. KI/EtONa is categorized as homogenous catalyst due to having same phase with reaction phase (liquid), while on the other hand solid catalyst KI/Zeolite is considered as heterogenous catalyst. High selectivity of homogenous catalyst causes higher reaction rate, thus allowing more formation of product with less amount of catalyst. Therefore, KI/EtONa can stimulate reactions of DEC synthesis better than KI/Zeolite.

3.4 P-T Diagram of Multicomponent in DEC Reactor
The fluid phase study on the synthesis of DEC from CO$_2$, ethanol and epoxides (ethylene oxide / butylene oxide / propylene oxide) was carried out by conducting 4 runs of experiment and using experimental data taken from Wang et al. [8] as shown in Table 13.

| Properties                   | This Work | Wang et al. [8] |
|------------------------------|-----------|-----------------|
|                              | Run 1     | Run 2 | Run 3 | Run 4 | Initial time | Final time |
| Temperature (°C)              | 177       | 170   | 170   | 170   | 150          | 150        |
| Pressure (bar)                | 35        | 30    | 30    | 30    | 50           | 50         |
| Reaction Time (hours)         | 3         | 3     | 3     | 3     | 0            | 3          |
| Ethanol                       | 86.100    | 0.520 | 0.745 | 0.011 | 0.304        | 0.255      |
| CO$_2$                        | 7.700     | 99.330 | 0.162 | 0.988 | 0.446        | 0.443      |
| Ethylene Oxide                | 5.400     | 0.150 | -     | -     | -            | -          |
| Butylene Oxide                | -         | -     | 0.037 | 0.001 | -            | -          |
| Propylene Oxide               | -         | -     | -     | -     | 0.250        | 0.232      |
| DEC                           | 0.400     | 0.0002| 0.016 | 0.023 | 0.000        | 0.035      |
| Ethylene Glycol               | 0.400     | 0.0002| -     | -     | -            | -          |
| 1,2-Butanediol                | -         | -     | 0.016 | 0.023 | -            | -          |
| Propylene Glycol              | -         | -     | -     | -     | 0.000        | 0.035      |

The PT diagram of multicomponent in DEC Reactor was obtained using Aspen Hysys V8.8, as shown in Figures 3 to 5.
The red dots indicate the operating conditions for the DEC synthesis reaction. DEC synthesis reaction can run in the liquid or vapor phase at a temperature of 177 °C and a pressure of 35 bar. This is evidenced by the presence of ethanol, CO$_2$ and EO components in the vapor and liquid phases, which can be seen in Table 14. In this case there is simultaneous between phase equilibrium and chemical reaction.

### Table 14. Chemical composition in liquid and vapor phase for Run 1

| Component          | Initial Time (t = 0 hour) | Final Time (t = 3 hours) |
|--------------------|---------------------------|--------------------------|
|                    | Vapour        | Liquid       | Vapour       | Liquid       |
| Ethanol            | 0.5596        | 0.8701       | 0.5556       | 0.8651       |
| CO$_2$             | 0.4022        | 0.0720       | 0.4074       | 0.0725       |
| Ethylene Oxide     | 0.0383        | 0.0580       | 0.0357       | 0.0541       |
| DEC                | 0.0000        | 0.0000       | 0.0010       | 0.0041       |
| Ethylene Glycol    | 0.0000        | 0.0000       | 0.0003       | 0.0042       |

While Figure 3b shows that the reaction runs in the superheated vapor phase at 170 °C and 30 bar.

(a) Run 3

(b) Run 4

**Figure 3. PT diagram for Run 1 and Run 2**

**Figure 4. PT diagram for Run 3 and Run 4**
4. Conclusions

Thermodynamics and kinetics study of diethyl carbonate (DEC) synthesis from CO₂, ethanol, and epoxides with various catalysts has been conducted in this study. DEC synthesis reaction with ethylene oxide produces the smallest Gibbs Energy, which means that this reaction is the most spontaneous compared to butylene oxide and propylene oxide as dehydrating agent. At temperature of 403 – 463 K, reaction constant continuously rose. On the other hand, at temperature of 483 K, reaction constant experienced a decrease. The activation energy for DEC synthesis is 55.62 kJ/mol if calculated based on the assumption of elementary reaction and 54.80 kJ/mol if assuming the reaction is non-elementary.

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