Modelling and simulation of hydrogenation of dimethyl oxalate in ethylene glycol production

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Abstract. In this work, the production of ethylene glycol was studied through a syngas-derived ethylene glycol route known as the indirect syngas-to-ethylene glycol process via oxalates. The improvement of hydrogenation of dimethyl oxalate process is pivotal in production of ethylene glycol. Therefore, it is noteworthy to analyse the effect of certain operating parameters on the reactor’s performance. Simulation analysis is an effective approach that allows to study the effect of hydrogen to dimethyl oxalate mole ratio (HDMR), Methyl Glycolate to Dimethyl Oxalate Mole Ratio (MDMR) and temperature on the conversion and selectivity of ethylene glycol. The kinetic of hydrogenation reaction in gas phase in the presence of catalyst was developed in Langmuir-Hinshelwood and Hougen-Watson form. A process model within plug flow reactor was developed using the RPLUG in Aspen Plus V10 simulator. The simulation data from literature was used to validate the model. The error obtained in validation for main product (ethylene) and by-product (methanol) found were below 10% which was acceptable. From the simulation, the reactor temperature and HDMR have significant effects on the conversion of dimethyl oxalate and yield of ethylene glycol. On the other hand, MDMR has little influence on the responding variable.

1. Introduction
Malaysia is one of the leading industries in production of petroleum and petrochemicals industry. Ethylene glycol is widely used industrial organic intermediate and it is ranked as the top 20 organic chemicals in the United States [1]. Ethylene glycol is organic dio-lipid which is an organic solvent that poisonous if indigested because it can cause dramatic toxicity [2]. It is colorless, odorless, viscous dihydroxy alcohol, clear and completely soluble in water. Its structural formula and molecular weight are C₂H₆O₂ and 62.068 g/mole, respectively [3]. The current industrial production of ethylene glycol worldwide mostly adopts the utilization of ethylene oxide as its main raw material which is non-sustainable sources. Thus, the production of ethylene glycol using syngas as its raw material has attracted researchers due to its cheap and abundance resources. The process is a two-stage reaction that involves coupling reaction of carbon monoxide in syngas and hydrogenation reaction of dimethyl oxalate using fluidized bed reactor in the presence of catalyst.

To improve the hydrogenation of dimethyl oxalate in production of ethylene glycol, it is vital to understand the effect of certain operating parameters on the conversion, yield and selectivity values. Nevertheless, experimental based study restricts a wide range of manipulating variables to be studied at a time. Sensitivity analysis is an effective tool that provides the complete analysis of the effect of changing in manipulated variables on performance of the process. It can be used to manipulate one or
more flowsheet variables and study the effect of the variation on other flowsheet variables. From the previous studies, the research works were focused on one or small number of manipulating parameter at a time, instead of the cumulative effect of all relevant combined factors on the selectivity of ethylene glycol. Most of the studies were experimental approach which was time consuming and tedious whereas simulation-based yielded fast results and was less prone to human error. Simulation-based approach have been carried out by Yu and Chien [4] which analyzed the hydrogen to dimethyl oxalate mole ratio (HDMR), Methyl Glycolate to Dimethyl Oxalate Mole Ratio (MDMR) and temperature on the conversion of ethylene glycol. Hence, in this work, to have better understanding on the parameters that effect the conversion, yield and selectivity cumulatively, sensitivity analysis tool in Aspen Plus was used for quick respond to study the process performance.

2. Reaction kinetic

The reaction system considered in this simulation work is the hydrogenation reactor in the ethylene glycol production plant. In this reaction, the dimethyl oxalate feed is hydrogenated into methyl glycolate which is an intermediate product to produce the desired ethylene glycol. The reaction takes place in gas phase in the presence of catalyst.

I. Dimethyl oxalate hydrogenation reaction towards intermediate product methyl glycolate and methanol

\[ C_4H_6O_4 + 2H_2 \rightarrow C_3H_6O_3 + CH_2O \]
dimethyl oxalate (DMO) hydrogen (H) methyl glycolate (MG) methanol (ME)

II. Methyl glycolate further hydrogenation reaction towards main product ethylene glycol methanol

\[ C_3H_6O_3 + 2H_2 \rightarrow C_2H_6O_2 + CH_4O \]
methyl glycolate (MG) hydrogen (H) ethylene glycol (EG) methanol (ME)

III. Side reaction: ethylene glycol hydrogenation reaction towards ethanol and water

\[ C_2H_6O_2 + H_2 \rightarrow C_2H_6O + H_2O \]
ethylene glycol (EG) hydrogen (H) ethanol (EOH) water (W)

The kinetic expressions for the two-step dimethyl oxalate to ethylene glycol reactions are shown in equation 1, 2 and 3 respectively [4].

\[ r_1 = \frac{k_1(P_{DMO} - \frac{P_{MG}P_{ME}}{K_{P1}P_{H}^2})}{1 + K_{EG}P_{EG} + K_{ME} + \frac{K_{DMO}P_{MG}P_{ME}}{K_{P1}P_{H}^2} + \frac{K_{MG}P_{EG}P_{ME}}{K_{P2}P_{H}^2} + K_{H}P_{H}} \]  

(1)

\[ r_2 = \frac{k_2\left(P_{MG} - \frac{P_{EG}P_{ME}}{K_{P2}P_{H}^2}\right)}{1 + K_{EG}P_{EG} + K_{ME} + \frac{K_{DMO}P_{MG}P_{ME}}{K_{P1}P_{H}^2} + \frac{K_{MG}P_{EG}P_{ME}}{K_{P2}P_{H}^2} + K_{H}P_{H}} \]  

(2)

\[ r_3 = \frac{k_3P_{EG}}{1 + K_{EG}P_{EG} + K_{ME} + \frac{K_{DMO}P_{MG}P_{ME}}{K_{P1}P_{H}^2} + \frac{K_{MG}P_{EG}P_{ME}}{K_{P2}P_{H}^2} + K_{H}P_{H}} \]  

(3)

Where, \(K_i\) is adsorption equilibrium constant for different species, \(i = \text{EG, ME, H, MG, and DMO}\), \(K_{pi}\) is reaction equilibrium constant, \(i = 1\) and \(2\), \(P_i\) is partial pressure for different species, \(i = \text{EG, ME, H, MG, and DMO}\) and \(k_i\) is pre-exponential factor for reactions, \(i = 1-3\).
3. Modeling and sensitivity procedure

In this work, simulation-based work was done to simulate the hydrogenation of dimethyl oxalate reaction in the production of ethylene glycol using Aspen Plus V10. Only, the second-stage hydrogenation reactor was chosen to be simulated since the first-stage reaction of producing dimethyl oxalate can be achieved up to 99.99 mole % according to Jiang et al. [6].

From thermodynamic point of view, DMO hydrogenation reactions are exothermic, and are thermodynamically favorable [4]. The reactor that was used for the catalytic hydrogenation reaction of dimethyl oxalate was a fluidized bed reactor. According to Zhu et al. [7] fluidized bed reactor can give high conversion, effectively remove heat and provide near-uniform temperature profile inside the reactor. To simplify the simulation of reactor without losing the capability of qualitatively illustrating the reaction performance and due to unavailability of this type of reactor in Aspen Plus version 10 database, isothermal plug flow reactor model was selected to model and simulate the hydrogenation reaction. The heat duty was assumed to be removed to maintain the reactor at the targeted temperature [4]. Schematic diagram of a plug flow reactor is shown in Figure 1.

The Non-Random Two Liquid Redlich-Kwong, NRTL-RK property method was considered as the thermodynamic model. The components involved in the reaction was dimethyl oxalate, water, methanol, ethylene glycol, methyl glycolate, ethanol and hydrogen. There were gas components in this system, thus Henry’s law was included to model the dissolution of gases into liquid [8].

![Figure 1: RPLUG Reactor Model](image)

The specification inputs to the RPLUG hydrogenation of dimethyl oxalate reactor block for Aspen simulation are shown in the Table 1 and Table 2.

| Specification         | Value   | Unit     |
|-----------------------|---------|----------|
| Total feed            | 7059.97 | kmol/hr  |
| Pressure              | 25.5    | bar      |
| Temperature           | 210     | °C       |
| Dimethyl oxalate      | 1.79    | mole %   |
| Methanol              | 26.42   | mole %   |
| Methyl glycolate      | 0.05    | mole %   |
| Hydrogen              | 71.69   | mole %   |
| Carbon monoxide       | 0.01    | mole %   |
Table 2: Reactor and Catalyst Specification [4]

| Specification                      | Value | unit |
|------------------------------------|-------|------|
| Length of reactor                  | 3.0   | m    |
| Diameter of reactor                | 1.0   | m    |
| Catalyst bed voidage              | 0.5   | -    |
| Particle density                   | 980   | kg/m³|
| Valid phase / process stream       | Vapor | -    |

The kinetic parameters for the main and side reaction for dimethyl oxalate hydrogenation are shown in the Table 3.

Table 3: Information of Reaction and Kinetics [4]

| Kinetic parameters | Pre-exponential factor (kmolkgeat⁻¹ h⁻¹ MPa⁻¹) | Activation energy (kJ/kmol) |
|--------------------|-----------------------------------------------|-----------------------------|
| k₁                 | 1.75E+06                                      | 37710                       |
| k₂                 | 3.87E+07                                      | 44284                       |
| k₃                 | 8.78E+13                                      | 137380                      |

| Equilibrium constant | Pre-exponential factor (MPa) | Activation energy (kJ/kmol) |
|----------------------|------------------------------|----------------------------|
| K_ME                 | 5.49E-12                     | 66356                      |
| K_EG                 | 1.85E-04                     | 18883                      |
| K_MG                 | 2.65E-02                     | 19242                      |
| K_DMO                | 7.92E-05                     | 118170                     |
| K_H₂                 | 1.20E-03                     | 8348                       |
| K_P₁                 | 1.63E+02                     | 17759                      |
| K_P₂                 | 2.87E-01                     | 15921                      |

The summary result of the simulation by Aspen Plus was compared with the results from literature. The feed was fed to the reactor at a specific temperature, pressure, hydrogen to dimethyl oxalate ratio as stated in Table 1. In this step, ethylene glycol, dimethyl oxalate and methyl glycolate was compared with the literature.

\[
\text{Error (\%)} = \frac{\text{simulated value} - \text{literature value}}{\text{literature value}} \times 100\% \quad (4)
\]

In this work, sensitivity analysis was carried out on the dimethyl oxalate hydrogenation reactor by manipulating several operating conditions, namely reactor temperature, methyl glycolate to dimethyl oxalate mole ratio (MDMR) and hydrogen to dimethyl oxalate ratio (HDMR) on the conversion of dimethyl oxalate and ethylene glycol selectivity. The formulas to calculate the conversion of dimethyl oxalate and selectivity of ethylene glycol are shown in the equations below.
\[
\text{Dimethyl oxalate conversion (\%)} = \frac{\text{inlet flow dimethyl oxalate} - \text{outlet flow dimethyl oxalate}}{\text{inlet flow dimethyl oxalate}} \times 100\% \quad (5)
\]

\[
\text{Overall ethylene glycol selectivity (\%)} = \frac{\text{ethylene glycol}}{\text{ethylene glycol} + \text{ethanol}} \times 100\% \quad (6)
\]

The range of manipulating variables used for sensitivity analysis is shown in Table 4.

| Parameter               | Lower range | Upper range |
|-------------------------|-------------|-------------|
| Reactor temperature (°C)| 160         | 240         |
| HDMR                    | 20          | 100         |
| MDMR                    | 1           | 10          |

### 4. Results and discussions

The results and analysis of model comparison and sensitivity study are presented in the following sections.

#### 4.1 Comparison of Simulation Results with Literature

In this step, ethylene glycol, methanol and hydrogen was compared with the results from Yu and Chien [4]. Table 5 shows the comparison of simulation results from simulation that was carried in Aspen Plus with those presented by Yu and Chien [4].

| product | literature | simulation result | % error |
|---------|------------|-------------------|---------|
|         | fraction   | mole flow(kmol/h) | fraction | mole flow(kmol/h) |
| MEOH    | 0.3112     | 2117.43           | 0.3091   | 2107.82            | 0.45 |
| H\textsubscript{2} | 0.6692     | 4553.28           | 0.6709   | 4574.38            | 0.46 |
| EG (main) | 0.0187     | 127.24            | 0.0169   | 115.57             | 9.17 |

From Table 5, it can be observed that the error obtained for the main product, ethylene glycol was only 9.17%. The error obtained for methanol and hydrogen were below 10% which was acceptable. Hence, it can be concluded that the RPLUG reactor model used in this study is acceptable and can be used for further analysis.

#### 4.2 Sensitivity Analysis of Hydrogenation Reaction Model

The sensitivity of conversion of dimethyl oxalate, yield and selectivity of ethylene glycol towards key operating variables were analyzed as mentioned earlier in the methodology. The sensitivity analysis was carried out by manipulating temperature, hydrogen to dimethyl oxalate mole ratio (HDMR) and methyl glycolate to dimethyl oxalate mole ratio (MDMR) in order to study their respective effects on dimethyl oxalate conversion, ethylene glycol selectivity and yield. Table 6 shows operating conditions for each case studied in the sensitivity analysis.
Table 6: Operating Conditions for Each Case Carried in Sensitivity Analysis

| Operating conditions | Case 1   | Case 2   | Case 3   |
|----------------------|----------|----------|----------|
| Temperature          | 160-240  | 210      | 210      |
| HDMR                 | 40       | 20-100   | 40       |
| MDMR (%)             | 2.8      | 2.8      | 1-10     |

Case 1: Effect of Reactor Temperature Towards Conversion of Dimethyl Oxalate and Yield of Ethylene Glycol

The effect of reactor temperature on conversion of dimethyl oxalate (DMO) and yield of ethylene glycol (EG) is shown in Figure 2.

Figure 2: Effect of Reactor Temperature on Conversion of DMO and Yield of EG

Based on Figure, it can be observed that conversion of dimethyl oxalate increases from 9% to 100% when the temperature increases from 160 to 220°C [5]. This indicate that the reactor temperature has significant effect on the dimethyl oxalate conversion and the high temperature seems beneficial for the reaction. However, when temperature increases above 220°C, it has almost no influence on dimethyl oxalate conversion because dimethyl oxalate has been almost 100% converted under the given reaction conditions.

From reaction point of view, for a reaction to occur, the reactant molecules must collide with each other which will occur when energy is greater than the activation energy. When the temperature increases, the reactant molecules move faster and collide more frequently with each other. Increase the temperature will increases the rate of a reaction and thus increases the conversion.

As shown in Figure, when temperature increases from 160 to 210°C, ethylene glycol (EG) yield increase from 24 to 96%, while selectivity of ethylene glycol decreases from 99.9 to 94.6 %. The yield increases because the conversion increases while the formation of ethanol is still low as it favours high temperature. Selectivity of ethylene glycol decrease when the temperature exceeds 210°C. This is because when the reaction temperature is too high, further hydrogenation of ethylene glycol occurs, which leads to the formation of ethanol as the side product [5]. Since the conversion maintains at maximum value constantly, while the selectivity tends to decrease. Therefore, the yield obtained also decreases at this condition.

According to Yu and Chien [4], the formation of ethanol which is the side product has higher activation energy (137380 kJ/kmol) than the formation of ethylene glycol which is the main product (44284 kJ/kmol). Consequently, at temperature higher than 210°C, the formation of ethanol will occur
Thus, the formation of side product become more prominent and the yield and selectivity of ethylene glycol decreases with the increase in reactor temperature.

**Case 2: Effect of Hydrogen to Dimethyl Oxalate Mole Ratio Towards Conversion of Dimethyl Oxalate and Yield of Ethylene Glycol**

The effect of HDMR on conversion of dimethyl oxalate (DMO) and yield of ethylene glycol (EG) is shown in Figure 3.

![Figure 3: Effect of Hydrogen to Dimethyl Oxalate Mole Ratio on Conversion of DMO and Yield of EG](image)

From Figure 3, it can be observed that the dimethyl oxalate conversion increases from 54 to 100% when HDMR increases from 20 to 54. This shows that hydrogen to dimethyl oxalate mole ratio plays an important role in the hydrogenation reaction [5]. However, increase in HDMR above 54, shows almost no influence on dimethyl oxalate conversion because dimethyl oxalate has almost 100% converted which means dimethyl oxalate has already finish reacted.

As shown in Figure 3, the ethylene glycol selectivity increases slightly when the HDMR increases. The yield rises from 75 to 99 % when HDMR rises from 20 to 100. This shows that hydrogen to dimethyl oxalate mole ratio has significant effect on the yield of ethylene glycol. As observed, when hydrogen to dimethyl oxalate mole ratio is low, the yield is also low.

According to Yu and Chien [4], under low hydrogen to dimethyl oxalate mole ratio, the hydrogenation reaction rate will be low. When the hydrogenation reaction rate is low, conversion of methyl glycolate (intermediate product) to ethylene glycol will be low. Hence a longer residence time required to achieve certain ethylene glycol yield. This may lead to the formation of other side products. This will also cause the accumulation of methyl glycolate in the reactor which will in turn leads to plugging of catalyst pores and catalyst deactivation.
Case 3: Effect of Methyl Glycolate to Dimethyl Oxalate Mole Ratio Towards Conversion of Dimethyl Oxalate and Yield of Ethylene Glycol

The effect of MDMR on conversion of dimethyl oxalate (DMO) and yield of ethylene glycol (EG) is shown in Figure 4.

![Figure 4: Effect of Methyl Glycolate to Dimethyl Oxalate Mole Ratio on Conversion of DMO and Yield of EG](chart)

From Figure 4, it can be observed that the conversion of dimethyl oxalate, decreases from 96 to 93% when MDMR increases from 1 to 10%. This shows that MDMR has little influence on the conversion of dimethyl oxalate. Methyl glycolate (C₃H₆O₃) is an intermediate product which produce under reversible reaction from dimethyl oxalate conversion. Hence, when mole flowrate of methyl glycolate increases at the inlet stream of the reactor, the reaction will favour backward reaction. This will in turn produce dimethyl oxalate and thus lead to lower conversion of dimethyl oxalate. Therefore, increase in methyl glycolate to dimethyl oxalate mole ratio will decrease the conversion [4].

From Figure 4, selectivity of ethylene glycol remains unchanged while yield of ethylene glycol rises slightly. This shows that MDMR has little influence on the yield of ethylene glycol. Methyl glycolate conversion to ethylene glycol is a reversible reaction. Thus, when methyl glycolate mole flowrate increases, the reaction will favour forward reaction. The conversion of methyl glycolate to ethylene glycol will increase and lead to high yield of ethylene glycol.

5.0 Conclusion

From the sensitivity test, it is clearly shown that two out of three manipulating variables studied which are reactor temperature, and HDMR have significant effects on the conversion of dimethyl oxalate and yield of ethylene glycol. On the other hand, MDMR has little influence on the responding variable. On the other hand, the productivity of dimethyl oxalate hydrogenation reaction is sensitive to two of the variable mentioned earlier.

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