

**SIMULATION AND OPTIMIZATION OF ETHYLENE
GLYCOL PRODUCTION**

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**SIMULATION AND OPTIMIZATION OF ETHYLENE
GLYCOL PRODUCTION**

by

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NOMENCLATURES

Symbols	Description	unit
k_1	Rate constant of dimethyl oxalate hydrogenation	kmol/(kgcat.h.Mpa)
k_2	Rate constant of methyl glycolate hydrogenation	kmol/(kgcat.h.Mpa)
k_3	Rate constant of ethylene glycol hydrogenation	kmol/(kgcat.h.Mpa)
K_{ME}	Adsorption equilibrium constant of methanol	MPa ⁻¹
K_{EG}	Adsorption equilibrium constant of ethylene glycol	MPa ⁻¹
K_{MG}	Adsorption equilibrium constant methyl glycolate	MPa ⁻¹
K_{DMO}	Adsorption equilibrium constant of dimethyl oxalate	MPa ⁻¹
K_H	Adsorption equilibrium constant of hydrogen	MPa ⁻¹
K_{P1}	Equilibrium constant reaction 1	MPa ⁻¹
K_{P2}	Equilibrium constant reaction 2	MPa ⁻¹
r_1	Reaction rate of dimethyl oxalate hydrogenation	kmol/(kgcat.h)
r_2	Reaction rate of methyl glycolate hydrogenation	kmol/(kgcat.h)
r_3	Reaction rate of ethylene glycol hydrogenation	kmol/(kgcat.h)
P_{DMO}	Partial pressure of dimethyl oxalate	MPa
P_{MG}	Partial pressure of methyl glycolate	MPa
P_{EG}	Partial pressure of ethylene glycol	MPa
P_{ME}	Partial pressure of methanol	MPa
P_H	Partial pressure of hydrogen	MPa
DMO	Dimethyl oxalate	-
EG	Ethylene glycol	-
MEOH	Methanol	-
HDMR	Hydrogen to dimethyl oxalate mole ratio	-
HDER	Hydrogen to diethyl oxalate mole ratio	-
MDMR	Methyl glycolate to dimethyl oxalate mole ratio	-

SIMULASI DAN PENGOPTIMUMAN PENHASILAN ETILENA GLIKOL

ABSTRAK

Penghasilan etilena glikol dari syngas menggunakan hidrogenasi dimetil oksalat fasa-gas pada pemangkin berasaskan tembaga adalah salah satu teknologi penting. Pengoptimuman terhadap penukaran, selektiviti dan hasil pengeluaran berskala industri sukar dilakukan menggunakan pendekatan asas eksperimen. Oleh itu, perisian simulasi Aspen Plus Versi 10 digunakan untuk simulasi, menguji sensitiviti parameter operasi ke arah penukaran, selektiviti dan hasil pengeluaran, dan mengoptimumkan pengeluaran etilena glikol menggunakan model reaktor RPLUG dengan ciri-ciri akhir produk yang dikehendaki. Hasil simulasi yang diperoleh boleh diterima kerana kesilapan yang dikira untuk pengeluaran etilena glikol apabila dibandingkan dengan kesusasteraan hanya sekadar 9.17 %. Analisis sensitiviti yang dijalankan menunjukkan penukaran dimetil oksalat dan hasil etilena glikol adalah maksimum pada suhu reaktor, tekanan dan hidrogen kepada nisbah mole dimetil oksalat sebanyak 212 °C, 29 bar dan 46 masing-masing. Metil glikolat kepada nisbah mol dimetil oksalat tidak menunjukkan kesan yang signifikan ke atas penukaran dan hasil pengeluaran. Oleh itu, pembolehubah tersebut tidak termasuk dalam kajian pengoptimuman. Selepas pengoptimuman, penukaran maksimum dimetil oksalat, selektiviti etilena glikol dan hasil pengeluaran etilena glikol masing-masing adalah 100 %, 98 % dan 99.7 %. Tindak balas ini telah dioptimumkan pada 200 °C, 37 bar, kepekatan dimetil oksalat pada 23.6 wt. % dan hidrogen kepada nisbah mol dimetil oksalat sebanyak 64.

SIMULATION AND OPTIMIZATION OF ETHYLENE GLYCOL PRODUCTION

ABSTRACT

Ethylene glycol production from syngas using gas-phase hydrogenation of dimethyl oxalate on a copper-based catalyst is one of the crucial technologies. Optimization on the conversion, selectivity and yield of industrial scale production is difficult to be done using experimental base approach. Hence, Aspen Plus Version 10 simulation software is used to simulate, test the sensitivity of operating parameter towards conversion, selectivity and yield, and optimize the production of ethylene glycol using RPLUG reactor model with desired end-product characteristics. The simulation results obtained is acceptable since the error calculated for the ethylene glycol production when compared with literature is only 9.17 %. Sensitivity analysis conducted shows that the conversion of dimethyl oxalate and yield of ethylene glycol were maximum at reactor temperature, pressure and hydrogen to dimethyl oxalate mole ratio of 212 °C, 29 bar and 46 respectively. Methyl glycolate to dimethyl oxalate mole ratio do not show significant effect on the conversion and yield. Hence, the variable not included in the optimization study. After optimization, the maximum conversion of dimethyl oxalate, selectivity of ethylene glycol and yield of ethylene glycol obtained are 100 %, 98 % and 99.7 % respectively. This reaction has been optimized at 200 °C, 37 bar, 23.6 wt. % of dimethyl oxalate concentration and hydrogen to dimethyl oxalate mole ratio of 64.

CHAPTER ONE

INTRODUCTION

1.1 Ethylene Glycol Production Process

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 (Schwaar, 1997). Ethylene glycol is organic dio-lipid which is an organic solvent that poisonous if indigested because it can cause dramatic toxicity (Brent et al., 1999). It is colorless, odorless, viscous dihydroxy alcohol, clear and completely soluble in water. Its structural formula and molecular weight are $C_2H_6O_2$ and 62.068 g/mole, respectively (Inyang, 2017). Ethylene glycol is widely used as an ingredient of electrolytic condensers, hydraulic brake fluid and synthetic waxes.

Heavy industrialization in countries such as Japan, China, and India have contributed significantly to the glycols demand over the recent years. The global glycols demand was exceeded 19,300 kilo tons in 2015 and is estimated to grow at a Compound Annual Growth Rate of 4.6% from 2016 to 2025 (Research, 2017). Asia Pacific is expected to witness the largest growth in next nine years and is expected to grow at an estimated CAGR of 5.0% from 2016 to 2025 (Research, 2017). The world consumes over 5 billion gallons of ethylene glycol per year and analysts expect that global demand will continue growing around 7% per year (Washington, 2011). These statistics prove that ethylene glycol has well-established market which contributed to its mass production around the world.

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 and investors 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. This route is only commercialized in china, because of its rich coal resources (Luo et al., 2012). Hence, optimization on the operating variables of ethylene glycol plant is vital to have a maximum production of ethylene glycol.

The production of ethylene glycol using syngas is gaining importance worldwide and thus the process needs to be optimized fully in term of the operating variables, so that the selectivity and yield of ethylene glycol are maximized. With the development of computer aided simulation software such as Aspen Plus V10, it is possible to simulate certain process with desired end-product characteristics. Proper optimization can significantly improve the selectivity and quality of the desired product as well as make the process safer with less formation of unwanted by-product (Taqvi et al., 2016).

Moreover, to find the optimum operating parameter is not easy without Aspen Plus software. Experimental based study on the optimum operating parameter is not accurate as the plant operate with large amount of substances. To maximize the production, it is vital to understand the effect of certain operating parameters on the production of ethylene glycol. However, experimental based study is time consuming. With Aspen Plus V10, sensitivity analysis tool can be used for quick respond of process performance to change in the input operating variables. This enables a wide range of manipulating variables to be studied at a time and a set of results of the user's choice can be tabulated easily. Hence, Aspen Plus software makes easier to find the optimum operating parameter.

1.2 Problem Statement

Most of the ethylene glycol produced in the world are using ethylene as their raw material. Ethylene is a petroleum-based feedstock which is a non-renewable source. Hence, ethylene glycol synthesis from syngas has drawn more attention as the alternative routes (Song et al., 2013). Since the production of ethylene glycol using syngas plant is currently only established in china according to Luo et al. (2012), it is utmost importance that the process optimization is carried out to obtain high production of ethylene glycol.

Furthermore, optimization analysis is addressed by repeatedly carrying out experiment until the optimum condition for the process is obtained. However, optimizing ethylene glycol production using plant information in collecting data is time-consuming to be performed. Hence, this work tries to simulate the dimethyl oxalate hydrogenation reaction which is the second-stage reaction using Aspen Plus V10 to achieve higher production of ethylene glycol.

Next, to have higher 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. The worst is the plant need to be disturbed or stopped for a while which lead to loss in the production line. Luckily, with Aspen Plus V10, sensitivity analysis tool can be used for quick respond to study the process performance.

Moreover, since the previous research works have been mostly experimental based on this topic, the parameters studied have also been limited and their combined effect on the yield of ethylene glycol is not thoroughly explored. Thus, this causes lack of optimum set of reaction conditions. Therefore, optimization studies using Aspen Plus need to be done to find out the best optimum parameter conditions for maximum yield of ethylene glycol cumulatively.

From the market demand statistics, the global demand and consumption for ethylene glycol will continue to grow in the upcoming decades. Hence, comes the importance of optimizing the ethylene glycol production process to increase the quality and yield. Research must be done efficiently to improve the ethylene glycol production process to supply the ever-increasing needs of the market. Therefore, in this work, the Aspen Plus V10 software is used to study the individual and combined effects of the various manipulating variables on the yield of ethylene glycol using sensitivity analysis tool. Then followed by optimization of the to maximize the production of ethylene glycol.

1.3 Research Objectives

The objectives for this work are as follows:

1. To simulate the hydrogenation reaction of dimethyl oxalate to produce ethylene glycol in the isothermal plug flow reactor, RPLUG model.
2. To investigate the effect of operating variables towards the conversion of dimethyl oxalate, yield and selectivity of ethylene glycol.
3. To carry out optimization study on the production of ethylene glycol.

1.4 Scope of Work

In this work, simulation-based work is done to simulate the hydrogenation of dimethyl oxalate reaction in the production of ethylene glycol using Aspen Plus V10. This work focuses solely on simulation-based approach rather than experimental-based approach to study the effect of the various operating variables on the production of ethylene glycol. Only, the second-stage hydrogenation reactor is 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. (2012).

Firstly, Aspen Plus V10 is used to develop simulation flowsheet for the isothermal plug flow reactor, RPLUG model of dimethyl oxalate hydrogenation process. The simulation results obtained are then compared with Yu and Chien (2017). If the simulation results obtained is comparable with the literature, sensitivity analysis is then carried on the operating variables using the sensitivity analysis tool. This analysis is done to find out the effect of operating variables towards the production of ethylene glycol.

The effect of temperature, pressure, concentration of dimethyl oxalate, hydrogen to dimethyl oxalate mole ratio and methyl glycolate to dimethyl oxalate mole ratio on the conversion of dimethyl oxalate and selectivity of ethylene glycol are studied to obtain the optimum set of operating conditions for the dimethyl oxalate hydrogenation reaction. Finally, the optimization of the ethylene glycol production is performed using the optimization tool in Aspen Plus by maximizing the yield of ethylene glycol. The optimum reaction conditions are essential to produce high dimethyl oxalate conversion and ethylene glycol selectivity in the production plant.

1.5 Thesis organization

This thesis consists of five chapters. The following are the thesis organization in this study:

Chapter one (Introduction) gives a general overview about the ethylene glycol process, problem statement, objectives and scope of work for this simulation study.

Chapter two (Literature Review) outline the literature review about the production of ethylene glycol from general point of view that includes petroleum-derived and syngas derived ethylene glycol process. Next, reaction mechanism of the ethylene glycol from syngas and previous study regarding this process are briefly described in this chapter.

Chapter three (Materials and Methods) shows the steps regarding this simulation study to achieve all the objectives. Firstly, develop the plug flow reactor model (RPLUG) and compare the simulation result with Yu and Chien (2017). Then, investigate the effect of operating variables towards the conversion of dimethyl oxalate, yield and selectivity of ethylene glycol using sensitivity analysis tool. Finally, carry out optimization study on the production of ethylene glycol using optimization tool in Aspen Plus V10.

Chapter four (Results and Discussion) presents the results and discussion of the simulation study. The simulated result is compared with Yu and Chien (2017). The effect of operating variables towards the conversion of dimethyl oxalate, yield and selectivity of ethylene glycol are briefly explained and justified in term of reaction point of view. Finally, results obtained from optimization are discussed in this chapter.

Chapter five (Conclusions) concludes the findings from this simulation study. Recommendations to improve the current simulation results are also presented in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1 Manufacture of Ethylene Glycol

2.2 Indirect Syngas-to-ethylene Glycol Process via Oxalates

In this work, the production of ethylene glycol is studied through a syngas-derived ethylene glycol route known as the indirect syngas-to-ethylene glycol process via oxalates. The indirect method to produce ethylene glycol from syngas requires two-stage reaction. First, coupling reaction of carbon monoxide to form oxalate. Then, the oxalate is further hydrogenated to form ethylene glycol which is the targeted product. The oxalate can be separated to very high purity with a high recovery (Jiang et al., 2012).

2.2.1 Coupling Reaction

Coupling reaction of carbon monoxide to dimethyl oxalate is an interesting catalytic process not only because of the increasing coproduction of ethylene glycol but also due to the emerging perspectives to provide a sustainable and economical route for ethylene glycol production. This method are more promising methods for ethylene glycol synthesis than the use of petroleum. The conversion of carbon monoxide to oxalate opened a new route for the production of oxalate from abundant and cheap sources (Song et al., 2013).

According to Song et al. (2013), research on catalyst activity focused on palladium, Pd loaded on α -Al₂O₃ with different co-catalysts has been reported for CO coupling reaction. Zhao et al. (2004) found that increasing the specific surface area, pore size or volume of the support improved the catalytic activity of the catalyst which lead to high conversion. A co-catalyst dispersed palladium is more efficient because it decreases the palladium particle size and hence increased the conversion (Zhao et al., 2004).

2.2.2 Hydrogenation of Oxalate

2.3 Reaction Mechanism and Kinetics

The study of detailed process of reaction mechanism is vital because it helps in understanding and controlling chemical reactions. Most reaction of great commercial importance can proceed by more than one reaction path. Hence, knowledge of the reaction mechanism involve may make it possible to choose reaction condition favoring one path over another, thereby giving maximum amounts of desired products and minimum amounts of undesired products. Moreover, sometime it is possible to predict the course of untried reaction (Mare, 2017).

Figure 2.1 shows the mechanism scheme of the hydrogenation of dimethyl oxalate on Cu/SiO₂. Firstly, Hui et al. (2012) have discovered that CH₃O-M and CH₃OC(O)(O)C-M formed after the dissociative adsorption of dimethyl oxalate on the catalyst via cleavage of C-O bond adjacent to the carbonyl group. In the actual reaction process, only small amount of CH₃OC(O)(O)C-M will produce CH₃O-M and M-C(O)(O)C-M by further dissociation. Most CH₃OC(O)(O)C-M will react with hydrogen atom to produce methyl glycolate fast after it formed. Hence, the reaction mainly proceeds along Route 2 and only small amounts of CH₃OC(O)(O)C-M will react along Route (1) as shown in Figure 2.1 (Hui et al., 2012).

This indicates that the dissociation adsorption is slower than hydrogenation. Methanol and methyl glycolate are produced by CH₃O-M and HOC(O)(O)C-M reacting with hydrogen atom. Some methyl glycolate are desorbed as by-product, however, other methyl glycolate will produce CH₃O-M and HOCH₂(O)C-M after dissociative adsorption on the active site of the catalyst. Most of HOCH₂(O)C-M will produce ethylene glycol

after hydrogenation proceeds, the rest will be adsorbed strongly on silica to form the residual species Si-OH-HOCH₂C(O)-OSi (Hui et al., 2012).

Figure 2.1 shows the mechanism scheme of the hydrogenation of dimethyl oxalate on Cu/SiO₂.

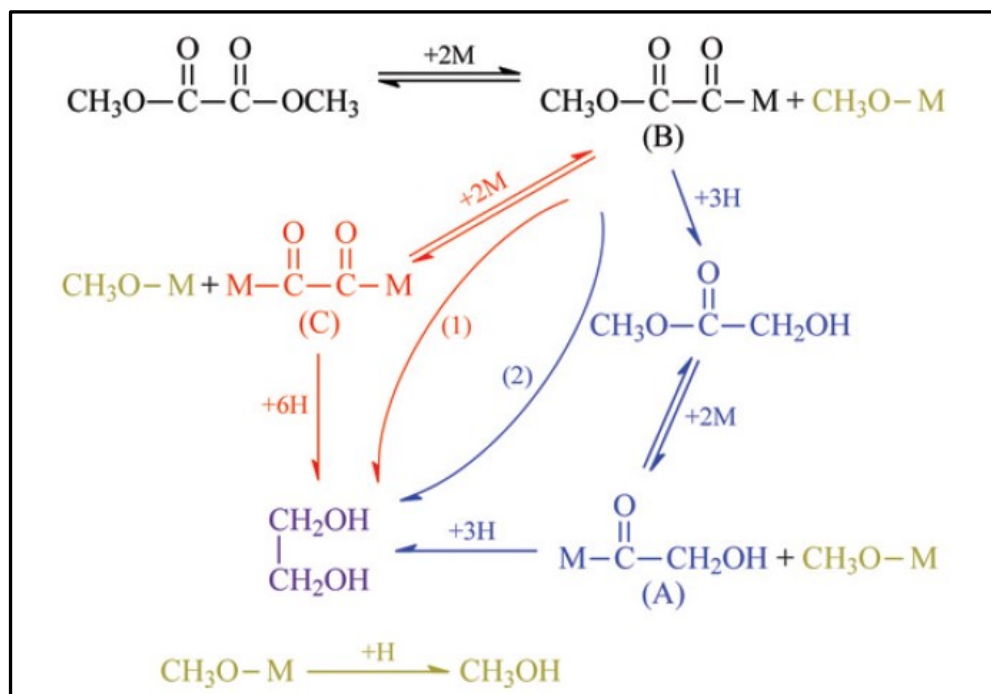


Figure 2.1: Proposed Scheme for the Hydrogenation Mechanism of Dimethyl Oxalate Over Cu/SiO₂ (Hui et al., 2012)

Li et al. (2015) has propose kinetic expressions for the mechanism of dimethyl oxalate hydrogenation in Langmuir-Hinshelwood form. From thermodynamic point of view, the reactions are exothermic and thermodynamically feasible. There are several important design variables in this reaction such as dimethyl oxalate concentration, hydrogen to dimethyl oxalate mole ratio, reaction temperature and pressure. The kinetic expressions for the two-step dimethyl oxalate to ethylene glycol reactions are shown in Equations 2.1, 2.2 and 2.3 respectively (Li et al., 2015).

$$r_1 = \frac{k_1(P_{DMO} - \frac{P_{MG}P_{ME}}{K_{P1}P_H^2})}{1 + K_{EG}P_{EG} + K_{ME} + \frac{K_{DMO}P_{MG}P_{ME}}{K_{P1}P_H^2} + \frac{K_{MG}P_{EG}P_{ME}}{K_{P2}P_H^2} + K_H P_H} \quad (2.1)$$

$$r_2 = \frac{k_2(P_{MG} - \frac{P_{EG}P_{ME}}{K_{P2}P_H^2})}{1 + K_{EG}P_{EG} + K_{ME} + \frac{K_{DMO}P_{MG}P_{ME}}{K_{P1}P_H^2} + \frac{K_{MG}P_{EG}P_{ME}}{K_{P2}P_H^2} + K_H P_H} \quad (2.2)$$

$$r_3 = \frac{k_3 P_{EG}}{1 + K_{EG}P_{EG} + K_{ME} + \frac{K_{DMO}P_{MG}P_{ME}}{K_{P1}P_H^2} + \frac{K_{MG}P_{EG}P_{ME}}{K_{P2}P_H^2} + K_H P_H} \quad (2.3)$$

2.4 Hydrogenation of Oxalate to Ethylene Glycol in the Presence of Catalyst

Several researches in recent years have shown the correlation of factors such as reaction temperature and pressure, dimethyl oxalate concentration, hydrogen to dimethyl oxalate mole ratio (HDMR) and weight liquid hourly space velocity (WLHSV) on the dimethyl oxalate conversion and yield of ethylene glycol using syngas feedstock. As Aspen Plus simulation-based researches are very limited, this section will discuss mainly on few experimental literatures done on the factors affecting dimethyl oxalate conversion and ethylene glycol yield in the presence of catalysts.

Matteoli et al. (1988) reported noble-metal-catalyzed homogeneous hydrogenation of oxalate. The selectivity for ethylene glycol reached 82% while the conversion of dimethyl oxalate reached 95% under conditions of 180 °C/ P_{H_2} (rt) = 20 MPa and using $Ru(CO)_2(CH_3COO)_2(P^iBu_3)_3$ as the catalyst. Ethylene glycol may be obtained selectively from dimethyl oxalate by hydrogenation in homogeneous phase in the presence of $Ru_2(CO)_4(CH_3COO)_2(P^iPr_3)_2$ to obtain complete conversion of dimethyl oxalate that carried out at 120 °C (Matteoli et al., 1991). Ru catalyst have outstanding catalytic performance, however their drawbacks such as high costs, preparation difficulties, short lifetimes and difficulties in catalyst separation, have restricted their industrial applications (Matteoli et al., 1988, Matteoli et al., 1991).

Research on hydrogenation of ethylene glycol has focused on gas-phase methods where the performance of various catalysts has been reported. Huang et al. (1996) used a supported Cu-Cr/SiO₂ catalyst to catalyze the hydrogenation of diethyl oxalate. They obtained 99.8% conversion of diethyl oxalate and 95.3% ethylene glycol selectivity. The reaction was carried out under conditions of 205 to 240 °C with 2.5 to 3.0 MPa. The molar ratio of hydrogen to oxalate used in the experiment is 60 (Huang et al., 1996).

Xu et al. (1995) used a Cu-Zn/SiO₂ catalyst to catalyze the hydrogenation of diethyl oxalate to ethylene glycol. The reaction was carried out under conditions of 200-250 °C and at a pressure of 3.0 MPa. The molar ratio of hydrogen to diethyl oxalate (HDER) is around 30 to 100. They obtained a 95% conversion of diethyl oxalate and more than 90% ethylene glycol selectivity. They also studied the reaction kinetic of the catalytic hydrogenation of diethyl oxalate to ethylene glycol in the vapor phase over a copper-base catalyst. The experiments were carried out in a continuous flow microreactor where the kinetic model obtained follows the Langmuir-Hinshelwood mechanism in which hydrogen adsorbs dissociatively (Xu et al., 1995). Li et al. (2004) studied Cu/SiO₂ catalyst under conditions of 205 °C and pressure of 2.5 MPa with hydrogen to oxalate mole ratio of 80; the ethylene glycol yield reaches 99.1%.

Based on previous research, dimethyl oxalate is first dissolved in methanol with 15-30 wt.% dimethyl oxalate concentration and then the solution is reacted with hydrogen with high HDMR. According to Yin et al. (2008), dimethyl oxalate solution concentration has little influences on dimethyl oxalate concentration. However, ethylene glycol selectivity rises with increasing dimethyl oxalate solution. At 473 K, 2.5 MPa, HDMR of 40 and 15 wt.% of dimethyl oxalate concentration in methanol, both the selectivity of ethylene glycol and conversion of dimethyl oxalate exceed 99% (Yin et al., 2008).

Zhang et al. (2007) reported that conversion of dimethyl oxalate and ethylene glycol selectivity improved at higher temperature, higher pressure, higher HDMR and lower space velocity (SV), however, selectivity of byproduct also increased. The optimum conditions were: pressure of 2 MPa, temperature of 205-210 °C, hydrogen to dimethyl oxalate mole ratio of 80-100 and space velocity of 10 mmol/(g.h). It also been reported that Langmuir-Hinshelwood model with non-dissociative hydrogen adsorption is suitable for this reaction (Zhang et al., 2007).

HDMR plays a significant role in the hydrogenation reaction. The hydrogenation rate will be too low if the HDMR is low. This means a longer residence time is required to achieve certain ethylene glycol yield and may lead to the formation of other side products. According to Tahara (1984) the residence time should be less than 5s. Furthermore, the conversion of methyl glycolate to ethylene glycol will be low and accumulation of methyl glycolate is likely to occur that cause plugging of catalyst pores if the reaction rate is low. While, if the hydrogen to dimethyl oxalate mole ratio is too high, the ethylene glycol will further undergo hydrogenation to form ethanol (Tahara, 1984).

Simulation-based approach has been done by Yu and Chien (2017) that studies the HDMR, methyl glycolate to dimethyl oxalate mole ratio and temperature on the selectivity of ethylene glycol. Furthermore, the economic performance while optimizing the ethylene glycol and complete design flowsheet including the separation part such as distillation column has been explored. This lead to less focus on the reactor and the cumulative parameter that effect the conversion of dimethyl oxalate and ethylene glycol selectivity. Hence, in this work to have better understanding on the parameters that effect the conversion and selectivity cumulatively, the reactor is simulated again and include the parameters that abandoned by Yu and Chien (2017).

From the above studies, it can be observed that the research works has been focused on one or small number of manipulating parameter at a time, instead of the cumulative effect of all relevant factors combined to maximize the selectivity of ethylene glycol their respective experimental and simulation approach. Most of the studies are experimental approach which is time consuming and tedious whereas Aspen Plus simulation software yield fast results and are less prone to human error.

Aspen Plus V10 is a computer-aided software which utilizes underlying physical relationships including material and energy balance, thermodynamic equilibrium and rate of equations to accurately and efficiently predict process behavior (Eden, 2012). Moreover, the software explores flexibility through the Aspen Plus Model Sensitivity Tool. Here it can quickly study the sensitivity of process performance to changes the key operating parameters.

Consequently, a wide range of operating parameters can be studied at a time which is advantageous than the previous experimental-based research works. Utilizing a base set of initial condition from sensitivity analysis, Aspen Plus Optimization Tool uses its algorithm to determine local maxima in the objective function. Hence, the production of ethylene glycol could be optimized by maximizing the yield of ethylene glycol.

Table 2.1 shows the summary of hydrogenation of oxalate to ethylene glycol research work. Experimental approach limits the number of parameter studied on the dimethyl oxalate conversion, selectivity and yield of ethylene glycol which result in one parameter being studied at a time. Wide range of optimum parameter obtained from the experiment namely hydrogen to oxalate mole ratio, represent less accurate results as it not specific to a value and the studies limited to certain catalyst.

Table 2.1: Summary of Hydrogenation of Oxalate to Ethylene Glycol Research Work

	Author	Year	experiment	simulation	optimization	model
1	(Tahara)	1984	yes	no	no	no
2	(Matteoli et al.)	1988	yes	no	no	no
3	(Matteoli et al.)	1991	yes	no	no	no
4	(Xu et al.)	1995	yes	no	no	yes
5	(Huang et al.)	1996	yes	no	no	no
6	(Zhang et al.)	2007	yes	no	no	no
7	(Yin et al.)	2008	yes	no	no	no
8	(Yue et al.)	2012	yes	no	no	no
9	(Huang et al.)	2013	yes	no	no	no
10	(Wen et al.)	2014	yes	no	no	no
11	(Popa et al.)	2015	yes	no	no	no
12	(Li et al.)	2015	yes	no	no	yes
13	(Song et al.)	2015	yes	no	no	no
14	(Zheng et al.)	2015	yes	no	no	yes
15	(Wen et al.)	2015	yes	no	no	no
16	(Li et al.)	2016	yes	no	no	no
17	(Yu and Chien)	2017	no	yes	yes	yes
18	(Satapathy et al.)	2017	yes	no	no	no
19	(Qi et al.)	2018	yes	no	no	no
20	(Yang et al.)	2018	no	yes	yes	yes
21	(Wei et al.)	2018	yes	no	yes	no

	Author	Year	Parameter studied
1	(Tahara)	1984	Residence time, catalyst performance
2	(Matteoli et al.)	1988	Catalyst performance
3	(Matteoli et al.)	1991	Catalyst performance
4	(Xu et al.)	1995	Reaction temperature, HDER, kinetic model
5	(Huang et al.)	1996	Reaction temperature, pressure, catalyst performance
6	(Zhang et al.)	2007	Reaction temperature, pressure, HDMR, SV
7	(Yin et al.)	2008	Dimethyl oxalate concentration
8	(Yue et al.)	2012	Catalyst performance
9	(Huang et al.)	2013	Catalyst performance
10	(Wen et al.)	2014	Catalyst performance
11	(Popa et al.)	2015	Catalyst, temperature, pressure, WLHSV
12	(Li et al.)	2015	Catalyst performance, kinetic model
13	(Song et al.)	2015	Catalyst performance, reaction temperature
14	(Zheng et al.)	2015	Catalyst performance, kinetic model
15	(Wen et al.)	2015	Catalyst performance, reaction temperature, LHSV
16	(Li et al.)	2016	Catalyst performance
17	(Yu and Chien)	2017	Simulation model, kinetic model, reaction temperature, MDMR, HDMR
18	(Satapathy et al.)	2017	Catalyst performance
19	(Qi et al.)	2018	Catalyst performance
20	(Yang et al.)	2018	Mathematics model based on industrial data
21	(Wei et al.)	2018	Reactor and column design

CHAPTER THREE

MATERIALS AND METHODS

3.1 Overview of Research Methodology

To achieve the research objective mentioned in chapter one, a process model for hydration of dimethyl oxalate to ethylene glycol is developed using the Aspen Plus V10 simulator. The process model created is then used to study the relationship of reactor temperature, liquid hourly space velocity, hydrogen to dimethyl oxalate mole ratio, methyl glycolate to dimethyl oxalate and concentration and pressure towards the conversion of dimethyl oxalate and selectivity of ethylene glycol.

Firstly, a suitable reactor block in Aspen Plus is chosen to simulate the data obtained from literature. Suitable information and assumptions are considered for the reactor block. The simulation data from literature is used to validate the model to determine whether the model is comparable with the simulation data. If the validation succeeded, operating variables such as reactor temperature, liquid hourly space velocity and hydrogen to dimethyl oxalate ratio are manipulated using the Sensitivity Analysis Tool in Aspen Plus. Lastly, the optimization of the dimethyl oxalate hydrogenation reaction is done by maximizing the selectivity of ethylene glycol by using Optimization Tool in Aspen Plus. A general flow of the methodology is shown in Figure 3.1.

3.2 Research Methodology Steps

Figure 3.1: Methodology Flow Chart shows the summary of methodology steps involved in this research work.

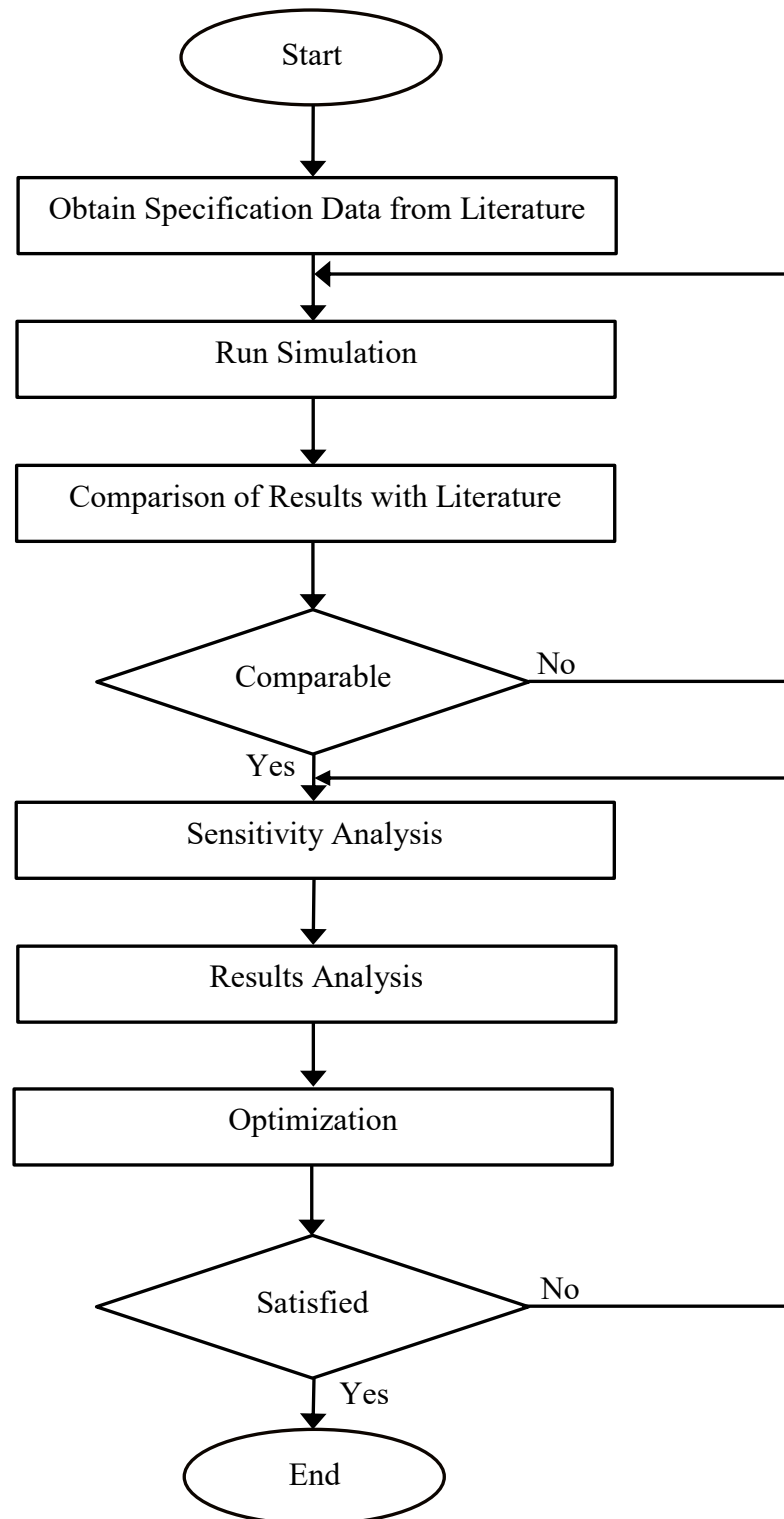
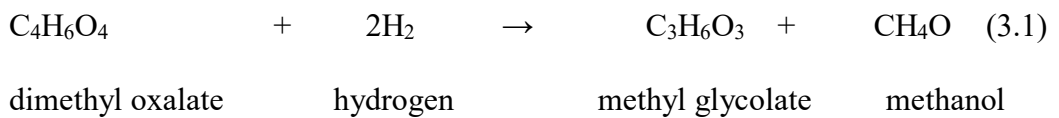


Figure 3.1: Methodology Flow Chart

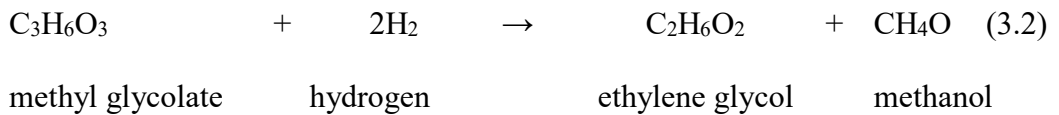
3.2.1 Collection of Data

The system considered in this simulation and optimization work is the hydrogenation reactor in the ethylene glycol production plant. It is the reaction where 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



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



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

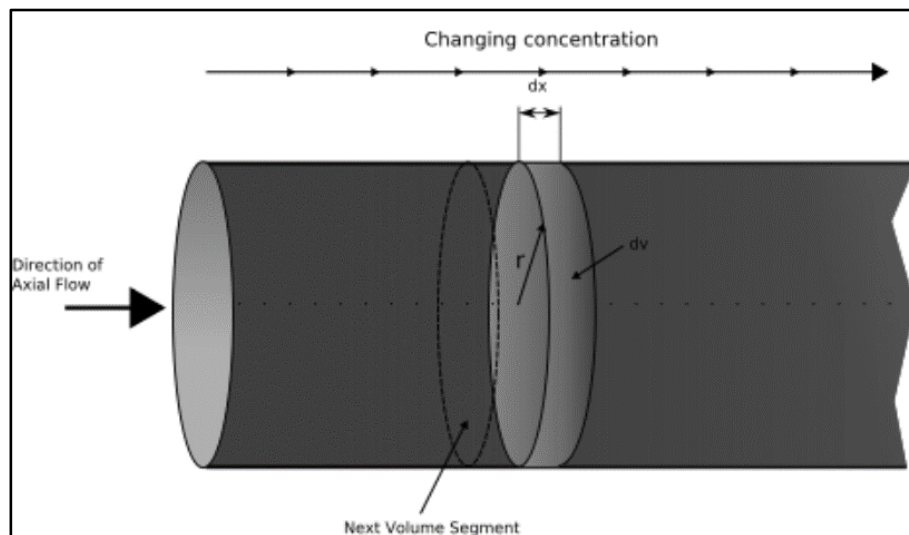
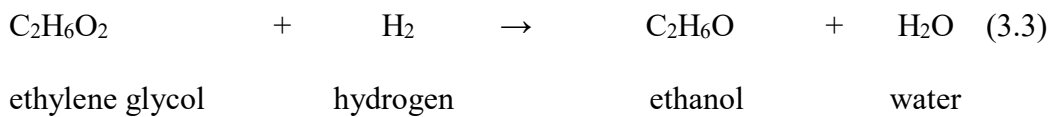


Figure 3.2: Schematic Diagram of a Plug Flow Reactor

The reactor that is used for the catalytic hydrogenation reaction of dimethyl oxalate is a fluidized bed reactor. According to Zhu et al. (2014) fluidized bed reactor can reach 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 is chosen to model and simulate the hydrogenation reaction as shown in Figure 3.3. Schematic diagram of a plug flow reactor is shown in Figure 3.2.

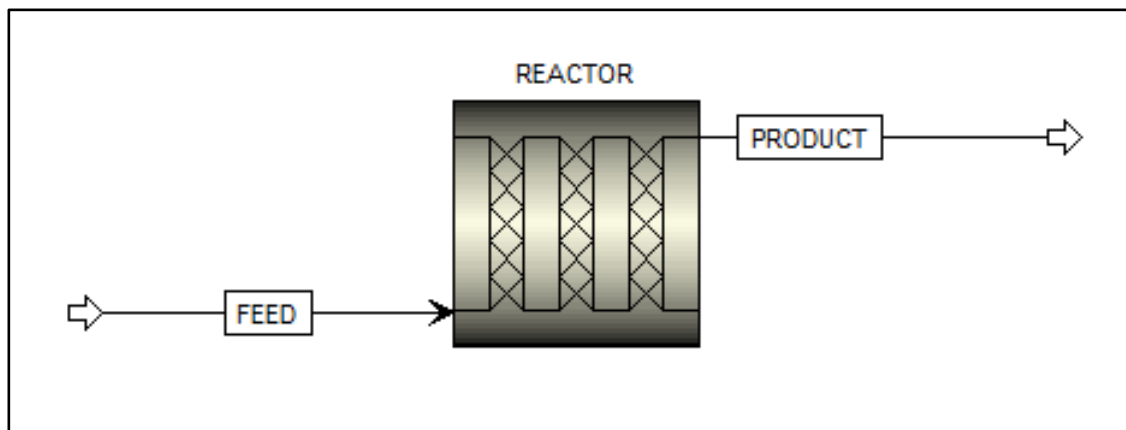


Figure 3.3: RPLUG Reactor Model

The Non-Random Two Liquid Redlich-Kwong, NRTL-RK property method is chosen as the thermodynamic model. The components involve in the reaction is dimethyl oxalate, water, methanol, ethylene glycol, dimethyl carbonate, methyl glycolate, ethanol, hydrogen and carbon monoxide. There are gas components in this system, thus Henry's law is included to model the dissolution of gases into liquid (Eden, 2012).

The specification inputs to the RPLUG hydrogenation of dimethyl oxalate reactor block for Aspen simulation are shown in the Table 3.1 and Table 3.2.

Table 3.1: Feed Specification (Yu and Chien, 2017)

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 3.2: Reactor and Catalyst Specification (Yu and Chien, 2017)

Specification	Value	unit
Length of reactor	3.0	m
Diameter of reactor	1.0	m
Catalyst bed voidage	0.5	-
Particle density	980	kg/m ³
Valid phase / process stream	Vapor	-

The kinetic parameters for the main and side reaction for dimethyl oxalate hydrogenation are shown in the Table 3.3.

Table 3.3: Information of Reaction and Kinetics (Yu and Chien, 2017)

Kinetic parameters		
	Pre-exponential factor (kmolkgcat⁻¹ h⁻¹ MPa⁻¹)	Activation energy (kJ/kmol)
k ₁	1.75E+06	37710
k ₂	3.87E+07	44284
k ₃	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

Assumption made in the simulation of hydrogenation of dimethyl oxalate process model are stated below:

1. Since there is no fluidized-bed reactor in Aspen Plus database, an isothermal plug flow reactor (RPLUG) model is chosen to simulate the reaction.
2. The components included in this work are dimethyl oxalate, water, methanol, ethylene glycol, dimethyl carbonate, methyl glycolate, ethanol, hydrogen and carbon monoxide.
3. Formation of some heavier by-products like diethylene glycol, 1,2-propane-diol and 1,2-butane-diol, poly-glycol and so on are not included due to the slight amount in production and the lack of kinetic and experimental data of these heavier by-products.
4. Feed to the hydrogenation process is at 99.99 mole% dimethyl oxalate and 1% of dimethyl carbonate (Jiang et al., 2012).
5. Methanol decomposition to form carbon monoxide during hydrogenation reactions is negligible.
6. Hydrogen is fed to the reactor at 99.999 mole% hydrogen and the remainder is carbon monoxide. This because the fresh hydrogen is assumed to be one of the products from a pressure swing adsorption unit.
7. No accumulation in the reactor.

3.2.2 Run Simulation

The hydrogenation process simulation model is run using the following steps as shown below:

1. Nine components are considered and keyed-in in the Aspen model: dimethyl oxalate, water, methanol, ethylene glycol, dimethyl carbonate, methyl glycolate, ethanol, hydrogen and carbon monoxide.

2. Different property method can yield different prediction for various thermophysical properties used in mass and energy balance calculations. NRTL-RK, Non-Random Two Liquid Redlich Kwong thermodynamic model is chosen for the simulation of dimethyl oxalate hydrogenation reactions.
3. Run Property Analysis.
4. Isothermal plug flow reactor is simulated using RPLUG model in process flowsheet , with one feed stream and one product stream.
5. Feed specification namely inlet temperature, pressure, total feed flowrate and mole fraction of each components are inserted into Aspen model.
6. RPLUG setup configuration such as reactor length and diameter as well catalyst specifications which includes catalyst bed voidage and particle density are keyed-in.
7. Using the kinetic expressions in Langmuir-Hinshelwood, LHHW form reaction model, kinetic data for the hydrogenation reactions and side reaction are entered.

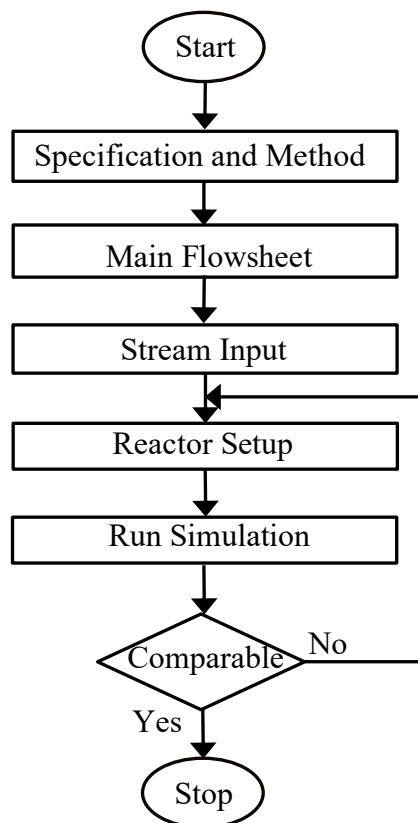


Figure 3.4: Aspen Simulation Flow Chart

3.2.3 Comparison of Simulation Results with Literature

The summary result of the simulation by Aspen Plus is to be compared with the results from literature. The feed is fed to the reactor at a specific temperature, pressure, hydrogen to dimethyl oxalate ratio as stated in Table 3.1. In this step, ethylene glycol, dimethyl oxalate and methyl glycolate is compared with the literature.

$$\text{Error (\%)} = \frac{\text{simulated value} - \text{literature value}}{\text{literature value}} \times 100\% \quad (3.4)$$

3.2.4 Sensitivity Analysis

Sensitivity analysis is an effective tool that allows user to study the effect of changes in input variables on process outputs. It will be used to manipulate one or more flowsheet variables and study the effect of the variation on other flowsheet variables. In this work, sensitivity analysis is carried out on the dimethyl oxalate hydrogenation reactor by manipulating several operating conditions, namely reactor temperature, reactor pressure, 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.

Dimethyl oxalate conversion

$$= \frac{\text{inlet flow dimethyl oxalate} - \text{outlet flow dimethyl oxalate}}{\text{inlet flow dimethyl oxalate}} \times 100\% \quad (3.5)$$

Overall ethylene glycol selectivity

$$= \frac{\text{ethylene glycol}}{\text{ethylene glycol} + \text{ethanol}} \times 100\% \quad (3.6)$$

By using the sensitivity analysis tool in Aspen Plus, the reactor temperature is varied from 160°C to 240°C in case 1. Typical temperature range used by Li et al. (2015) is in between 180°C and 220°C, however a wider range is used to explore possibilities of ethanol formation. In case 2, the reactor pressure is varied from 15 to 40 bar (Li et al., 2015). The range of hydrogen to dimethyl oxalate mole ratio is selected based on literature, however; a wider range is used to explore possibilities of ethylene glycol selectivity. Hydrogen to dimethyl oxalate mole ratio carried out is from 20 to 100. Dimethyl oxalate concentration is varied from 10 to 30 wt.% (Yin et al., 2008). The range of manipulating variables used for sensitivity analysis is shown in Table 3.4.

Table 3.4: Range of Manipulating Variables Used for Sensitivity Analysis

Parameter	Lower range	Upper range
Reactor temperature (°C)	160	240
Reactor pressure (bar)	15	40
HDMR	20	100
MDMR	1	10
DMO Concentration	10	30

To perform sensitivity analysis on the hydrogenation reactor using Aspen Plus V10, a new case can be setup from the Sensitivity folder under Model Analysis Tool. Firstly, flowsheet variables must be defined in the Input Define tab. The flowsheet variable defined here can be the variable to which a design specification is desired or can be a part of an expression used to achieve a design specification. Since sensitivity analysis is carried out to study the effect of changes in operating variables on the conversion of dimethyl oxalate and selectivity of ethylene glycol in this work, hence inlet mole flowrate of dimethyl oxalate is keyed-in as the variable to be defined.

Next, manipulated variables for the sensitivity analysis are defined on the input Vary sheet. In this work, operating variables namely, reactor temperature, reactor pressure, HDMR, MDMR and dimethyl oxalate concentration are specified as the manipulated variables. Each manipulated variable is defined accordingly with desired range as stated in the Table 3.4. Lastly, the variables to be tabulated by the sensitivity analysis are specified under Tabulate sheet by supplying optional heading for the table columns or by choosing from the variables that is defined on the Sensitivity Input Define sheet. After the required information is inserted, the simulation can be run to observe the changes of each manipulating variable on the measured variable, which is in this case, is the conversion of dimethyl oxalate and selectivity of ethylene glycol.

Figure 0.3 below shows the general flowchart methodology to perform sensitivity analysis using Aspen Plus V10.

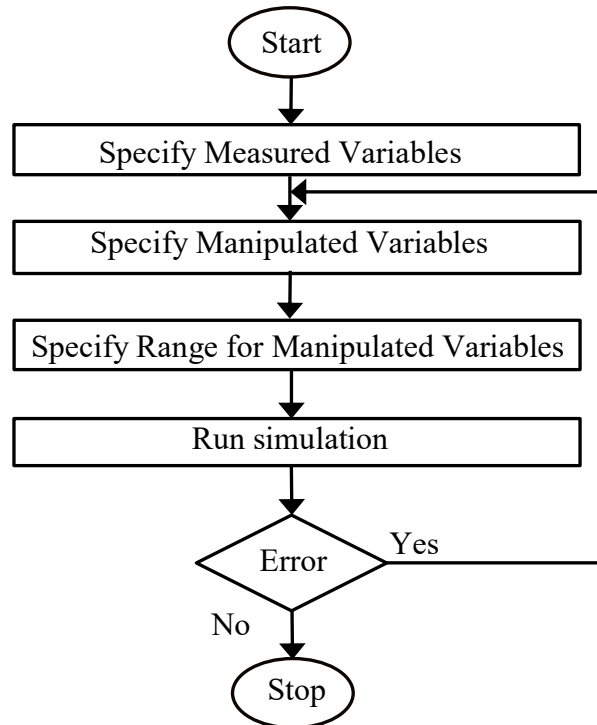


Figure 3.2: Sensitivity Analysis Flow Chart