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REACTIVE DISTILLATION FOR SYNTHESIS OF GLYCEROL CARBONATE
VIA GLYCEROLYSIS OF UREA

Mr. Noppon Lertlukkanasuk

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

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งานวิจัยนี้ได้ทำการพัฒนากระบวนการใหม่ สำหรับการสังเคราะห์กลีเซอรอลคาร์บอเนต ผ่านกระบวนการกลีเซอโรไลซิสของยูเรียในระบบการกลั่นแบบเกิดปฏิกิริยา โดยการใช้โปรแกรมแอสเพนพลัส ตัวแปรทางเทอร์โมไดนามิก ที่ไม่ทราบค่าของกลีเซอรอลคาร์บอเนต (เช่น พลังงานอิสระกิบส์ของการเกิด) ของกลีเซอรอลคาร์บอเนตสามารถทำการประมาณได้โดยวิธีรู้ปคอนทริบิวชัน เช่น วิธีของโจแบค วิธีของกานี และวิธีของเบนสัน จากการศึกษาพบว่าวิธีของกานีมีความคลาดเคลื่อนน้อยที่สุด นอกจากนี้ตัวแปรในแบบจำลองการเกิดปฏิกิริยาแบบสมดุลและแบบจลนศาสตร์สามารถหาได้จากการทำการทดลองแบบกะและนำไปประยุกต์ใช้ในมอดูล RADFRAC ของโปรแกรมแอสเพนพลัสที่กำหนดให้เป็นชั้นสมดุลเพื่อศึกษาผลของค่าตัวแปรออกแบบและตัวแปรปฏิบัติการของระบบการกลั่นแบบเกิดปฏิกิริยาที่มีผลต่อค่าการเปลี่ยนแปลงของกลีเซอรอลค่าผลได้และความบริสุทธิ์ของกลีเซอรอลคาร์บอเนต จากผลการจำลองพบว่าการเพิ่มจำนวนชั้นของสตีปปีง ชั้นของปฏิกิริยา และการลดจำนวนชั้นของเรกติฟายอิงจะให้ค่าการเปลี่ยนแปลงของกลีเซอรอลที่สูง เนื่องจากลดการสูญเสียสารตั้งต้นที่ขอดหอ นอกจากนี้กลีเซอรอลและยูเรียในผลิตภัณฑ์ขอดหอสามารถถูกรีไซเคิลกลับมาในส่วนของปฏิกิริยาได้ โดยการเพิ่มอัตราส่วนการป้อนกลับ จากการศึกษาพบว่าค่าตัวแปรออกแบบและตัวแปรปฏิบัติการที่เหมาะสมคือ จำนวนชั้นของสตีปปีง 3 ชั้น ชั้นของปฏิกิริยา 3 ชั้น ไม่มีชั้นของเรกติฟายอิง พลังงานหม้อต้มซ้ำ 15 กิโลวัตต์ และค่าอัตราส่วนการป้อนกลับเท่ากับ 2 ซึ่งทำให้ได้ค่าการเปลี่ยนแปลงของกลีเซอรอล 93 เปอร์เซ็นต์ ค่าผลได้ของกลีเซอรอลคาร์บอเนต 96 เปอร์เซ็นต์ และค่าความบริสุทธิ์ของกลีเซอรอลคาร์บอเนต 100 เปอร์เซ็นต์ และเมื่อทำการเปรียบเทียบกับกระบวนการผลิตแบบปกติ พบว่าระบบการกลั่นแบบเกิดปฏิกิริยาจะให้ค่าการเปลี่ยนแปลงของ กลีเซอรอลที่สูงกว่า และใช้พลังงานในระบบน้อยกว่า

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NOPPON LERTLUKKANASUK: REACTIVE DISTILLATION FOR
SYNTHESIS OF GLYCEROL CARBONATE VIA GLYCEROLYSIS OF
UREA. ADVISOR: PROF. SUTTICHAJ ASSABUMRUNGRAT, Ph.D.
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This study developed a new process for synthesis of glycerol carbonate via glycerolysis of urea in reactive distillation using Aspen plus program. Missing thermodynamic parameters (e.g. Gibb's free energy of formation) of glycerol carbonate were estimated by the group contribution methods including Joback's, Gani's and Benson's methods. The results showed that Gani's method provided the lowest deviation among the three methods. Equilibrium and kinetic model parameters were obtained from batch experiment and applied to the simulation. A RADFRAC module in Aspen Plus program with equilibrium stage was used in the simulation to investigate the effects of design and operating parameters of reactive distillation on conversion of glycerol and yield and purity of glycerol carbonate. The simulation results showed that high conversion of glycerol could be obtained by increasing the number of stripping and reaction stages as well as decreasing the number of rectifying stages due to reducing reactant loss in the distillate. Moreover, glycerol and urea in distillate were recycled to reactive section by increasing reflux ratio. The suitable design and operating parameters can achieve at 3 stripping stages, 3 reaction stages, no rectifying stage, reboiler heat duty of 15 kW and reflux ratio of 2 – this offers 93% conversion of glycerol, 96% yield, and 100% purity of glycerol carbonate in the final product. Compared to a conventional process, reactive distillation provided higher conversion of glycerol and lower energy consumption.

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NOMENCLATURE

A	pre-exponential factor	[mol ml ⁻¹ min ⁻¹]
E_a	activation energy	[kJ mol ⁻¹]
G_i^o	standard Gibbs free energy of formation of species i	[kJ mol ⁻¹]
ΔG	Gibbs free energy change of reaction	[kJ mol ⁻¹]
ΔH^o	standard enthalpy change of reaction	[kJ mol ⁻¹]
k^+	forward rate constant of reaction	[mol ml ⁻¹ min ⁻¹]
k^-	backward rate constant of reaction	[mol ml ⁻¹ min ⁻¹]
K_{eq}	equilibrium constant of reaction	[-]
N_{Rec}	number of stage in rectifying section	[-]
N_{Rxn}	number of stage in reaction section	[-]
N_{Str}	number of stage in stripping section	[-]
P	pressure	[bar]
r_i	reaction rate of species i	[mol ml ⁻¹ min ⁻¹]
R	gas constant	[J mol ⁻¹ K ⁻¹]
ΔS^o	standard entropy change of reaction	[J mol ⁻¹ K ⁻¹]
T	temperature	[K]
x_i	mole fraction in liquid phase of species i	[-]
X_i	conversion of species i	[-]
y_i	mole fraction in gas phase of species i	[-]
Y_i	yield of species i	[-]

Subscripts

0	initial value at time = 0
eq	equilibrium
GC	glycerol carbonate
Gly	glycerol
i	species i
p	product
r	reactant

CHAPTER I

INTRODUCTION

1.1 Rationale

At present, there are great concerns about the depletion of petroleum fuels and global warming over the world. The rising use of renewable energy is expected following energy security perspectives. Nowadays, biodiesel is become an important renewable fuel for transportation sector. Biodiesel can be produced from many feedstocks but its production typically leads to the same byproduct of glycerol.

Glycerol is produced with the amount as one-tenth of biodiesel production (Li *et al.*, 2010). Most glycerol is removed from the biodiesel product during a purification process. At the present, the amount of glycerol for industrial utilization is around 160,000 tonnes per year and increases at an annual rate of 2.8% (Pagliaro *et al.*, 2008). While a biodiesel production capacity is around 8 Million tonnes per year and increases at an annual rate of 16.6 % (European Biodiesel Board, 2008). Therefore a glut of glycerol would be expected in a near future. On account of the rapid decrease in its price, researchers and industry have been developing at new uses for glycerol to substitute petrochemical-base materials. Recently several examples have been reported: glycerol oxidation to dihydroxyacetone, glyceric acid, tartronic acid and glyceraldehyde, dehydration of glycerol to acrolein, hydrogen or syngas production by reforming (Fernandez *et al.*, 2009), hydrogenolysis of glycerol to propylene glycol (Mohanprasad *et al.*, 2005), polymerization to polyglycerol, halogenation to epichlorohydrin, and carboxylation to glycerol carbonate.

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is an important derivative of glycerol as well as a new high value-added product. Glycerol carbonate is a colorless protic polar liquid, non-toxic, low evaporation rate, low flammability, and high boiling point. Glycerol carbonate can be used for many applications e.g. a solvent for plastics and resins (such as cellulose acetate, nylon, and polyacrylonitrile), the additives in lithium battery, liquid membrane for carbon dioxide and nitrogen

separation, a solvent in cosmetic, personal care, and medicinal applications. In addition, the hydroxyl group of glycerol carbonate can be reacted with anhydrides to form ester linkages or with isocyanates to form urethane linkages. Therefore, heated glycerol carbonate can react with phenols, alcohols, and carboxylic acid to form not only ethers or esters of glycerol, but also polymers such as polyesters, polyurethane, and polycarbonate (Pagliaro *et al.*, 2008).

Glycerol carbonate can be produced from glycerol by different routes. The reaction of glycerol with phosgene results in glycerol carbonate, but phosgene is very toxic. Glycerol carbonate can be prepared by the reaction of glycerol with cyclic carbonate such as propylene carbonate, and ethylene carbonate. Ethylene carbonate is obtained from the reaction of ethylene oxide with carbon dioxide, however ethylene carbonate is an expensive reagent. Another route of producing glycerol carbonate is from the conversion of glycerol with carbon dioxide which suffers from the drawback of high pressure operation, and low conversion owing to its thermodynamic limitation (Aresta *et al.*, 2006). Therefore, this route requires improvement of catalytic performance. In addition, glycerol carbonate could be prepared by the reaction between glycerol and dimethyl carbonate but it has high cost of organic carbonate which is used at high molar ratio of dimethyl carbonate to glycerol. In addition, it needs to shift the reaction equilibrium, and expensive lipase catalyst (Kim *et al.*, 2007). An alternative route is glycerolysis of urea which is the interesting reaction that converts two wastes into an added value product. Glycerol and urea are both cheap reagents and easily available.

Normally, the glycerolysis of urea has to operate under vacuum condition or using sweep gas to eliminate ammonia as a byproduct in gas phase for shifting equilibrium of the reaction (Climent *et al.*, 2010). Moreover, most researchers performed the glycerolysis of urea in batch operation that make it difficult to apply in the large industrial scale. Another difficulty is a use of traditional soluble catalyst i.e. zinc sulfate catalyst which can cause complicatedness and high cost of catalyst recovery and product purification. Compared with the homogeneous catalyst reactions, heterogeneous catalyst reactions propose the advantages in term of product purification. Catalysts can be easily recovered and reused. There are some researches on the glycerolysis of urea with heterogeneous catalysts. For example, γ -zirconium

phosphate was employed as a heterogeneous catalyst for the reaction of glycerol and urea. At a pressure of 20 Pa, 140°C and 1.5 h, conversion of 80% and high selectivity was achieved (Aresta et al.,2009).

In this research we will develop a new process to synthesize glycerol carbonate via glycerolysis of urea by combination reaction and separation unit with reactive distillation. Furthermore, the thermodynamic equilibrium of the reaction can be shifted by controlling the reflux ratio of column to eliminate ammonia as a byproduct at atmospheric pressure, and continuous operation, which lead to increase potential industrial application. In addition, we discuss the effect of design and operating variables on the conversion of glycerol, yield and purity of glycerol carbonate including determination the reaction model parameters.

1.2 Objectives

To develop of a new continuous process via reactive distillation for the conversion of glycerol into valuable glycerol carbonate via glycerolysis of urea.

1.3 Scope of works

1. The synthesis of glycerol carbonate from glycerolysis of urea in reactive distillation is considered.
2. A suitable method for estimating thermodynamic properties among Benson's, Joback's and Gani's methods is selected to determine missing thermodynamic properties of glycerol carbonate (Gibb's free energy of formation) which is required for simulations of the process. The suitable method is selected based on estimation of known thermodynamic properties of some chemicals with similar structures of glycerol carbonate such as propylene carbonate and ethylene carbonate.
3. Experiments in a batch reactor are carried out to obtain data for validation of the thermodynamic property estimation method for glycerol carbonate and reaction model parameters.

4. Simulations of the reaction in reactive distillation using Aspen Plus program are performed to determine effects of various design and operating parameters such as heat duty, number of stages, and reflux ratio on reaction performance.
5. Comparison simulation results for synthesis of glycerol carbonate from conventional method and reactive distillation are determined.

CHAPTER II

THEORY

In this chapter, the necessary information for the synthesis of glycerol carbonate from the reaction of glycerol as a starting material was described.

2.1 Glycerol

Glycerol (or glycerine, propan-1,2,3-triol) is a polyol chemical which is colorless, odorless, sweet-tasting, low toxicity, and viscous liquid. From its properties in Table 2.1, glycerol is normally used in pharmaceutical industry. Three hydrophilic hydroxyl groups of glycerol result to be completely soluble in water and alcohol and its hygroscopic property. Glycerol can form salts as a sodium glyceroxide.

Table 2.1 Physical and chemical properties of glycerol at 20 °C. (Pagliaro *et al.*, 2008)

Chemical formula	$C_3H_5(OH)_3$
Molecular mass	$92.09382 \text{ g mol}^{-1}$
Density	1.261 g cm^{-3}
Viscosity	1.5 Pa.s
Melting point	$18.2 \text{ }^\circ\text{C}$
Boiling point	$290 \text{ }^\circ\text{C}$
Free energy	4.32 kcal g^{-1}
Flash Point	$160 \text{ }^\circ\text{C}$ (closed cup)
Surface tension	64.00 mNm^{-1}
Temperature coefficient	-0.0598

Glycerol is obtained as a byproduct in many processes as shown in Table 2.2. The soap-making process provides glycerol as a byproduct from the saponification of animal fats. Therefore, glycerol which is obtained from this process has sodium

hydroxide and water as impurities. Another route of obtaining glycerol is a byproduct of the production of fatty acid from hydrolysis reaction, so water dissolves in glycerol. While glycerol can be obtained from the production of biodiesel as a byproduct via transesterification. The obtained glycerol is also mixed with methanol. The production of biodiesel from transesterification reaction between methanol and vegetable oil using potassium hydroxide as a catalyst provides 10.5 kg of glycerol from 100 kg of produced biodiesel (Pagliaro *et al.*, 2008).

Table 2.2 Glycerol production and by-product.

Glycerol production	Main by-product in glycerol
Saponification of animal fats (by-product of soap-making)	NaOH and H ₂ O
By-product of the production of biodiesel via transesterification	Methanol
By-product of the production of fatty acid via hydrolysis	H ₂ O

Impurities in a crude glycerol are methanol, water, or sodium hydroxide depending on process production. Crude glycerol normally contains 40 to 88% of glycerol. Moreover, technical grade glycerin is a high purity of glycerol after refinery. Therefore, amounts of methanol, water and sodium hydroxide are less. A USP grade glycerin is a pharmaceutical grade of glycerol which uses in special applications.

Table 2.3 Specifications of glycerol (Ref.: SRS engineering corporation)

Properties	Crude Glycerin	Technical Grade Glycerin	99.7 - USP Grade Glycerin
Glycerol Content	40 - 88%	98.0 Min	99.70%
Ash	2.0% Max	N/A	N/A
Moisture Content	N/A	2.0% Max	0.3% Max
Chlorides	N/A	10 ppm Max	10 ppm Max
Color	N/A	40 Max(Pt - Co)	10 Max. (APHA)

Table 2.3 continued

Specific Gravity	N/A	1.262 (@25C)	1.2612 Min
Sulfate	N/A	N/A	20 ppm Max
Assay	N/A	N/A	99.0 - 101.0%
Heavy Metals	N/A	5 ppm Max	5 ppm Max
Chlorinated Compounds	N/A	30 ppm Max	30 ppm Max
Residue on Ignition	N/A	N/A	100 ppm Max

Glycerol is a versatile material for many industrial applications. Glycerol is used directly as an additive in many applications such as a sweetener, and wetting agent in tobacco, or it can be converted to other value-added products. Many processes which convert glycerol into other products are presented in the literatures. The processes that use glycerol as a raw material are aqueous phase reforming process (APR) to syngas, hydrogenolysis to propylene glycol, the synthesis of epichlorohydrin, dehydration of glycerol to acrolein, oxydehydration reaction of glycerol to acrylic acid, dehydration (biotechnological production) to 3-hydroxypropionald (3-HPA), butylation of glycerol glycerol tert-butyl ethers (GTBEs), anionic polymerization to polyglycerol, nitration to nitroglycerine poly(glycidyl nitrate) (PGN), selective oxidation of glycerol to oxidized glycerol derivatives, and the carboxylation of glycerol to glycerol carbonate.

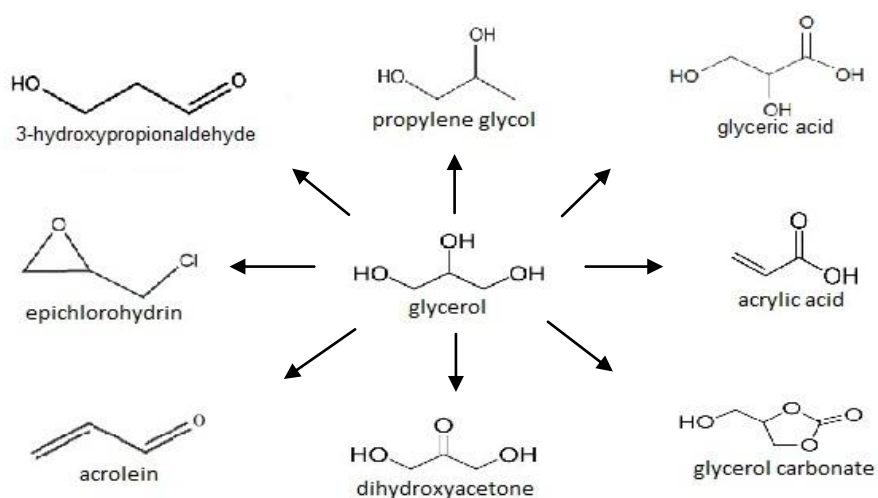


Figure 2.1 add-value chemicals from the process of the reaction of glycerol

Table 2.4 Price lists of add-value product from the conversion process of glycerol

Product	Price (Ref. Sigma-Aldrich)
Glycerol (refined glycerol)	5.2 USD/100g
Propylene glycol	5.2 USD/100g
1,3-dichloro-2-propanol	47.7 USD/100g
Epichlorohydrin	34.6 USD/100g
Glycerol tert-butyl ethers (GTBEs)	1,698 USD/100g
Glycerol carbonate	504 USD/100g
Dihydroxyacetone	42.3 USD/100g
Propylene	113.5 USD/100g
Propylene oxide	1,238 USD/100g

2.2 Glycerol carbonate

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is an important product from the conversion process of glycerol. It is a stable and clear liquid at room temperature, high boiling point, low toxicity, low flammability, good biodegradability, low evaporation rate, and moisturizing ability. Glycerol carbonate has a hydroxyl group which can react in many reactions such as the reaction with anhydrides to produce ester linkages, the reaction with isocyanates for the production of urethane linkages, and the production of multi-functional alkylene carbonates from the reaction with polyisocyanates.

Due to its properties, glycerol carbonate is widely used in many applications and expects to replace petroleum-based chemicals. Glycerol carbonate is used as a solvent in cosmetic, medicinal and pharmaceutical applications, a component in membrane gas separation of carbon dioxide and nitrogen, an additive in lithium battery, a surfactant component, including as a precursor in the production of polycarbonate, polyurethane, hyperbranched aliphatic polyethers, and in the plastic processing.

Table 2.5 Physical properties of glycerol carbonate (Jeffsol, Huntsman Corporation)

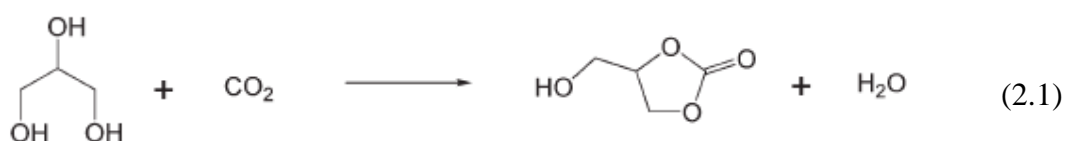
Boiling range at 0.1 mmHg	110-115 °C
Freezing point	-69 °C
Flash point, PMCC	>190 °C
Molecular weight	118
pH	4-6.5
Density at 25 °C	1.4 g/mL
Water solubility	Miscible

2.3 Synthesis of glycerol carbonate from the reaction of glycerol

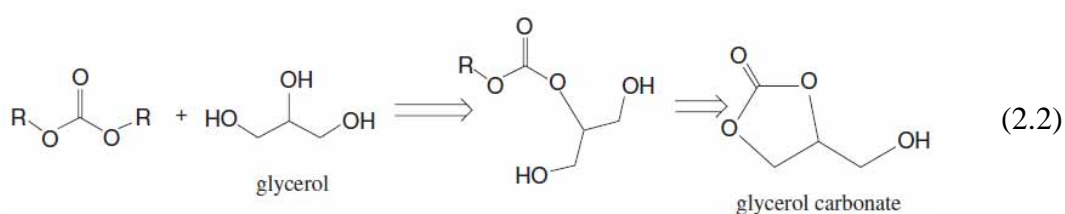
2.3.1 Reactions

Glycerol carbonate is an important chemical of glycerol derivatives which can be prepared from the reaction of glycerol in different methods. Firstly, glycerol carbonate could be prepared by the reaction of glycerol with phosgene. Nevertheless, phosgene is very toxic. The synthesis of glycerol carbonate from the reaction between glycerol and cyclic carbonate such as ethylene carbonate, and propylene carbonate could be provided, but the carbonate source is also expensive.

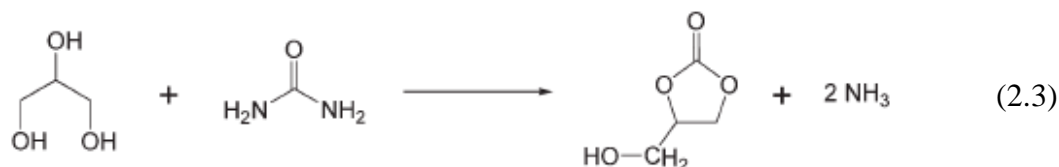
Accordingly, there are three main methods to produce glycerol carbonate from the reaction of glycerol.



Glycerol carbonate can be obtained from the reaction of glycerol and carbon dioxide. Several researchers attempt to develop this route, but the limitations such as equilibrium limitation, low yield of glycerol carbonate, and high pressure operation are main obstacle.



Glycerol carbonate can be prepared via transesterification of glycerol and dimethyl carbonate using lipase as a biocatalyst. However, lipase for the synthesis of glycerol carbonate is expensive, and several researches carried out with high molar ratio of expensive dimethyl carbonate to glycerol to shift equilibrium reaction.



Another method to the synthesis of glycerol carbonate is the glycerolysis of urea at a temperature between 90 °C and 220 °C using Lewis acid catalyst. In this process, high yield of glycerol carbonate is obtained by removing ammonia gas as a byproduct to shift equilibrium reaction with passing gas extraction, or operating under vacuum. Glycerol reacts with urea in a two-step carbamoylation/carbonation reaction to produce glycerol carbonate. The rate of reaction of the second step is slower than the first step, so the catalyst is an important component to improve this limiting step. (Claude *et al.* (US 006025504A))

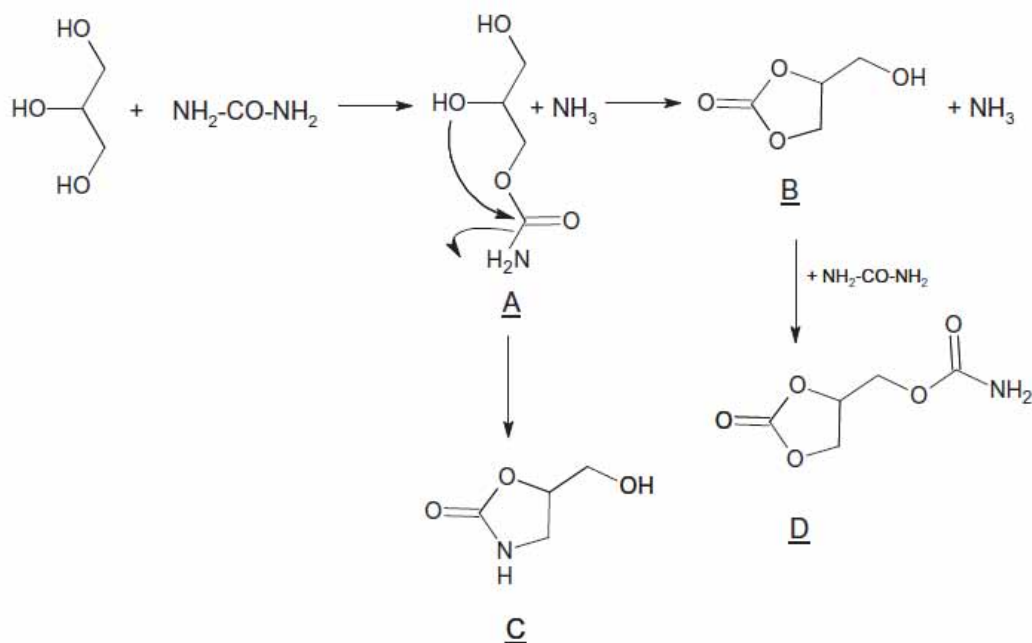


Figure 2.2 Reaction mechanism of the synthesis of glycerol carbonate from the glycerolysis of urea : (A)glycerol urethane, (B)glycerol carbonate, (C)5-(hydroxymethyl)oxazolidin-2-one, (D)(2-oxo,-1,3-dioxolan-4-yl)methyl carbamate. (Rubio-Marcos *et al.*, 2010)

From Figure 2.2, the synthesis of glycerol carbonate from the reaction between glycerol and urea has four steps of reaction mechanism. Firstly, glycerol reacts with urea to produce glycerol urethane as an intermediate and ammonia as a byproduct. Secondly, carbonation of glycerol urethane produces glycerol carbonate and ammonia. Thirdly, glycerol urethane is converted to 5-(hydroxymethyl) oxazolidin-2-one. Finally, glycerol carbonate reacts with urea to produce (2-oxo,-1,3-dioxolan-4-yl)methyl carbamate as a byproduct (Rubio-Marcos et al., 2010).

2.3.2 Thermodynamic equilibrium (Li et al. (2010))

The thermodynamic equilibrium of reaction affects to the yield of glycerol carbonate as a desired product. Therefore, chemical equilibrium constant is calculated and investigated.

The chemical equilibrium constant of reaction at standard condition (25 °C and 1 atm) can be calculated from the change of standard molar enthalpy ($\Delta_r H_m^\circ$), change of standard molar entropy ($\Delta_r S_m^\circ$), and the change of Gibbs energy of reaction ($\Delta_r G_m^\circ$) using following equations.

$$\Delta_r H_m^\circ = \sum_{product} n_i \Delta_f H_{m,i}^\circ - \sum_{reactant} n_j \Delta_f H_{m,j}^\circ \quad (2.4)$$

$$\Delta_r S_m^\circ = \sum_{product} n_i S_{m,i}^\circ - \sum_{reactant} n_j S_{m,j}^\circ \quad (2.5)$$

$$\Delta_r G_m^\circ = \Delta H_m^\circ - T \frac{\Delta_r S_m^\circ}{1000} \quad (2.6)$$

Therefore,
$$\ln K^\circ = \frac{-\Delta_r G_m^\circ}{RT} \quad (2.7)$$

The liquid phase standard molar enthalpy of formation ($\Delta_f H_l^\circ$) and the liquid phase standard molar entropy ($\Delta_f S_l^\circ$) is not reported in the literature. So, they could be calculated from following equations.

$$\Delta_r H_{m,l}^\circ = \Delta_f H_{m,g}^\circ - \Delta_v H_m^\circ \quad (2.8)$$

$$S_{m,l}^\circ = S_{m,g}^\circ - \frac{\Delta_v H_m^\circ}{T} \times 10^3 \quad (2.9)$$

The chemical equilibrium constant also depends on the reaction temperature which is shown in the following equations.

$$\left[\frac{\delta \Delta_r H_m}{\delta T} \right]_p = \Delta_r C_{p,m} \quad (2.11)$$

$$\left[\frac{\delta(\Delta_r G_m / T)}{\delta T} \right]_p = -\Delta_r H_m / T^2 \quad (2.12)$$

For the synthesis of glycerol carbonate from the glycerolysis of urea, high reaction temperature can provide high yield of glycerol carbonate because it is favorable in chemical equilibrium.

In the system which involves gas phase, the chemical equilibrium constant depends on the pressure operation. So, the chemical equilibrium constant is obtained from the following equations at constant temperature.

$$\left(\frac{\partial \Delta_r G_m}{\partial p} \right)_T = \Delta V_m \quad (2.13)$$

The gas phase in system is assumed to be ideal gas at low pressure, then

$$\left(\frac{\partial \Delta_r G_m}{\partial p} \right)_T = \Delta n RT \quad (2.14)$$

$$\text{So,} \quad \Delta_r G_m(T, P) = \Delta_r G_m(T, P^o) + \Delta n RT \ln(P / P^o) \quad (2.15)$$

$$\text{From,} \quad \Delta_r G_m(T, P) = -RT \ln K \quad (2.16)$$

The synthesis of glycerol carbonate from the reaction between glycerol and urea produces ammonia as a gas phase byproduct. Accordingly, the high yield of glycerol carbonate is obtained at low pressure operation.

Therefore, the chemical equilibrium constant of the reaction is calculated at different condition.

The dependence of the equilibrium constant on reaction temperature can be obtained from the Van't Hoff equation which can be derived from the Gibbs-Helmholtz equation as shown below:

$$\left(\frac{\partial(\Delta G^o / T)}{\partial(1/T)} \right)_P = \Delta H^o \quad (2.17)$$

The Van't Hoff equation can be expressed by substituting equation (2.16) and dividing by $-R$.

$$\left(\frac{\partial(\ln K_{eq})}{\partial(1/T)} \right)_P = -\frac{\Delta H^o}{R} \quad (2.18)$$

From this equation, ΔH^o can be obtained from slope by plotting $\ln K_{eq}$ on y axis and $1/T$ on x axis.

2.4 Reactive Distillation (Schmidt-Traub *et al.* (2006))

In many cases of reaction, the yield of desired product is low due to the equilibrium limitation. Accordingly, several researches attempt to shift the equilibrium reaction by using excess reactant which increases the operation cost. Therefore, reactive distillation is used to solve these problems. Moreover, solving the difficult separation of mixtures, high desired product purity, reduction of plant cost, and decrease the energy consumption are obtained with using reactive distillation. Whereas, using reactive distillation results in some disadvantages such as the requirement of the same operation windows for both reaction and separation.

The reaction and separation occur simultaneously within the reactive distillation column. In the reactive distillation process, the heterogeneous catalyst is appropriate to recover easily compared with homogeneous catalyst. The suitably internals effect to the efficiency of the column which can provide to mix completely of vapor and liquid streams.

Reactive distillation in the presence of heterogeneous catalyst involves three phases which react and transfer in the column. Several researches present the model that describes the phenomena at interface. Equilibrium stage model is used to explain the tray column and packed column with the concept of the Height Equivalent to a Theoretical Stage (HETS). The assumptions of this model are equilibrium in vapor and liquid at the end of stage, no entrainment, and completely mixed of vapor and liquid phase. However, this model is not suitable for the high reaction rate.

Another method is a rate-based approach which considers multicomponent mass and heat transfer. Therefore, this approach is more accurate than the equilibrium

stage model. There are many models that describe the vapor liquid mass transfer in the concept of rate-based approach such as Two-film model.

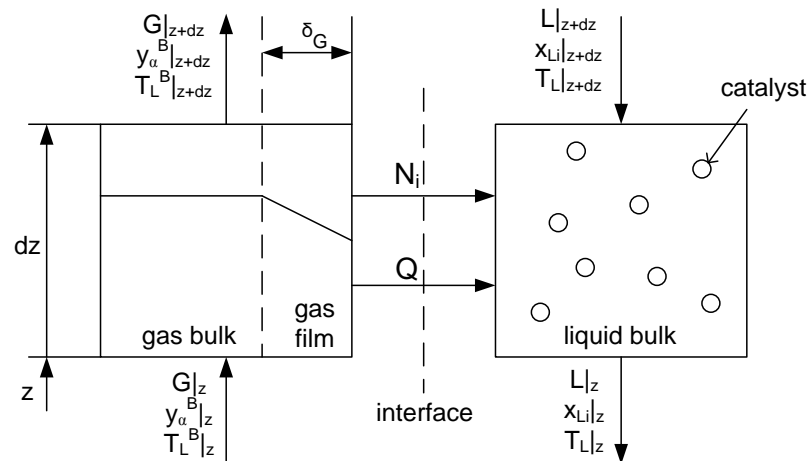


Figure 2.3 Film model for the packed column with heterogeneous catalyst.

For the two-film model, the component balance on the stage j is shown in following equations.

$$\frac{dn_{G,i}}{dt} = G_{j-1}y_{i,j-1} - G_j y_{i,j} - n_{i,j} a_j A_c dz \quad , i = 1, \dots, n_c \quad (2.17)$$

The interfacial mass transfer rates can be calculated from the Maxwell-Stefan equations. The diffusional flux is obtained from the following equations.

$$J = -c_{i,G}^{av} \cdot [k_G^{av} (y_{i,j}^I - y_{i,j})] = -c_{i,L}^{av} [k_L^{av} \Gamma_L^{av} (x_{i,j} - x_{i,j}^I)] \quad (2.18)$$

The energy balance for this system is obtained from the following equations.

$$\frac{dE_{L,z}}{dz} = L_{j+1} H_{L,j+1} - L_j H_{L,j} + q_j^I a_j A_c \Delta z \quad (2.19)$$

Whereas A_c is column cross section, a_i is the activity of component i , c is the molar concentration, G is a gas molar flow rate, L is a liquid molar flow rate, q is the heat flux, and Γ is the thermodynamic correction matrix, respectively.

The thermodynamic behavior becomes non-ideal in the reactive distillation process. The real behavior of liquid component can be estimated by different model such as UNIFAC model. Moreover, the cell model and differential model can be used to explain non-ideal flow patterns in the reactive distillation process.

2.5 Thermodynamic property estimation techniques (Poling *et al.* (2001))

The group contribution method was developed to estimate the missing properties of component. Since then, the experimental results could provide to determinate the alternative group contributions. In this study, three estimation techniques including method of Joback, Constantinou and Gani and Benson were examined.

2.5.1 Method of Joback

Method of Joback was developed from Lydersen's group contribution by adding several new functional groups and contribution values. The relation for the estimation properties are

$$T_c(K) = T_b [0.584 + 0.965 \{ \sum_k N_k (tck) \} - \{ \sum_k N_k (tck) \}^2]^{-1} \quad (2.20)$$

$$P_c(\text{bar}) = [0.113 + 0.0032 N_{atoms} - \sum_k N_k (pck)]^{-2} \quad (2.21)$$

$$T_b = 198 + \sum_k N_k (tbk) \quad (2.22)$$

$$\Delta G_f^0 = 53.88 + \sum_k N_k (gfk) \quad (2.23)$$

where tck and pck indicate the contributions. The estimation critical properties, Joback's method is reliable for T_c when the experimental boiling point is used. The error is increase if the estimated boiling point is used. For the compounds with 3 or more carbons, it is less. For P_c , the error is increase for the large molecules such as some ring compounds. For Gibb's free energy formation estimation, Joback's method is marginally accurate for all substances and slightly accurate for halogenated compounds.

2.5.2 Method of Constantinou and Gani (CG)

Constantinou and Gani developed a more complex function based on UNIFAC group for contribution at a "Second order" level. These contributions provide more

flexibility to estimate special configuration compound such as isomer and resonance structure. The Constantinou and Gani relations are

$$T_c(K) = 181.128 \ln \left[\sum_k N_k (tc1k) + W \sum_j M_j (tc2j) \right] \quad (2.24)$$

$$P_c(\text{bar}) = \left[\sum_k N_k (pc1k) + W \sum_j M_j (pc2j) + 0.10022 \right]^{-2} + 1.3705 \quad (2.25)$$

$$T_b(K) = 204.359 \ln \left[\sum_k N_k (tb1k) + W \sum_j M_j (tb2j) \right] \quad (2.26)$$

$$\Delta G_f^o (\text{kJmol}^{-1}) = -14.83 + \left[\sum_k N_k (gf1k) + W \sum_j M_j (gf2j) \right] \quad (2.27)$$

Method of Constantinou and Gani is quite reliable for the estimation of all critical properties. Nevertheless, the large error could occur for very smallest molecule and very largest molecules. Second order contributions could improve absolute percent error except for the ring compounds and olefin. For normal boiling point estimation, method of Constantinou and Gani is more accurate than method of Joback. And for Gibb's free energy formation estimation, method of Constantinou and Gani is quite reliable for components with three or more carbon atoms. But the error increase for small molecules and perfluoro-groups compounds. The author's claim that method of Constantinou and Gani was tested for about 350 substances with average absolute errors of 4.8 kJ/mol in ΔG_f^o at 298.15K (Poling *et al.* (2001)).

2.5.3 Method of Benson

Benson developed the extensive method to estimate thermodynamic properties such as standard enthalpy of formation and standard Gibb's free energy of formation. This method is based on the next-nearest neighbor interactions and contributions of the bonding arrangements which the chosen groups can interact with other atom or group except for hydrogen. The Benson relations are

$$\Delta H_f^o (298.15K) = \sum_k N_k (\Delta H_{fk}^o) \quad (2.28)$$

$$S^o (298.15K) = \sum_k N_k (S_k^o + S_s^o) + S_s^o \quad (2.29)$$

$$S_{el}^o (298.15K) = \sum_e v_e (S_e^o) \quad (2.30)$$

$$\Delta G_f^o(298.15K) = \Delta H_f^o(298.15K) - 298.15[S^o(298.15K) - S_{el}^o(298.15K)] \quad (2.31)$$

The symmetry entropy(S_s^o), is independent of T and given below

$$S_s^o = R \ln(N_{oi}) - R \ln(N_{ts}) \quad (2.32)$$

where N_{oi} is the number of structural isomers of the molecule that especially equal to 1 and N_{ts} is the total symmetry number. N_{ts} can be obtained from two distinct types of indistinguishability including internal (N_{is}) and external (N_{es}). The rotating terminal groups to interior groups can provide the value of N_{is} . And N_{es} can be obtained from indistinguishability if the rigid molecule is rotated. Moreover, N_{ts} can be obtained from

$$N_{ts} = N_{es} \cdot \prod_{k=term} (N_{is})_k \quad (2.33)$$

Normally, Benson's method is the most accurate and reliable estimation method. For the comparison of three group contribution methods, the author's claim that Benson's method provided the smallest errors when the absolute property is less than 10 kJ/mol (Poling *et al.* (2001)). Whereas, this method is more complicate than Joback's and Gani's method which has many group contributions.

Joback's method is the simplest method for estimation of missing properties; however, this method can occur large errors for some components.

CHAPTER III

LITERATURE REVIEWS

In this chapter, three common routes of glycerol carbonate production are reviewed and discussed from the literatures. There are conversion of glycerol with carbon dioxide, reaction of glycerol with dimethyl carbonate, and glycerolysis of urea. Each method is described in details below.

3.1 Conversion of glycerol with carbon dioxide

The reaction of glycerol and carbon dioxide is one of the interesting routes among scientific researches. This route is more attractive and economic to convert glycerol and carbon dioxide to glycerol carbonate which is a higher value-added product (Behr *et al.*, 2008).

So many researches have attempted to develop this route to be more efficient such as improving activity of carbon dioxide, finding an appropriate catalyst, and adding solvent medium. One alternative route is the use of supercritical carbon dioxide to improve the conversion of the reaction. Vieville *et al.* (1998) studied the synthesis of glycerol carbonate with supercritical carbon dioxide as a reaction medium and a reactant. The reaction conditions were 13 MPa and 347K. The results showed that the synthesis of glycerol carbonate was possible under the condition of supercritical carbon dioxide. However, the disadvantage of this system had low yield (4.7%) because of the low solubility of glycerol in supercritical medium. Another route of improving the conversion of glycerol and carbon dioxide is selection of appropriate catalysts which increase the activity of carbon dioxide. Aresta *et al.* (2006) examined the carboxylation of glycerol to glycerol carbonate with carbon dioxide at 450 K with Sn-catalysts. The $n\text{-Bu}_2\text{Sn}(\text{OCH}_3)_2$ catalyst could produce dimethyl carbonate and it could react with glycerol to produce glycerol carbonate, however, the conversion rate of the formation of dimethyl carbonate was lower than that of glycerol carbonate in the presence of $n\text{-Bu}_2\text{Sn}(\text{OCH}_3)_2$ catalyst. For all that,

the reaction offered a much lower rate for several hours, high pressure operation (5MPa), and still low conversion of glycerol. To improve the conversion of glycerol and carbon dioxide, a solvent medium can be added in the reaction mixture to increase the solubility of the reactant. George *et al.* (2009) reported the synthesis of glycerol carbonate from the reaction between glycerol and carbon dioxide in methanol as a solvent with $n\text{Bu}_2\text{SnO}$ (dibutyltin(IV)oxide) as a catalyst. They found that the addition of alcoholic solvent in reaction medium could increase the rate of reaction and yield of glycerol carbonate. In addition, this process is required to remove water from the system to prevent thermodynamic limitations. The yield of glycerol carbonate was 35% in 4 h.

At present, this route has been unsuccessful due to low selectivity of glycerol carbonate and high pressure operation, so it still challenges in scientific research because it is more economic to convert waste into a value-added product.

3.2 Reaction of glycerol with dimethyl carbonate

Glycerol carbonate can be produced by the transesterification between glycerol and ethylene carbonate (Cho *et al.*, 2010). Nevertheless, this carbonate reactant is expensive, and the formation of the high boiling point byproduct can cause the problem in purification process. However, this problem does not occur when using dimethyl carbonate as carbonate source in the synthesis of glycerol carbonate which leads to production of methanol as a by-product which can be removed by a simple separation.

There are many routes to improve the efficiency of the glycerol carbonate production. One alternative route is finding the appropriate catalyst for this system. Previously, the synthesis of glycerol carbonate from the reaction between glycerol and dimethyl carbonate was carried out by using lipase as a biocatalyst in many researches. Glycerol carbonate can be prepared from the reaction of glycerol with dimethyl carbonate in high yield which catalyzed by lipase (Pagliaro *et al.*, 2008). Kim *et al.* (2007) reported enzymatic synthesis of glycerol carbonate from the reaction of glycerol and dimethyl carbonate. They screened a variety of commercial lipase, and the results showed that immobilized lipase from *Candida Antarctica*

(CALB, Novozym 435) provided high catalytic activity. Moreover, they tested the effect of reaction parameters on the synthesis of glycerol carbonate such as the ratio of glycerol to dimethyl carbonate and reaction temperature. The results showed that high yield of glycerol carbonate was obtained when the ratio of dimethyl carbonate to glycerol became equimolar. It was suggested that the high yield of glycerol carbonate should be obtained with high molar ratio of dimethyl carbonate to glycerol because of shifting the equilibrium reaction. Another disadvantage from the use of lipase as a biocatalyst in this research is the deactivation of lipase at high temperature, resulting in limitation of reaction rate of glycerol carbonate formation. Another way to improve the yield of glycerol carbonate with the use of lipase as a biocatalyst is finding the optimum reaction conditions. Lee *et al.* (2010) examined the synthesis of glycerol carbonate from the reaction of glycerol and dimethyl carbonate using lipase as a biocatalyst in a solvent-free transesterification reaction. Moreover, they tested a variety of lipases for their catalytic activity in the reaction and optimized the reaction conditions. The results showed that Novozyme 435 provided high catalytic activity. The high yield of glycerol carbonate could be obtained at a molar ratio of dimethyl carbonate to glycerol of 10 and the reaction temperature of 70 °C. Furthermore, glycerol carbonate was synthesized with high yield (90%) for 48 h.

Nevertheless, the limitations from the use of lipase such as deactivation at high temperature and the higher price of lipase make it impossible to use in the large industrial scale. Therefore, many researches attempt to find inorganic catalysts for the replacement of the biocatalyst. One of that is K_2CO_3 which is the homogeneous catalyst and has high activity in this reaction. Herseczki *et al.* (2009) studied the synthesis of glycerol carbonate from the reaction between glycerol and dimethyl carbonate using K_2CO_3 as a catalyst. However, the reaction required a high molar ratio of dimethyl carbonate to glycerol to shift the reaction equilibrium. The results show that this system could provide high yield of glycerol carbonate. Ladero *et al.* synthesized glycerol carbonate from dimethyl carbonate and glycerol by using alkaline hydroxides and carbonates as catalysts at low temperature without any solvent. The results showed that the rate of reaction increased rapidly when K_2CO_3 was added. In addition, this system removed methanol as a by-product by distillation.

In this homogeneous reaction system, the catalyst was soluble in the reaction mixture, so it was difficult to remove and recycle in the next reaction cycles. Nowadays, there are great concerns to have economical processes. It is more economic to use a heterogeneous catalyst. Therefore, many researchers attempt to develop heterogeneous catalysts for the synthesis of glycerol carbonate even if the activity decrease slightly. Ochoa-Goómez *et al.* (2009) studied and screened homogeneous and heterogeneous catalysts for the synthesis of glycerol carbonate by transesterification between dimethyl carbonate and glycerol. Excess dimethyl carbonate was used to shift the chemical equilibrium. In addition, they optimized the reaction by using the active catalyst from screening. The results showed that catalytic activity depend on its basic strength. Therefore, CaO was the best heterogeneous catalyst for the synthesis of glycerol carbonate, and this catalyst could be removed from the reaction mixture and easily available.

One alternative route to improve the efficiency of this system is based on process development such as shifting the equilibrium reaction. As described above, several researches used a high molar ratio of dimethyl carbonate to glycerol to shift the reaction equilibrium. Moreover, dimethyl carbonate was more expensive than glycerol. Excess dimethyl carbonate must be removed and recycled for the next reaction cycles by specific distillation such as azeotropic distillation. In addition, the side reactions could occur in the system with excess dimethyl carbonate, so the yield of glycerol carbonate was decreased. Therefore, it has potential to solve these problems with using reactive distillation. Li *et al.* (2010) examined the synthesis of glycerol carbonate with coupling the reaction and azeotropic distillation. In addition, this process could shift the reaction equilibrium without using excess dimethyl carbonate by removing methanol as a by-product at distillate. They used calcium oxide (CaO) as the catalyst which could be separated from the reaction mixture to recycle in several times. Calcium oxide catalyst was used to replace an expensive lipase catalyst in the reaction. And the influence of the reaction parameters on yield of glycerol carbonate was studied. The results showed that benzene was the most efficient entrainer for the azeotropic distillation. Furthermore, the yield of glycerol carbonate insignificantly reduced when using reused CaO catalyst in this system. Coupling reaction and azeotropic distillation resulted in shifting the reaction

equilibrium which could provide high yield of glycerol carbonate even if using the deactivated catalyst. High yield (98%) of glycerol carbonate could be obtained with optimum condition which had molar ratio of dimethyl carbonate to glycerol 1:1, final temperature of tower bottom at 85°C, mass ratio of added benzene to methanol produced of 1.5 and reflux ratio of 4.

3.3 Glycerolysis of urea

Another method of the synthesis of glycerol carbonate is by the reaction between glycerol and urea which produces ammonia as a byproduct gas. The two steps reaction catalyzed by a mineral zinc sulfate could achieve high productivity and selectivity at a temperature between 90 and 220 °C and a pressure of 40 – 50 mbar by Lewis acid catalyst (Pagliaro *et al.*, 2008). High yield of glycerol carbonate is limited by the equilibrium reaction. Shifting the reaction equilibrium by removing ammonia from the system could carry out by passing air or nitrogen gas to extract ammonia gas or operating under vacuum pressure. Claude *et al.* (US 006025504A) examined the synthesis of glycerol carbonate by the carbamoylation/carbonation reaction between glycerol and urea using Lewis acid sites catalyst under vacuum operation. The equipment setup is illustrated in Fig.3.1. The results show that high yield (80%) of glycerol carbonate was obtained with using zinc sulfate as a catalyst under vacuum. However, it involved high operation cost due to very low pressure operation.

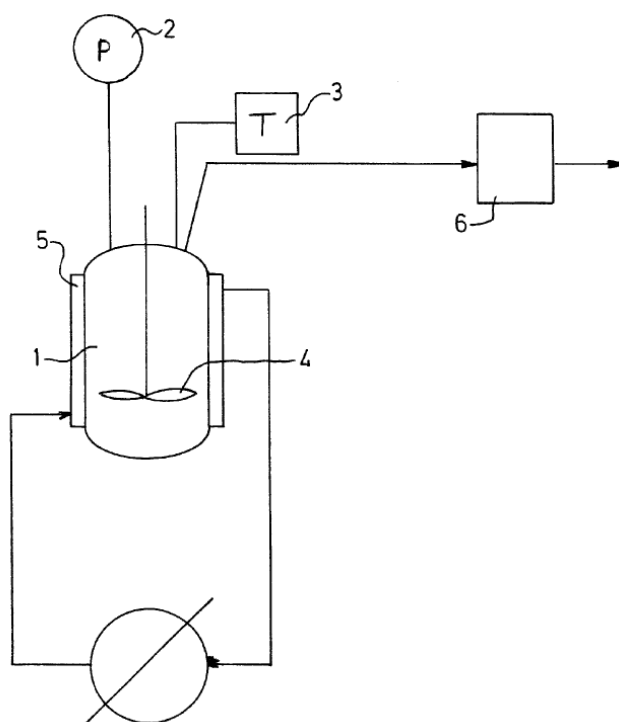


Figure 3.1 Installation batch operating experiment : 1-semi-closed reactor, 2-pressure sensor, 3-temperature sensor, 4-mechanical stirrer, 5-jacket, and 6-vacuum pump (Claude *et al.* (US 006025504A))

The purification process of glycerol carbonate from the reaction mixture was difficult due to the high boiling point of product. Consequently, a complicated purification was used such as high vacuum distillation, and chromatographic process. However, no technical method available to analyze and separate completely of glycerol carbonate from the reaction mixtures (glycerol, urea, and glycerol carbonate) exists in the literature. Fourdinier *et al.* (2010) studied a chemometric approach which was used in hydrophilic interaction liquid chromatography (HILIC) for the separation of glycerol carbonate, glycerol and urea. They tested with the Monochromdiol column for a mobile phase composed of 95% MeCN and 5% water. These conditions were confirmed that the analytical method was applicable for the quantitative analysis of glycerol, urea and glycerol carbonate. Nevertheless, this purification process is also difficult to operate in industrial scale.

Many researches improved the yield of glycerol carbonate by finding the appropriate catalyst. Several catalysts which provided high yield and selectivity of

glycerol carbonate were examined to find the optimal reaction conditions. Lelovský *et al.* (2009) studied the glycerolysis of urea with various catalysts. Furthermore, they concentrated on different zinc compounds and transition metal oxides and examined their catalytic activity in the reaction between glycerol and urea. From the reaction, the formation of many byproducts was observed such as Glycidol (2,3-epoxy-1-propanol), oligomers of glycerol, 4-hydroxymethyl oxazolidine-2-one and 2-oxodioxola-4-ylmethyl ester of carbamic acid. The results showed that the Lewis acidic catalyst such as zinc compounds and zeolites provided significant yields of glycerol carbonate. ZnO is very active at the initial state and then its activity decreased with the time whereas ZnSO₄.H₂O was stable. So, this catalyst provides good results in long time reaction. In addition, the reaction with ZnO catalyst could obtain high yield of glycerol carbonate at the lower pressure.

As described above, the reaction between glycerol and urea catalyzed by zinc sulfate could achieve with high yield and selectivity (Pagliaro *et al.*, 2008). However, this salt is soluble in reaction mixture and the reaction takes place under homogeneous catalysis reaction. Therefore, that was difficult to recover and recycle in several times. Using a heterogeneous catalyst for the synthesis of glycerol carbonate can help environmental issues. Aresta *et al.* (2009) tested and screened several catalysts which did not dissolve in the reaction mixtures to find the catalytic material which was easily recoverable and recyclable. In addition, they tested the effect of the reaction parameters on yield and selectivity of glycerol carbonate to find the optimum conditions. The results showed that γ -zirconium phosphate was the most active catalyst which could be recovered and recycled several cycles of the reaction. Moreover, the catalyst could maintain its efficiency and selectivity when used in several cycles with recovery and thermal treatment. Cyclic carbamate was a by-product which formed only after several cycle. The temperature and reaction time were tested to find the optimum conditions. The best condition to produce glycerol carbonate took place at 20 Pa 418 K for 3 h of reaction using an equimolar of two reactants with a catalyst load of 0.6 - 1.5% w/w with respect to glycerol. And that could obtain good conversion of glycerol (80%) and high selectivity. In this research, the disadvantage of the using γ -zirconium phosphate as a catalyst is difficult to

synthesize and high cost of the source for the preparation of catalyst. So those are difficult to operate in industrial scale.

The acid-base properties of catalyst can affect the activity of the reactants and the yield of glycerol carbonate. The catalyst with well balanced acid-base properties can activate the molecule of the reactants to achieve high yield of product. Therefore, many researches attempt to improve its properties of the catalyst. Climent *et al.* (2010) studied the synthesis of glycerol carbonate from the reaction of glycerol and urea using heterogeneous catalyst such as basic oxides (MgO and CaO), and mixed oxides obtained from hydrotalcites. In addition, they examined carbonylation of glycerol with urea to provide high yield of glycerol carbonate using recyclable heterogeneous catalyst with adequate acid-base pairs. The authors claimed that catalysts which had adequate acid and base properties were favorable to the synthesis of cyclic carbonates from the reaction between diols and urea to provide high yield of the cyclic carbonate. Besides, the reaction conditions were optimized at 145 °C reaction temperature, 30 Torr of pressure, and 5 h reaction time. The results of the synthesis of glycerol carbonate with using different catalysts showed that ZnO catalyst with a lower basic strength and high acidity of the conjugated acid could achieve high activity. However, they found that Al/Zn-mixed oxide was the most active and selective catalyst and provided 82% conversion and 88% selectivity of glycerol carbonate. To study deactivation of the catalyst, the yield of glycerol carbonate was reduced after the first cycle of the reaction and slightly decreased in the next cycles.

One alternative route to improve the yield of glycerol carbonate is to increase reactive surface of the catalyst such as nanodispersion which results in high yield of glycerol carbonate. Rubio-Marcos *et al.* (2010) reported a solvent-free preparation method to make hierarchical cobalt oxide nanoparticles (40-50 nm) dispersed zinc oxide microparticles (0.2-1 μm) for the synthesis of glycerol carbonate. The catalytic activity of catalysts was tested in the synthesis of glycerol carbonate from glycerol and urea. The system was operated at 1 atm and the shift of equilibrium reaction was enhanced by passing air through the reactor. Furthermore, they discussed the effect of the preparation procedure of $\text{Co}_3\text{O}_4/\text{ZnO}$ mixtures. The results showed that the best activity and selectivity of glycerol carbonate could obtain at moderate reaction

conditions (140 °C and 4 h.) with $\text{Co}_3\text{O}_4/\text{ZnO}$ prepared at room temperature in dry nanodispersion method. In addition, the catalyst system containing more cobalt oxide could obtain higher activity because the $\text{Co}_3\text{O}_4/\text{ZnO}$ catalyst prepared by dry nanodispersion created new reactive surfaces that were favorable to the synthesis of glycerol carbonate. From this research, the advantages of the use of heterogeneous catalyst ($\text{Co}_3\text{O}_4/\text{ZnO}$) were very fast preparation, eco-friendly, easily recoverable and recyclable in several times without any loss in activity and selectivity during the carbonylation of glycerol. The $\text{Co}_3\text{O}_4/\text{ZnO}$ catalyst has a potential to produce glycerol carbonate. And the distillation should exchange the separation of product, and reactant at the same time. The reactive distillation will be examined.

Table 3.1 Comparison between different reactions for glycerol carbonate production from glycerol

Process	Advantage	Disadvantage
the conversion of glycerol with carbon dioxide	- inexpensive reagent	- Low conversion - high pressure operation
glycerol and dimethyl carbonate in a reaction catalyzed by lipases	- no high pressure equipment - mild condition - high selectivity - Environmentally chemical	- high cost of organic carbonate - high molar ratio of dimethyl carbonate to glycerol - long reaction time - the lipase catalyst was expensive
reaction between urea and glycerol ,carbamylation–carbonation at 90 and 220 C in Lewis acid catalyst	- high yields - short reaction time - inexpensive reagent - no high pressure equipment - easily available	- reaction under vacuum - reaction in dehydrating agent (prefer)

3.4 Reactive distillation

Many systems cannot completely convert reactants to a desired product because of reaction equilibrium limitations. Therefore, integration of separation and reaction unit with reactive distillation is one alternative way to improve the yield of desired product by shifting equilibrium reaction. As described above, Li *et al.* (2010) coupled the reaction and azeotropic distillation to produce glycerol carbonate from the reaction between glycerol and dimethyl carbonate. In this paper, coupling the reaction and azeotropic distillation provided to produce continuously glycerol carbonate in high yield without excess expensive dimethyl carbonate. Dhale *et al.* (2004) studied to use a reactive distillation for propylene glycol and ethylene glycol recovery from aqueous solution in acetal formation reaction. The simulation of propylene glycol acetalization was carried out to compare the experimental results using the RADFRAC module column of Aspen Plus 11.1. The results show that high yield of propylene glycol was obtained by reactive distillation method. The kinetic rate-based model reaction for simulation with RADFRAC module column of Aspen Plus 11.1 can predict the experimental results.

Bonet *et al.* (2009) developed a new process to revalorize glycerol for synthesis of triacetin (glyceryl triacetate) by using reactive distillation. Aspen plus was used to simulate the production of triacetin from the reaction between glycerol and acetic acid by using UNIFAC method. Reactive distillation was based on equilibrium stage model and experimental kinetic reaction model. The design and operating variables of reactive distillation including number of stages, distillate flow rate and reflux ratio were studied. In addition, simulation results for synthesis triacetin by using reactive distillation were compared with the results from traditional process. The results showed that the suitable conditions for reactive distillation were 70 stages, reflux ratio of 2.51 and distillate flow rate of 26 kmol/h. Total conversion of glycerol and 99% purity of triacetin could be obtained by using reactive distillation due to shifting equilibrium reaction. Compared to traditional process, reactive distillation provided greater advantages.

Arisketa *et al.* (2010) studied the production of acetal (1,1 diethoxy butane) from acetalization reaction between ethanol and butanol by using reactive distillation.

In conventional reaction system, only 40-50 % conversion could be achieved due to equilibrium thermodynamic limitations. Kinetic model was determined from experimental batch reaction by using Arrhenius correlation. Moreover, synthesis of acetal by using reactive distillation was run experimentally in a semi pilot plant with Katapak SP-11 modules packing and Amberlyst 47 ion exchange resin as a catalyst packing. The effect of design and operating variables such as reflux ratio and number of stages were examined. The results showed that conversion decreased by increasing the number of rectifying stages for every reflux ratio because of more acetal as a high boiling point compound in reactive section. High conversion could be achieved by increasing the number of stripping stages due to a higher concentration of volatile compounds (the reactants) in the reactive section. Increasing the number of reaction stages resulted in increasing conversion. Furthermore, high reflux ratio caused to increase conversion. Appropriate column configurations for synthesis acetal from acetalization reaction were 3 reaction stages, 1 rectifying stage, 3 stripping stages and reflux ratio of 5.

The group contribution methods are useful for the estimation of missing thermodynamic properties. Moreover, these can be applied to estimate in several substances properties with no experimental data. Normally, method of Joback, Gani and Benson are investigated but any method is not completely reliable. Kiatkittipong *et al.* (2011) applied three group contribution methods to estimate the missing thermodynamic properties for glycerol ethers synthesis from glycerol etherification in reactive distillation. Besides, three group contributions were used to obtain the equilibrium composition by minimization of Gibb's free energy. The results showed that Gani's method provided the lowest percent deviation among the three methods and showed good agreement with experimental equilibrium compositions. However, the small adjustment (2%) of Gibb's free energy of formation from Gani's method provided closer to experimental results. Furthermore, the activity based Langmuir-Hinshelwood model gave the best agreement with experimental results in kinetic study. In reactive distillation study, a RADFRAC module in Aspen plus program was used to study for the synthesis of glycerol ethers from glycerol etherification. The effect of design variables including number of rectifying stages, reaction stages and

stripping stages was investigated. The results showed that the suitable configuration of reactive distillation is 6 reaction stages, 6 rectifying stages and no stripping stage.

As described above, it has potential to synthesize glycerol carbonate via the glycerolysis of urea with the reactive distillation and the high yield of glycerol carbonate can be obtained by shifting the equilibrium reaction.

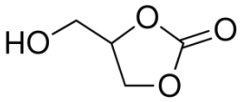
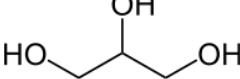
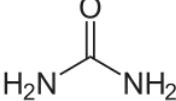
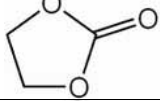
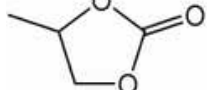
CHAPTER IV

EXPERIMENTAL DETAILS

4.1 Estimation of missing parameters:

Thermodynamic parameters of glycerol carbonate such as Gibb's free energy of formation cannot be obtained from the literature. Therefore, missing properties of glycerol carbonate were estimated by the group contribution methods. There are Joback's method, Gani's method and Benson's method. The substances having the similar structure to glycerol carbonate were estimated for its thermodynamic properties. Then percent deviations of some known physical properties are compared between different methods to select an appropriate one for glycerol carbonate. Table 4.1 summarizes the substances involved in this study.

Table 4.1 Lists of chemical substances for comparison.

Substances	Molecular formula	Molecular structure	G_f° database (kJ/mol)
glycerol carbonate	$C_4H_6O_4$		-
glycerol	$C_3H_8O_3$		-484.08
urea	CH_4N_2O		-177.43
ethylene carbonate	$C_3H_4O_3$		-435.21
propylene carbonate	$C_4H_6O_3$		-478.77

4.2 Catalyst Preparation

$\text{Co}_3\text{O}_4/\text{ZnO}$ was prepared by dry nanodispersion method (Rubio-Marcos et al., 2010). The dry dispersion procedure determined by shaking 10% wt. of Co_3O_4 nanoparticles (Aldrich) with ZnO microparticles (Aldrich) in a flask for 5 min. Before dry dispersion procedure, analytical grade materials were dried at 110 °C for 2h.

4.3 Catalyst Characterization

The particle size and morphology of $\text{Co}_3\text{O}_4/\text{ZnO}$ catalyst was characterized by using scanning electron microscopy (SEM) to confirm dispersion of Co_3O_4 nanoparticles on the interface of ZnO microparticles.

4.4 Batch reaction procedures

40 ml (0.55 mol) of glycerol (99.5%, Qrec), 32.9 g (0.55 mol) of urea (99.5%, Qrec) and 0.7566 g of $\text{Co}_3\text{O}_4/\text{ZnO}$, (urea/glycerol molar ratio = 1, catalyst load of 1.5% by weight with respect to glycerol) were mixed in the autoclave reactor (100 ml). The turbine, sampling port and thermocouple are installed on a reactor. The batch reaction is illustrated in Fig 4.1. The mixture was stirred at 1163 rpm to reduce the external mass transfer effect and heated in oil bath at determined reaction temperature under atmospheric pressure. After completed reaction, the catalyst was separated by centrifugation. The reaction mixture was analyzed by gas chromatography equipped with ZB-5HT capillary column and a flame ionization detector (FID).

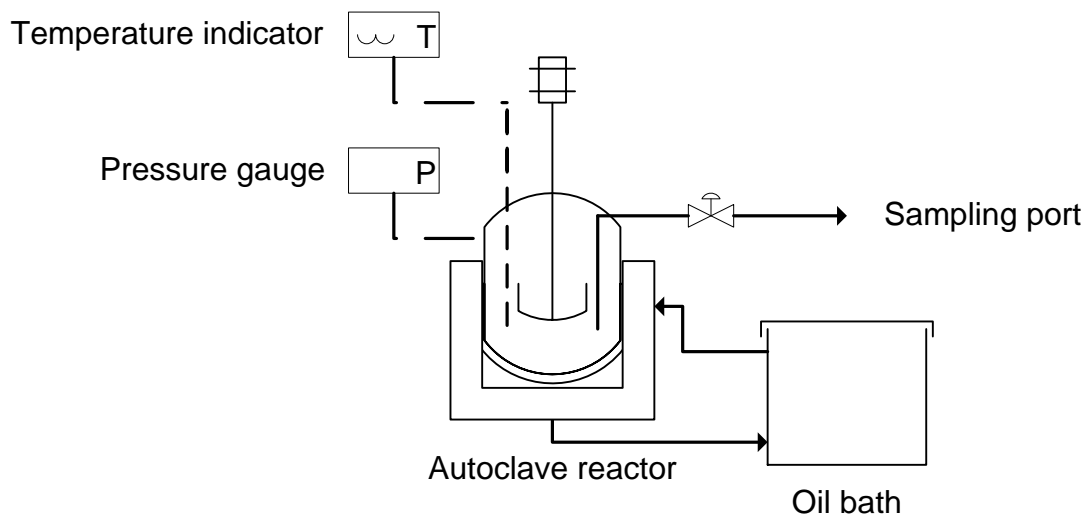


Figure 4.1 Schematic diagram of the batch experimental system.

Table 4.2 Operating conditions for gas chromatography

Gas Chromatography	Shimadzu GC-14B
Detector	FID
Column	ZB-5HT
- Column material	Phenyl-Dimethylpolysiloxane
- Length (m)	30
- Inner diameter (mm)	0.25
- Film Thickness (um)	0.25
- Maximum temperature (°C)	400
Carrier gas	N ₂ (99.999%)
Carrier gas flow (ml/min)	30
Column temperature	
- initial (°C)	50
- final (°C)	340
Injector temperature (°C)	310
Detector temperature (°C)	340
Analyzed compounds	High molecular weight compounds such as triglycerides, polymers

4.5 Determination of reaction model parameters and comparison with experimental results

The reaction model parameters were estimated from experimental results carried out at different temperatures including 100°C, 140°C, 160°C and 180°C. Firstly, the equilibrium compositions obtained from the experiment were applied to Aspen Plus (RGibbs reactor) to estimate Gibbs free energy and enthalpy of formation of glycerol carbonate. Then the reaction kinetic model was developed and the parameters which offered the best fit of the experimental results at different conditions were determined. The obtained kinetic parameters were then applied to conventional reactor with air flow and reactive distillation in the next study.

4.6 Reactive distillation simulation

The simulations were carried out by using the RADFRAC module in Aspen plus to predict the results of reactive distillation for the synthesis of glycerol carbonate from glycerol and urea. On each stage of the column, it is assumed to be vapor-liquid equilibrium and neglected pressure drop within the column. The Aspen plus component database provides physical and chemical properties of all species except glycerol carbonate which is estimated by using group contribution method such as boiling point and standard Gibb's free energy of formation. Fig.4.2 shows the diagram of the reactive distillation used in the research.

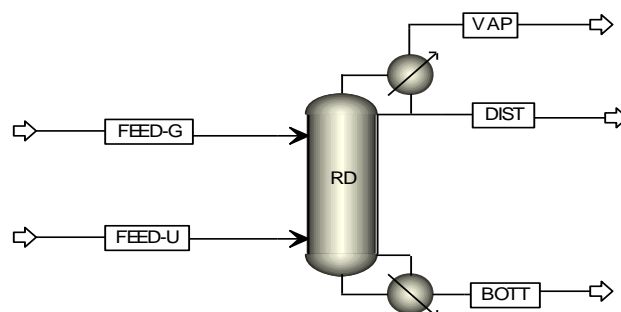


Figure.4.2 RD simulation in Aspen Plus program

The effects of design and operating variables including number of rectifying stage, stripping stage, reaction stage, reflux ratio and reboiler heat duty on the reactive distillation performance were studied.

4.7 Comparison between reactive distillation with conventional method

The results of reactive distillation simulation were compared with that of conventional method to synthesize glycerol carbonate. The conventional method including batch operation with using sweep gas was investigated to determine on conversion of glycerol, yield and purity of glycerol carbonate for comparison.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Catalyst characterization:

The heterogeneous $\text{Co}_3\text{O}_4/\text{ZnO}$ catalyst was prepared by dry nanodispersion method (Rubio-Marcos et al., 2010). Scanning electron microscopy (SEM) was used to check and confirm dispersion of Co_3O_4 nanoparticles on the interface of ZnO microparticles as shown in literature (Rubio-Marcos et al., 2010).

Figure 5.1 showed the agglomerate of spherical Co_3O_4 nanoparticles. The agglomerate of this particle results to decrease surface area of the catalyst. Figure 5.2 showed elongated prismatic ZnO microparticles. And $\text{Co}_3\text{O}_4/\text{ZnO}$ catalyst that was prepared by dry nanodispersion method is illustrated in Figure 5.3. It can be seen that the agglomerate of Co_3O_4 nanoparticles disappear. The great distribution of Co_3O_4 nanoparticles on the interface of ZnO microparticles can provide high activity of the catalyst.

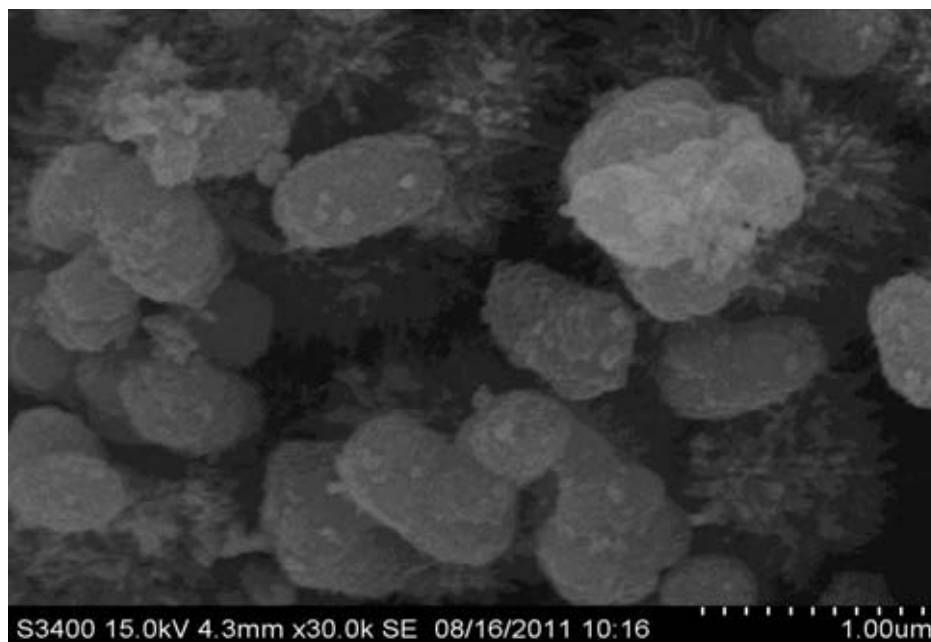


Figure 5.1 Scanning electron microscopy micrograph of Co_3O_4 nanoparticles agglomerates.

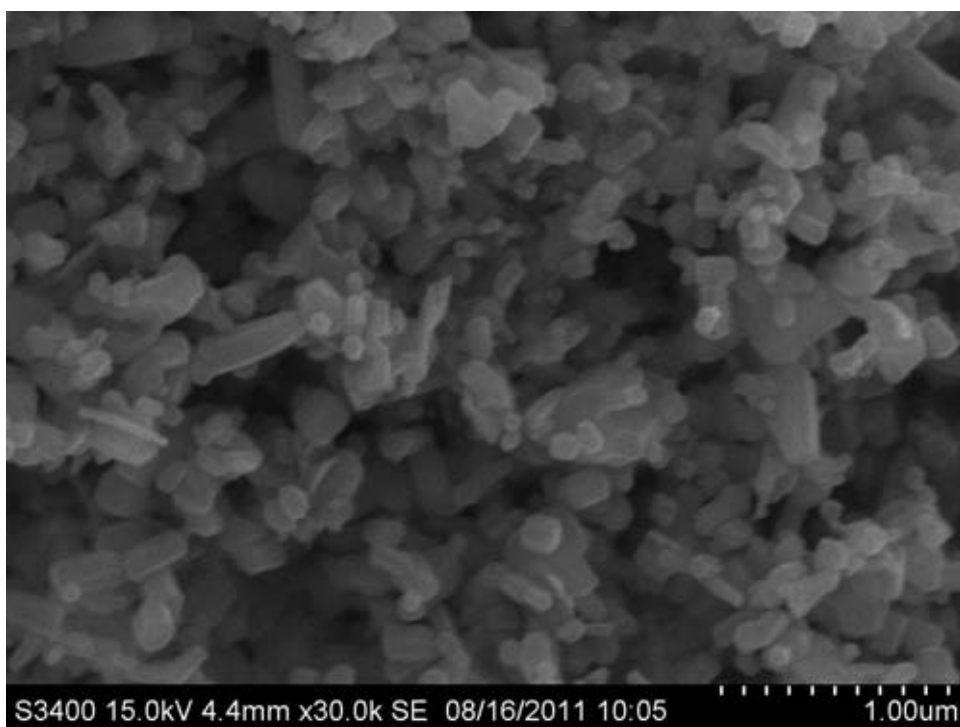


Figure 5.2 Scanning electron microscopy micrograph of ZnO microparticles.

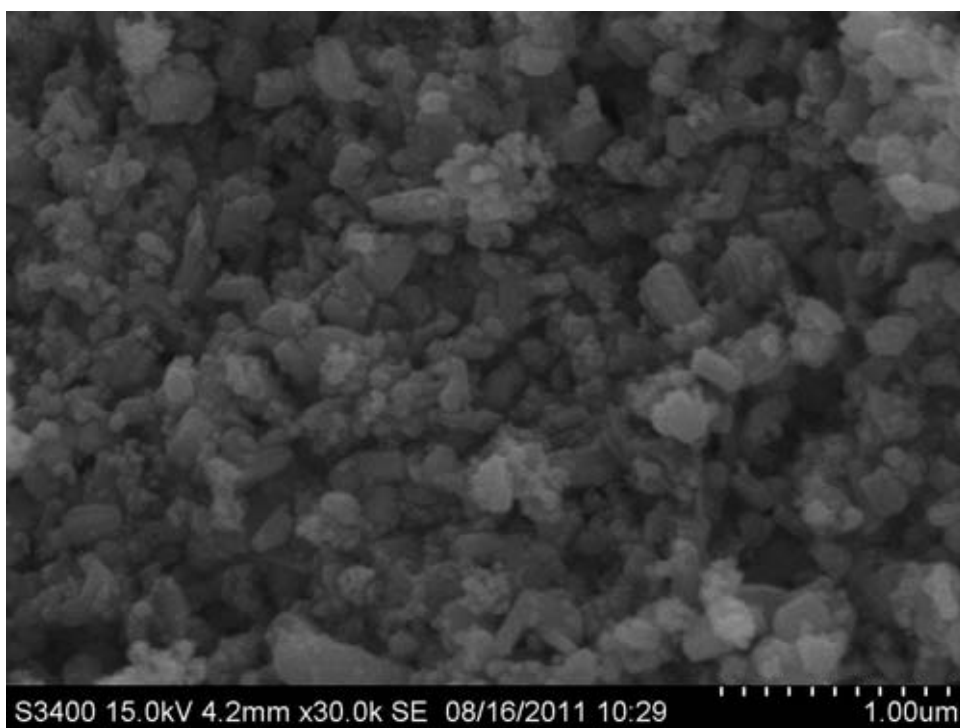


Figure 5.3 Scanning electron microscopy micrograph of $\text{Co}_3\text{O}_4/\text{ZnO}$ mixture.

5.2 Equilibrium thermodynamic analysis:

For synthesis of glycerol carbonate from the reaction between glycerol and urea, the equilibrium constant is based on equilibrium mole fraction of components in liquid phase as shown below:

$$K_{\text{eq}} = \frac{(x_{\text{GC}}) \cdot (x_{\text{NH}_3})^2}{(x_{\text{Gly}}) \cdot (x_{\text{Urea}})} \quad (5-1)$$

In addition, the equilibrium constant could be obtained from the Gibbs' free energy of components as shown in equations (5-2) and (5-3). However, the Gibbs' free energy of glycerol carbonate could not be obtained from the literature. Therefore, the group contribution methods were used for the estimation.

$$\Delta G(T, P) = -RT \ln K_{\text{eq}} \quad (5-2)$$

$$\Delta G^{\circ} = \sum_{\text{p}} n_{\text{p}} \Delta G_{\text{p}}^{\circ} - \sum_{\text{r}} n_{\text{r}} \Delta G_{\text{r}}^{\circ} \quad (5-3)$$

The missing thermodynamic properties of glycerol carbonate were determined by using three group contribution methods including Benson's, Joback's and Gani's methods. The missing properties of glycerol carbonate are required for simulation process in the next section. The estimation of missing parameters of glycerol carbonate by three group contribution methods using Aspen Plus program was shown in Table E.1 (Appendix E).

The appropriate group contribution method was selected based on estimation of known thermodynamic properties of some chemicals with similar structures of glycerol carbonate such as propylene carbonate and ethylene carbonate by comparison between known properties from database and those estimated from different methods. The estimated standard Gibbs' free energy and percent deviation were shown in Tables 5.1. The results showed that Gani's method provided the lowest percent deviation among the three methods. This method showed good agreement with cyclic carbonate compounds. Joback's method is the simplest method for estimation of

missing properties. However, this method could result in large errors for some components such as urea. Benson's method is the most complicated estimation technique, but this method provided the largest error for estimation of Gibb's free energy of some chemicals with similar structures of glycerol carbonate.

Table 5.1 Standard Gibbs free energy database and estimated value by group contribution methods

Substances	G° (kJ/mol) database	Estimated G° (kJ/mol)			Deviation (%)		
		Joback	Gani	Benson	Joback	Gani	Benson
Glycerol carbonate	-	-511.4	-539.3	-480.5	-	-	-
Glycerol	-484.1	-477.8	-493.5	-480.1	1.30	-1.95	0.82
Urea	-177.4	-52.1	-165.2	-201.1	70.62	6.89	-13.35
Ethylene carbonate	-435.2	-360.2	-385.5	-325.7	17.23	11.42	25.17
Propylene carbonate	-478.8	-361.2	-383.7	-256.7	24.56	19.87	46.39

Therefore, estimated thermodynamic properties of glycerol carbonate by using Gani's method were applied to simulate equilibrium conversion of glycerol by using RGibbs module in Aspen plus. The results were shown in Figure 5.4. It can be seen that the large error could occur from simulation. However, thermodynamic properties of glycerol carbonate could be calculated from experimental results.

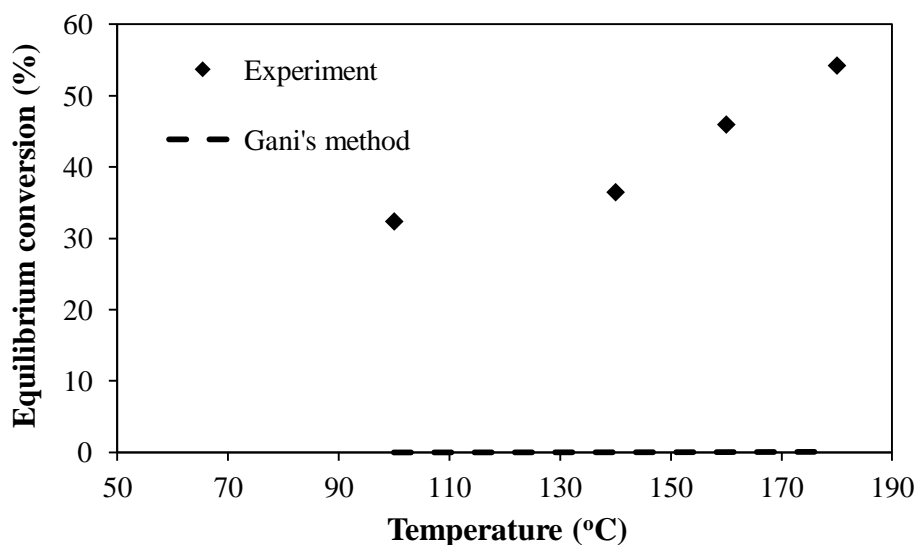


Figure 5.4 Dependence of equilibrium conversion of glycerol on reaction temperature from simulation by using group contribution method and experiment.

For synthesis of glycerol carbonate from the reaction between glycerol and urea, there are four steps of reaction mechanism. Firstly, reaction of glycerol with urea produces glycerol urethane and ammonia as a byproduct. Secondly, glycerol carbonate and ammonia are produced from carbonation of glycerol urethane. Thirdly, 5-(hydroxymethyl) oxazolidin-2-one is produced from the conversion of glycerol urethane. Finally, (2-oxo,-1,3-dioxolan-4-yl)methyl carbamate as a byproduct is produced from the reaction between glycerol carbonate and residue urea (Rubio-Marcos et al., 2010).

In this study, $\text{Co}_3\text{O}_4/\text{ZnO}$ was used as a catalyst for synthesizing glycerol carbonate. Near 100% selectivity could be obtained by using $\text{Co}_3\text{O}_4/\text{ZnO}$ as a catalyst (Rubio-Marcos et al., 2010). In this study, it could be confirmed by using C-NMR analysis. The reaction mixture from the reaction between glycerol and urea at 140 °C, 1 atm and 3 h of reaction time using $\text{Co}_3\text{O}_4/\text{ZnO}$ as a catalyst was analyzed by C-NMR. C-NMR spectrum of reaction mixture was shown in Figure 5.5. It can be seen that only signals of glycerol and glycerol carbonate were present. A set of three signals of by-products at 42, 62 and 77 ppm could not be observed. Accordingly, determination of the reaction model parameters is based on the main reaction pathway as shown below:

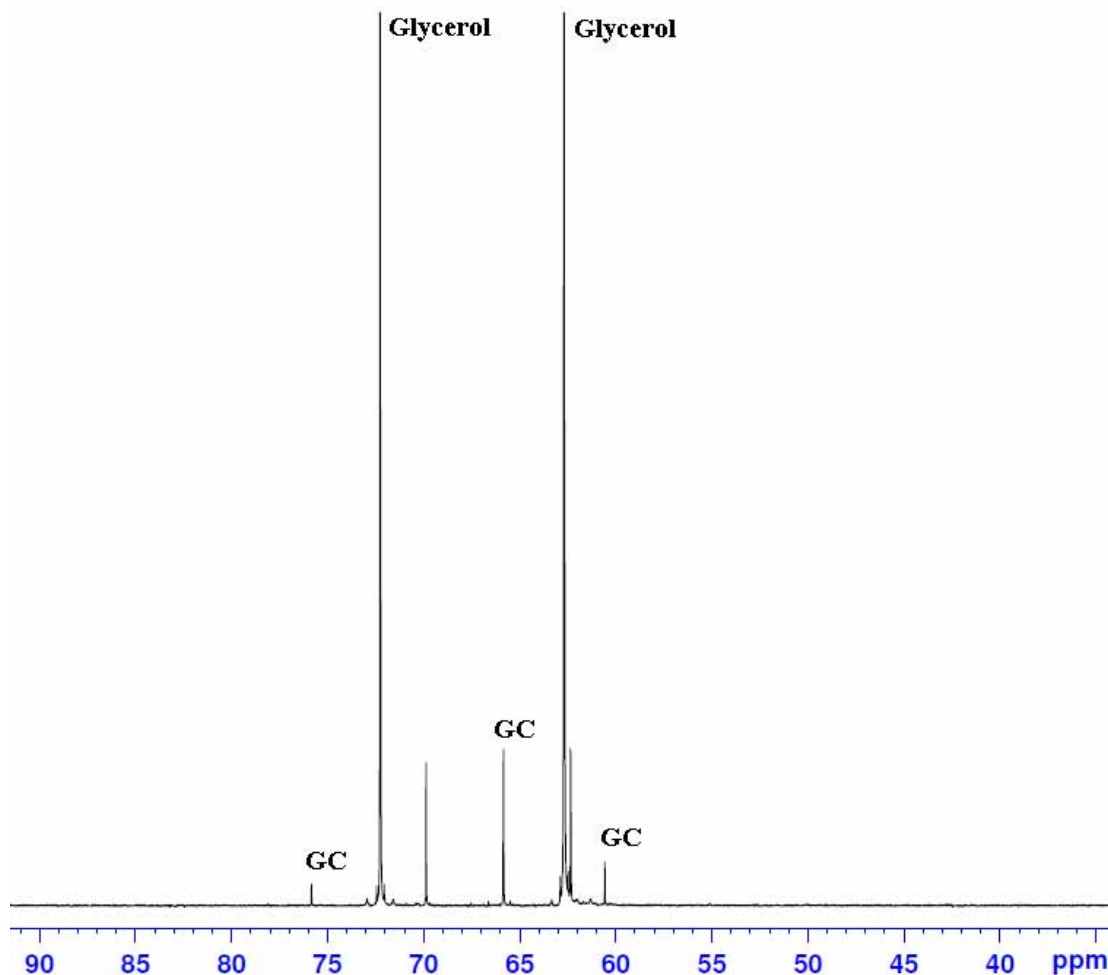


Figure 5.5 C-NMR (400 MHz, in D_2O) spectrum of the reaction mixture from the reaction conditions at 140°C , 1 atm and 3 h. reaction time with using $\text{Co}_3\text{O}_4/\text{ZnO}$ as a catalyst.

In this study, the reaction model parameters were determined by fitting the model with the experimental data at different temperatures including 100°C , 140°C , 160°C and 180°C . Then the obtained parameters were employed in the next simulation section.

Experimental results of conversion of glycerol with time at different temperatures were shown in Figure 5.6. It can be observed that conversion of glycerol increased with reaction time and became constant due to an equilibrium reaction. The

values of equilibrium conversion of 32%, 36%, 46% and 54% could be obtained at 100°C, 140°C, 160°C and 180°C, respectively.

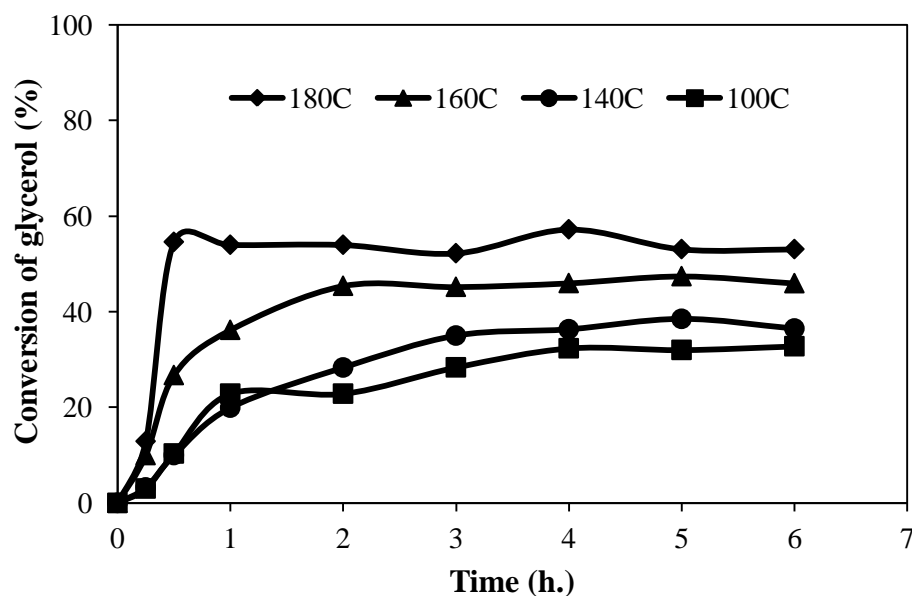


Figure 5.6 Experimental results at different temperatures (reaction conditions: 1 atm, equimolar ratio of reactants and 1.5% by weight catalyst with respect to glycerol).

Equilibrium model parameters were calculated from experimental results at equilibrium conditions. Equilibrium constant can be calculated from following equation (5-1).

Gibbs free energy of glycerol carbonate could be achieved from the equilibrium constant from equations (5-2) and (5-3) and compared with estimated results by the group contribution methods including Benson's, Joback's and Gani's methods as shown in Figure 5.7.

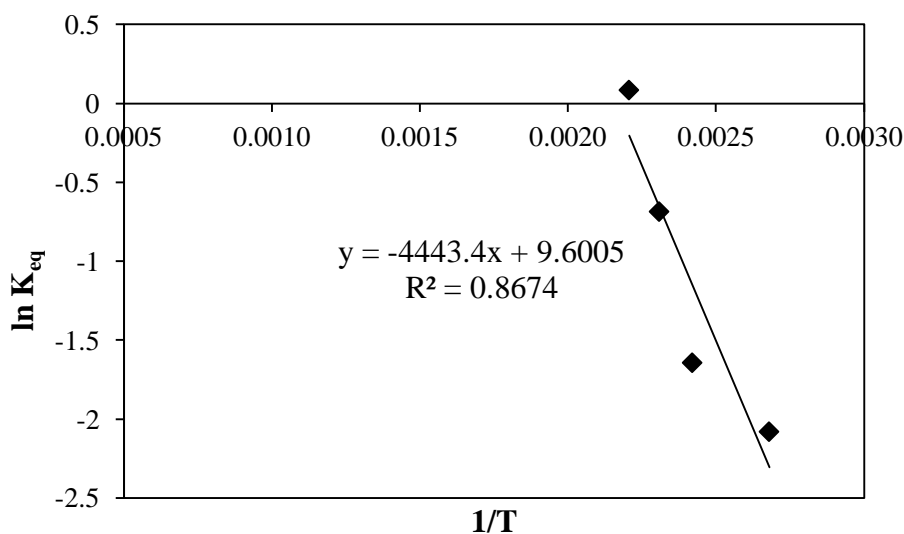


Figure 5.7 Van't Hoff's plots

Besides, enthalpy of formation of glycerol carbonate could be obtained from Van't Hoff plots as shown in Figure 5.7.

$$\ln K_{eq} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (5-5)$$

Figure 5.8 illustrated comparison of Gibbs free energy of glycerol carbonate at different temperatures from the experimental results and the estimated results by the group contribution methods. The results showed that Gibbs free energy of glycerol carbonate as a function of temperature had similar trend with the estimated results. Gani's method provided the best estimation results among the three methods which agreed with the results in the estimation of missing parameters section.

Table 5.2 summarizes thermodynamic properties of glycerol carbonate and compared with literature. It can be observed that the calculated enthalpy of formation of glycerol carbonate is close to the value from Li *et al.* (2010).

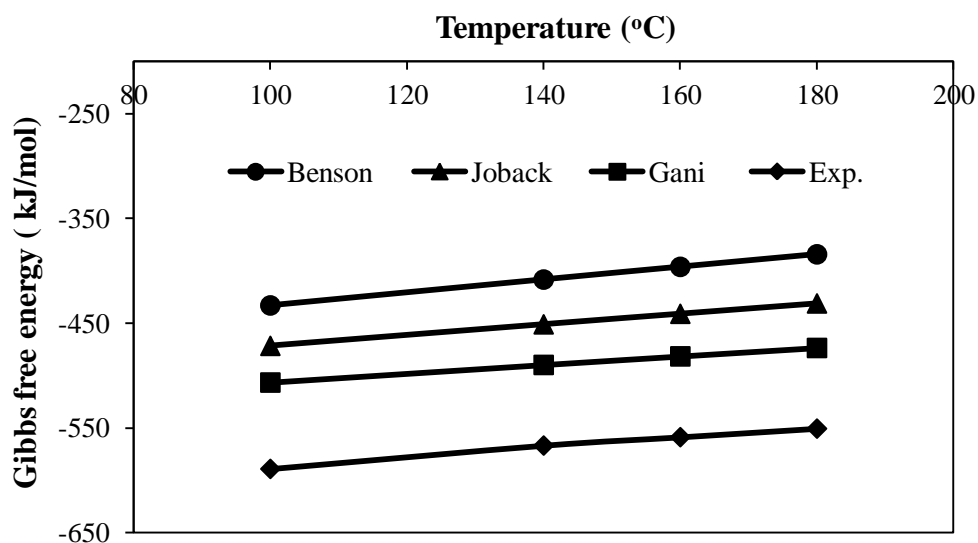


Figure 5.8 Comparison of Gibbs free energy of glycerol carbonate from experimental results and estimated results by the group contribution methods.

Table 5.2 Summary of the thermodynamic properties of glycerol carbonate from this work and from literature.

Thermodynamic properties of glycerol carbonate	In this study	Li <i>et al.</i> (2010)
Gibbs free energy of formation (kJ/mol)	-600.8	-
Enthalpy of formation (kJ/mol)	-784.8	-785.3

Thermodynamic properties of glycerol carbonate including Gibbs free energy of formation and Enthalpy of formation were applied in Aspen plus program by using RGibbs module to simulate equilibrium conversion and compare with experimental results as shown in Figure 5.9. Ideal method was used to predict the reaction between glycerol and urea. It can be seen that simulation results by using the group contribution methods was not in agreement with experimental results. Nevertheless, adjusted simulation results by using thermodynamic properties of glycerol carbonate calculated from the equilibrium reaction provided more reliable prediction.

In addition, MATLAB was used to solve equilibrium model parameters and to provide equilibrium constant as a function of temperature. The results were shown below:

$$\ln K_{eq} = A + B(1/T) + C \ln(T) + D(T) \quad (5-6)$$

where, $A = -8,041.00$, $B = 291,370.00$
 $C = 1,316.80$, $D = -1.4475$

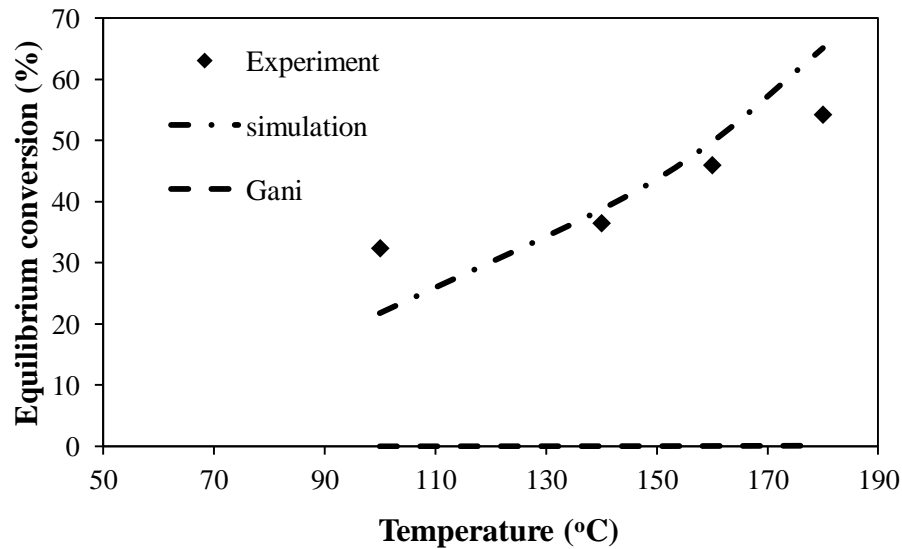


Figure 5.9 Dependence of equilibrium conversion of glycerol on reaction temperature from simulation and experiment.

5.3 Kinetic study

In this section, the kinetic model parameters were calculated from experimental results by using Arrhenius's plot at three different temperatures (100°C, 140°C and 160°C). Polymath 5.1 program was used to fit the reaction data and to determine the reaction rate constants.

By performing material balances for a batch reactor, the rate expressions could be written as:

$$-r_{Gly} = -r_{Urea} = r_{GC} = \frac{r_{NH_3}}{2} = k^+ \left(x_{Gly} x_{Urea} - \frac{x_{NH_3}^2 x_{GC}}{K_{eq}} \right) \quad (5-7)$$

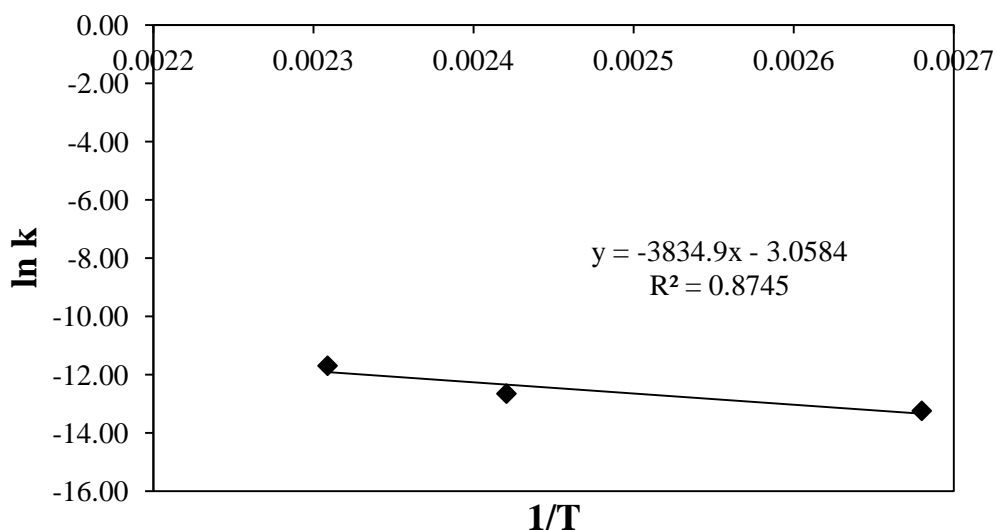


Figure 5.10 Arrhenius's plots.

From Arrhenius's plots as shown in Figure 5.10, the activation energy and the pre-exponential factor could be calculated from the slope and the intercept, respectively

$$\ln k = -\frac{Ea}{RT} + \ln A \quad (5-8)$$

where, $Ea = 31.89 \text{ kJ mol}^{-1}$

$$A = 0.05 \text{ mol ml}^{-1}\text{min}^{-1}$$

Furthermore, this kinetic model was applied to simulate the synthesis of glycerol carbonate by using Aspen plus program to compare simulation results with the experimental results from literature at the same reaction conditions. That can be seen in section 5.4.2 (conventional method for synthesis glycerol carbonate).

The obtained reaction model (equation (5-7)) was used to predict results and to compare with experimental results as shown in Figure 5.11. The results showed that the reaction model were in good agreement with experiments. For reaction temperature of $180 \text{ }^\circ\text{C}$, error could occur at initial time.

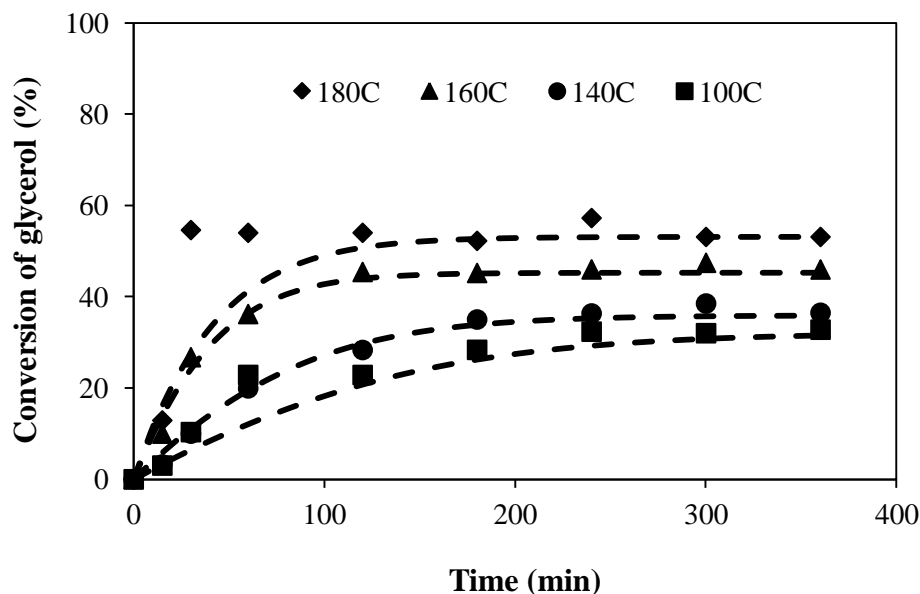


Figure 5.11 Conversion of glycerol at different temperatures (symbols: experimental results and dashed line: reaction model).

5.4 Simulation of the glycerol carbonate synthesis process:

5.4.1 Vapor-liquid equilibrium consideration:

Considering vapor-liquid equilibrium of the system for synthesis of glycerol carbonate reveals that ammonia is produced in vapor phase as a byproduct. Therefore, liquid and vapor phase of ammonia may be in equilibrium where the rate of evaporation equals to the rate of condensation. Boiling point diagrams are widely used to consider in vapor-liquid equilibrium. These diagrams are easily provided by Aspen Plus program and shown in Figure 5.12.

Figure 5.12 shows vapor-liquid equilibrium diagrams at atmosphere pressure and mole fraction of vapor and liquid phase at various temperatures. The intersections at vertical axis ($x = 0, 1$) represent pure component boiling point. The results showed that each component could be easily separated from the others. Ammonia is the lowest boiling point substance. Therefore, it would be achieved at the distillate of reactive distillation column. Glycerol carbonate is the heaviest boiling point substance

that would be achieved at the bottom of the column. Moreover, the reaction mixture does not form any azeotrope due to no intersection of any curves.

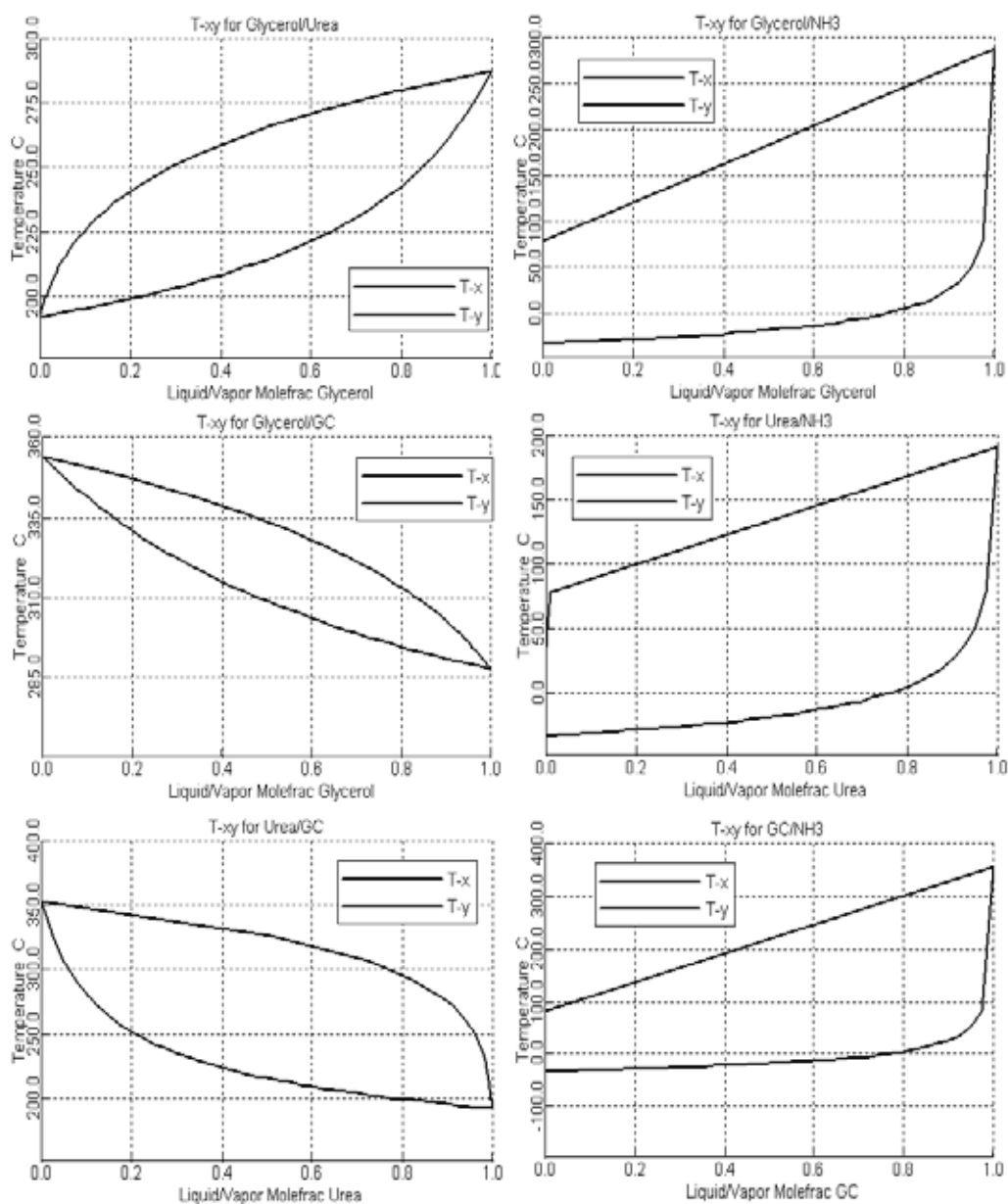


Figure 5.12 Vapor-liquid equilibrium diagrams from Aspen Plus program for the system of synthesis of glycerol carbonate.

5.4.2 Conventional method for synthesis of glycerol carbonate

For synthesis of glycerol carbonate, its high yield is limited by the equilibrium reaction. In a conventional method, shifting the reaction equilibrium by removing ammonia from the system could be carried out by operating the batch system under vacuum pressure or using sweep gas such as nitrogen and air (Climent et al., 2010).

In this study, the conventional method for synthesis of glycerol carbonate comprised of a batch reactor operated with a sweep gas such as air and a distillation column as shown in Figure 5.13. The simulation of the conventional process was performed by using RBatch and DSTWU module in Aspen plus 11.1. NRTL model was used for simulation of conventional method. The kinetic model of the reaction was used to predict the reaction in batch operation with using $\text{Co}_3\text{O}_4/\text{ZnO}$ as a catalyst. The reaction conditions of this study followed the report of Rubio-Marcos *et al.* (2010). An equimolar reactant was fed in a batch reactor. The reaction was operated at 145 °C, 1 atm, 4 h of reaction time with air as a sweep gas for removal of ammonia. After completed the reaction, the outlet from the batch reactor was fed to a distillation column to separate glycerol carbonate from the mixture.

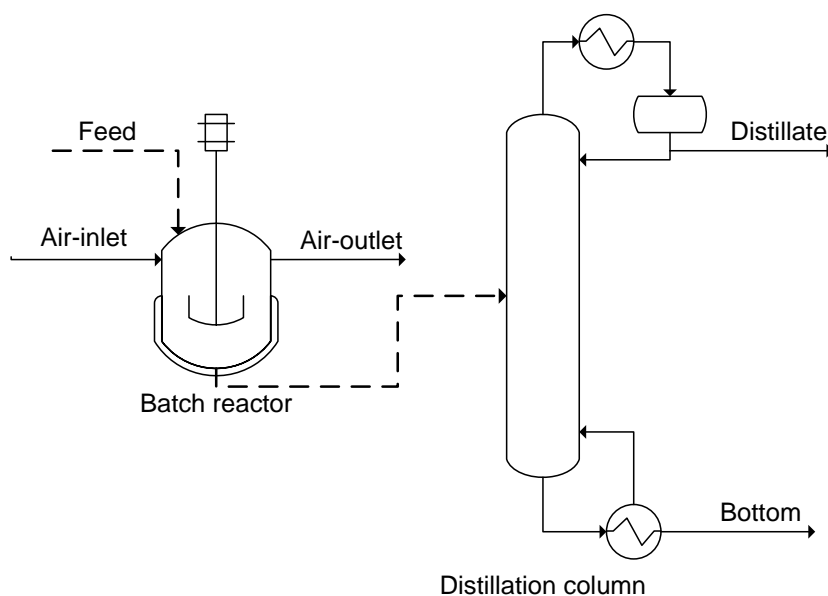


Figure 5.13 Conventional process for synthesis of glycerol carbonate.

The simulation results of the conventional process for synthesis of glycerol carbonate are shown in Table 5.3. The results showed that 72.52% conversion of glycerol could be achieved from this simulation which is close to the experimental results from Rubio-Marcos *et al.* (2010) at the same conditions (69% conversion of glycerol). Therefore, the reactor output contained glycerol carbonate and unreacted glycerol and urea. Most of ammonia in system was extracted by air passing as shown in air outlet stream. A distillation column was used to separate glycerol carbonate from the reaction mixture. Unreacted glycerol and urea were obtained in the distillate stream due to their lower boiling point values. In addition, high purity of glycerol carbonate (100%) could be obtained in the bottom stream.

Nevertheless, the limitations from shifting equilibrium reaction by operating under vacuum or using sweep gas and batch operation make it difficult to use in the large industrial scale.

Table 5.3 Conventional process streams for synthesis glycerol carbonate.

	FEED	R-OUT	DIST	BOTT	AIR-IN	AIR-OUT
Temperature, °C	25.00	145.00	134.27	352.92	25.00	145.00
Pressure, bar	1.00	1.00	1.00	1.00	1.00	1.00
Vapor Fraction	0.00	0.00	0.00	0.00	1.00	1.00
Mole Flow, mol/hr	200.00	119.32	47.34	71.98	100.00	253.20
Mole Flow mol/hr						
Glycerol	100.00	27.23	26.96	0.27	0.00	0.25
Urea	100.00	19.14	19.14	0.00	0.00	8.34
Ammonia	0.00	0.49	0.49	0.00	0.00	144.55
Glycerol carbonate	0.00	72.44	0.72	71.71	0.00	0.08
O ₂	0.00	0.03	0.03	0.00	100.00	99.97
Mole Fraction						
Glycerol	0.50	0.23	0.57	0.00	0.00	0.00
Urea	0.50	0.16	0.40	0.00	0.00	0.03
Ammonia	0.00	0.00	0.01	0.00	0.00	0.57
Glycerol carbonate	0.00	0.61	0.02	1.00	0.00	0.00
O ₂	0.00	0.00	0.00	0.00	1.00	0.39

5.4.3 Reactive distillation study

The aim of this section is to show that using reactive distillation for synthesis of glycerol carbonate can achieve higher conversion and lower energy consumption than the conventional process. Reactive distillation may also be adopted for synthesis of glycerol carbonate. Shifting thermodynamic equilibrium can be obtained by controlling the reflux ratio of column to eliminate ammonia as a byproduct at atmospheric pressure, and to achieve continuous operation.

5.4.3.1 Standard conditions

Reactive distillation simulation was studied by using an equilibrium stage model with RADFRAC module in Aspen plus program. Vapor-liquid equilibrium on each stage and neglecting pressure drop within the column are the assumptions of this study. Moreover, NRTL model is employed for simulation of reactive distillation. There are three sections in the reactive distillation column. The configuration of column is that the reactive section is in the middle of the column. Glycerol which is the less volatile reactant was fed at the top of reactive section. Moreover, urea was fed at the bottom stage of the reactive section. A scheme of this configuration is shown in Figure 5.14. Table 5.4 shows standard conditions of design and operating variables used to study the effect of each parameter at initially.

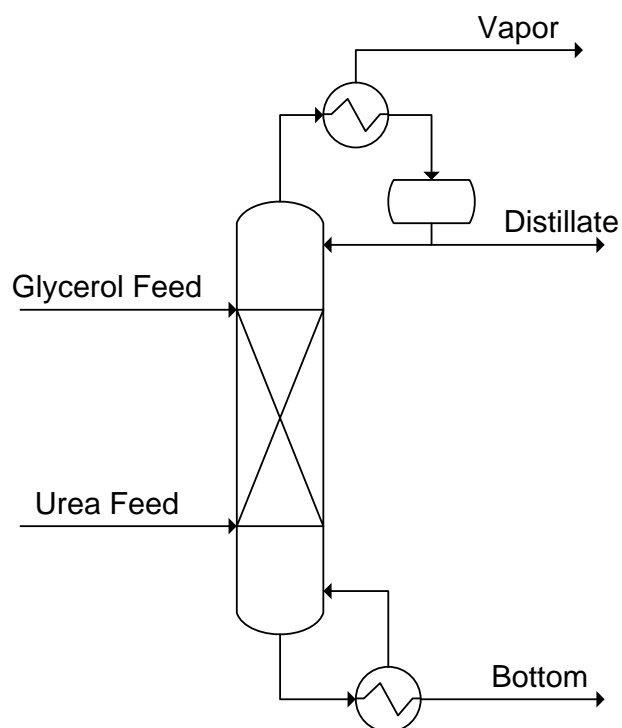


Figure 5.14 Reactive distillation process scheme for synthesis of glycerol carbonate.

Table 5.4 Standard conditions of reactive distillation column.

Feed conditions		Column specification	
Glycerol feed flow rate (mol/h.)	100	Rectifying stages	1
Urea feed flow rate (mol/h.)	100	Reaction stages	1
Temperature (°C)	25	Stripping stages	1
Pressure (bar)	1	Total stages	5
		Reflux ratio	2
		Reboiler heat duty (kW)	17
		Pressure (bar)	1

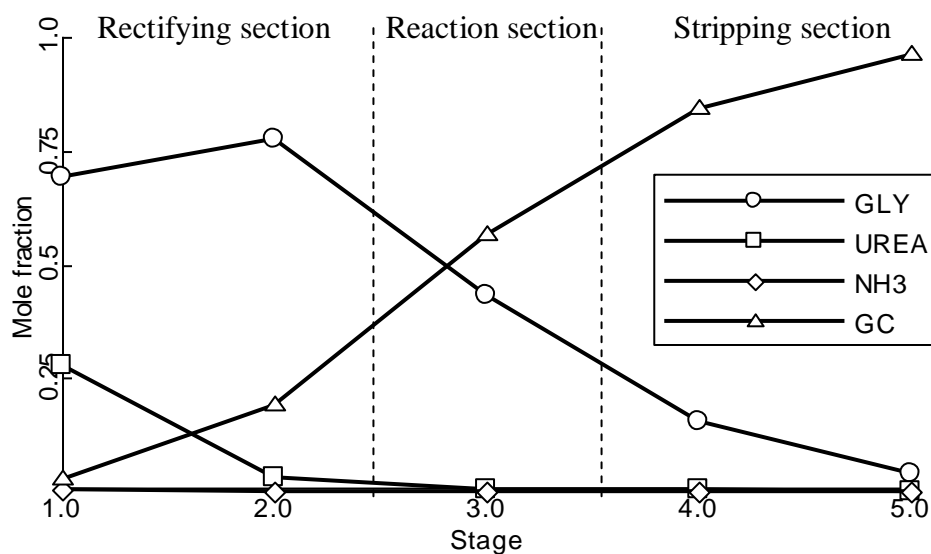


Figure 5.15 Mole fraction profile along reactive distillation column at standard conditions.

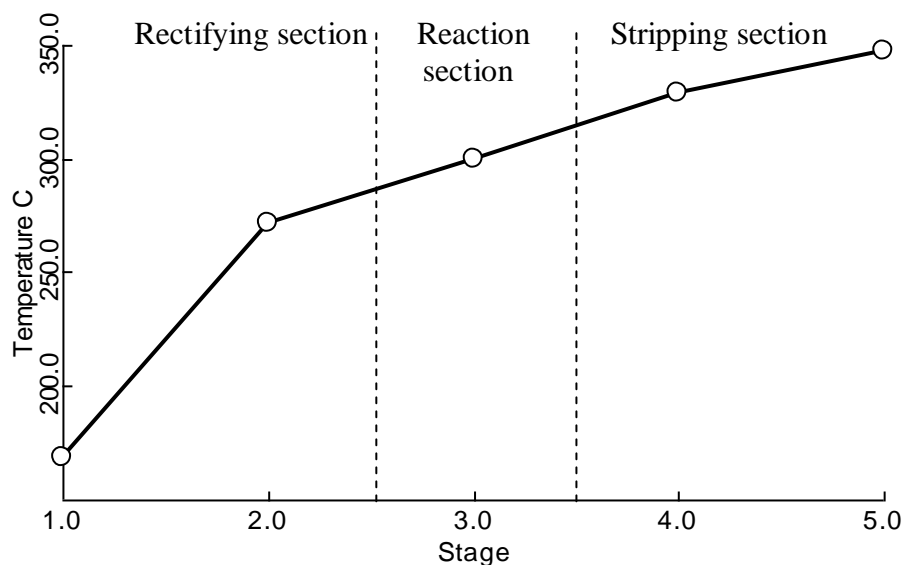


Figure 5.16 Temperature profile along reactive distillation column at standard conditions.

In this study, the kinetic model of the reaction between glycerol and urea (forward reaction) and between glycerol carbonate and ammonia (backward reaction) were used to predict the reaction in reactive section of column with using $\text{Co}_3\text{O}_4/\text{ZnO}$ as a catalyst. Figure 5.15 shows the simulation results of mole fraction profiles along

the reactive distillation column at the standard condition. The results showed that glycerol carbonate could be obtained in the bottom stream due to its high boiling point. There was more glycerol carbonate in the stripping section (stage 4) whose duty is to purify product in the bottom stream. Most of compositions changed occur at middle of column (stage 3) which is the reactive section. The reaction between glycerol and urea occurs in the reactive section to produce glycerol carbonate. Moreover, the rectifying section (stage 2) removed light component from the reactive section and prevented glycerol carbonate loss in the distillate stream. In distillate stream, there is more ammonia in vapor phase and glycerol and urea in liquid phase due to its lower boiling point compared with glycerol carbonate. Temperature profile was illustrated in Figure 5.16 It could be seen that high temperature was observed in the bottom of the column. Temperature was decreased at the middle of the column due to endothermic reaction between glycerol and urea.

The results of reactive distillation simulation were compared with those of a conventional method to synthesize glycerol carbonate. The reaction performance including conversion of glycerol, yield and purity of glycerol carbonate was considered. The conversion of glycerol (X_{Gly}) and yield of glycerol carbonate (Y_{GC}) are defined as follows:

$$X_{Gly} = \frac{\text{difference in molar flow rate of inlet and outlet of glycerol}}{\text{feed molar flow rate of glycerol}} \times 100 \quad (5-9)$$

$$Y_{GC} = \frac{\text{molar flow rate of glycerol carbonate in bottomstream}}{\text{difference in molar flow rate of inlet and outlet of glycerol}} \times 100 \quad (5-10)$$

At standard conditions, 80.3% conversion of glycerol and 99.8% yield of glycerol carbonate were obtained. Therefore, the effect of design and operating variables including reboiler heat duty, reflux ratio, the number of stripping, rectifying and reaction stages on conversion of glycerol and purity of glycerol carbonate were investigated.

5.4.3.2 The effect of design variables

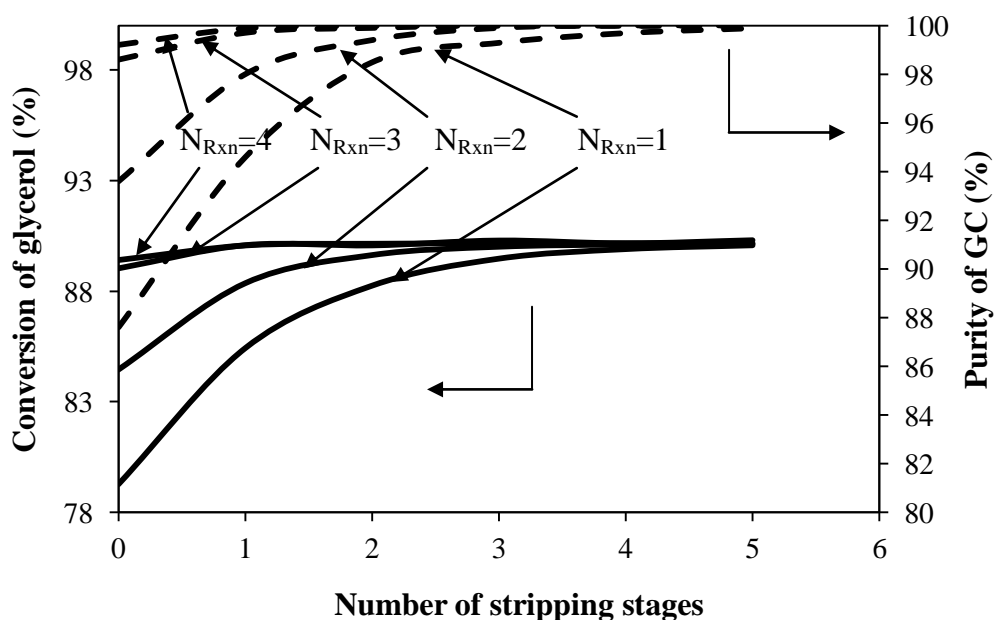


Figure 5.17 Effect of the number of stripping stages on the conversion of glycerol and purity of glycerol carbonate in bottom stream. (rectifying: 1 stage)

The effect of the number of stripping stages on the conversion of glycerol and purity of glycerol carbonate in the bottom stream are investigated and the results are shown in Figure 5.17. It is noted that the other design and operating variables including the number of rectifying stages, reflux ratio and reboiler heat duty were set at standard conditions. The relation between reaction stages and stripping stages were determined by varying the number of these stages from 0 to 5 stages. The results showed that conversion of glycerol and purity of glycerol carbonate increased by increasing the number of stripping stages for 1 to 3 reaction stages. Even though temperature of the reaction zone slightly decreased by increasing the number of stripping stages. However, more glycerol carbonate was introduced to the bottom of column when the number of stripping stages was increased that the equilibrium reaction in the reaction section was shifted to the forward direction. Therefore, the glycerol conversion and the desired product were increased. The stripping section

provided to purify glycerol carbonate in the residue and can achieve 100% purity of glycerol carbonate.

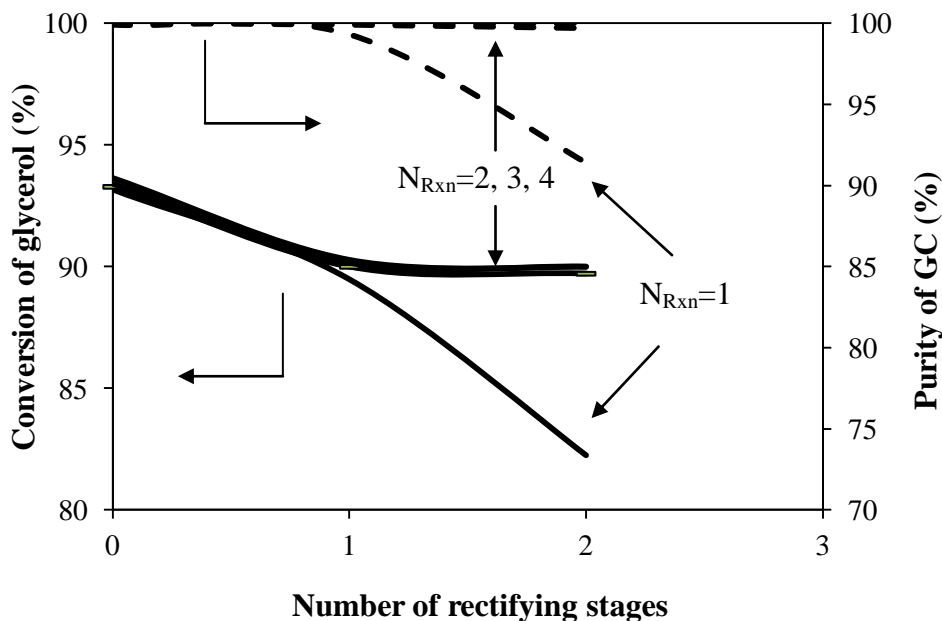


Figure 5.18 Effect of the number of rectifying stages on the conversion of glycerol and purity of glycerol carbonate in bottom stream. (stripping: 3 stages)

The effect of the number of rectifying stages on the conversion of glycerol and purity of glycerol carbonate are shown in Figure 5.18. The number of the stripping was fixed at 3 in the investigation of the effect of the number of rectifying stages. A rectifying section is provided to remove a light component from the reactive section. It was also observed that increasing the number of rectifying stages caused slight decreasing conversion of glycerol and purity of glycerol carbonate. The reason is because more urea, a light component, was removed in the distillate when the number of rectifying stages was increased that are not favorable to the reaction of glycerol with urea even though ammonia was removed together with urea. Accordingly, no rectifying stage is appropriate in order to have high conversion of glycerol.

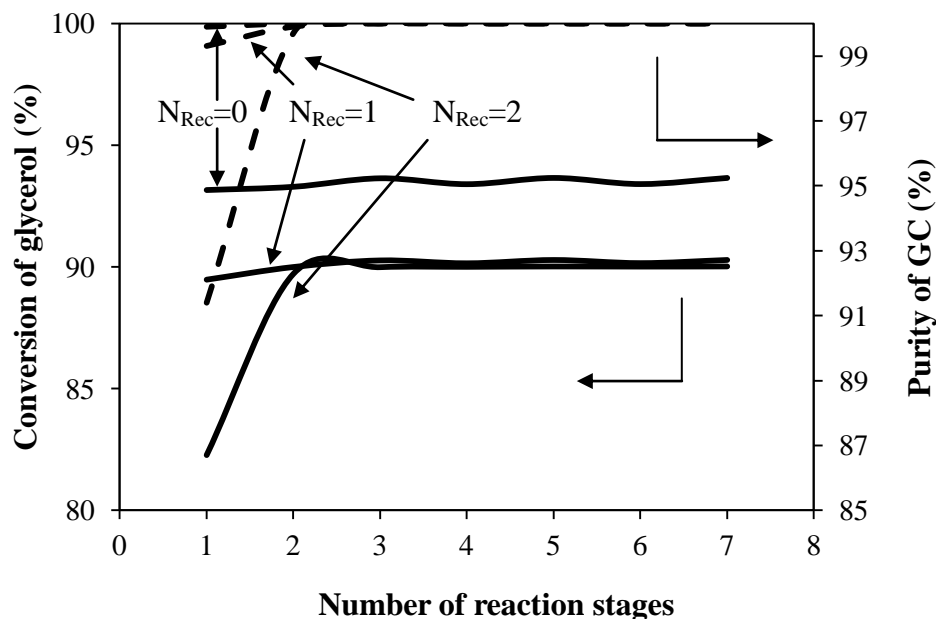


Figure 5.19 Effect of the number of reaction stages on the conversion of glycerol and purity of glycerol carbonate in bottom stream. (stripping: 3 stages)

The effect of the number of reaction stages on the conversion of glycerol and purity of glycerol carbonate in the bottom stream are shown in Figure 5.19. The results showed that conversion of glycerol and purity of glycerol carbonate in bottom stream were enhanced with increasing the number of reaction stages and become constant at 3 reaction stages due to increasing the residence time. It seemed that the number of reaction stages higher than 3 stages provides no significant improvement of the conversion of glycerol.

According to these results, it showed that the appropriate design for synthesis of glycerol carbonate with reactive distillation is 3 stripping stages and 3 reaction stages without rectifying stage. Nevertheless, further simulations were carried out by varying reflux ratio and reboiler heat duty.

5.4.3.3 The effect of operating variables

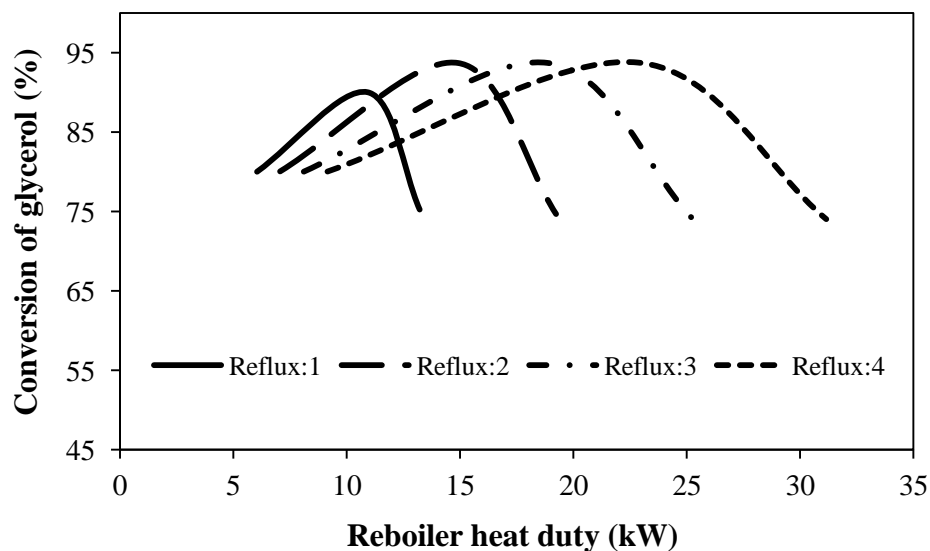


Figure 5.20 Effect of heat duty of reboiler on the conversion of glycerol at various reflux ratio. (stripping: 3 stages, reaction: 3 stages and without rectifying stage)

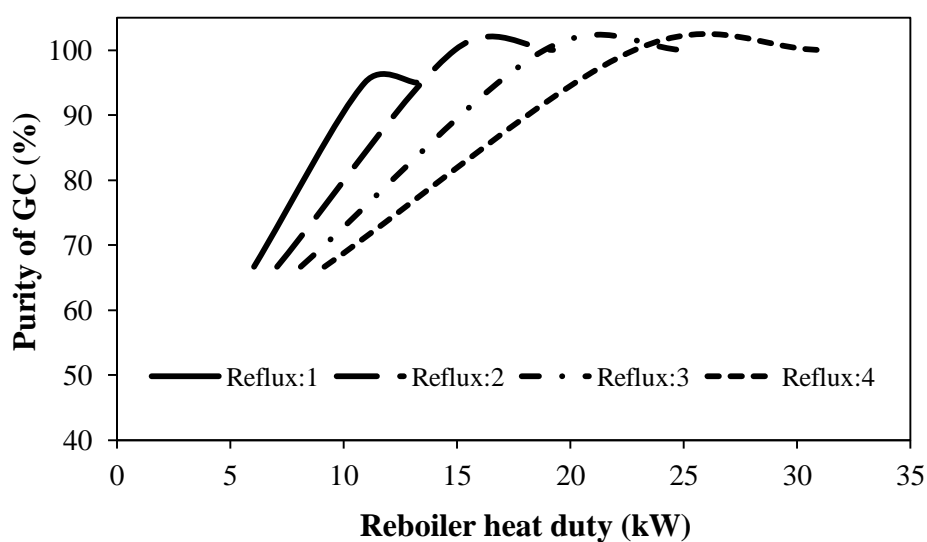


Figure 5.21 Effect of heat duty of reboiler on purity of glycerol carbonate in bottom stream at various reflux ratio. (stripping: 3 stages, reaction: 3 stages and without rectifying stage)

The effect of reflux ratio on the conversion of glycerol and purity of glycerol carbonate in bottom stream are shown in Figures 5.20 and 5.21. The purity of glycerol carbonate and conversion of glycerol increased by increasing reflux ratio because increasing reflux ratio could provide higher concentration of glycerol and urea in the reactive section of the column that could react to produce glycerol carbonate. Glycerol and urea in distillate were recycled to the reactive section. Accordingly, this was favorable to the reaction of glycerol with urea. As the reflux ratio increased over 2, the highest conversion of glycerol and purity of glycerol carbonate changed insignificantly.

The effect of heat duty of reboiler on the conversion of glycerol and purity of glycerol carbonate in bottom stream are illustrated in Figures 5.20 and 5.21. At any reflux ratio, the conversion of glycerol and purity of glycerol carbonate increased as heat duty of reboiler increased. This could occur because temperature in the reactive section was increased and more glycerol and urea was introduced in the reactive section. However, conversion of glycerol decreased when heat duty of reboiler was too high. This could occur because glycerol and urea was heated and removed from the reactive section to distillate and vapor stream. Whereas, these positive and negative effects of increasing heat duty of reboiler became smaller at higher reflux ratio. Therefore, an optimum heat duty of reboiler was set to get a high performance of reactive distillation column as shown in Figure 5.20. At reflux ratio was about 2, an optimum heat duty of reboiler was 15 kW to get the maximum purity of glycerol carbonate and conversion of glycerol.

5.4.3.4 Reactive distillation simulation results and comparison with conventional process

According to all simulation results, the suitable design and operating variables for synthesis glycerol carbonate via glycerolysis of urea with reactive distillation for the used glycerol and urea feed flow rate of 100 mol/h has the following characteristics:

- No rectifying stage
- 3 reaction stages

- 3 stripping stages
- Reflux ratio of 2
- Reboiler heat duty of 15 kW

There are 8 total stages in the column. Glycerol was fed at the top of reaction section (above stage 2) and urea was fed at the bottom of column (above stage 5). Mole fraction profiles of the components in the reactive distillation column with suitable conditions were shown in Figure 5.22. It can be seen that high purity of glycerol carbonate could be obtained at the bottom stream due to its high boiling point. High concentration of glycerol carbonate appeared in the stripping section (stage 5-7). Most of the compositions changed occur at the reaction section (stage 2-4). In the reaction section, reaction between glycerol and urea (forward reaction) and reaction between glycerol carbonate and ammonia (reverse reaction) could occur. At the top of column, there were more glycerol and urea which were the residues from the reaction and the loss of glycerol carbonate. Temperature profile in the reactive distillation column at suitable conditions are illustrated as shown in Figure 5.23. Temperature of reboiler and condenser are 353 and 131°C, respectively. Temperature decreased at the middle of the column (stage 2-4) due to an endothermic reaction between glycerol and urea to produce glycerol carbonate.

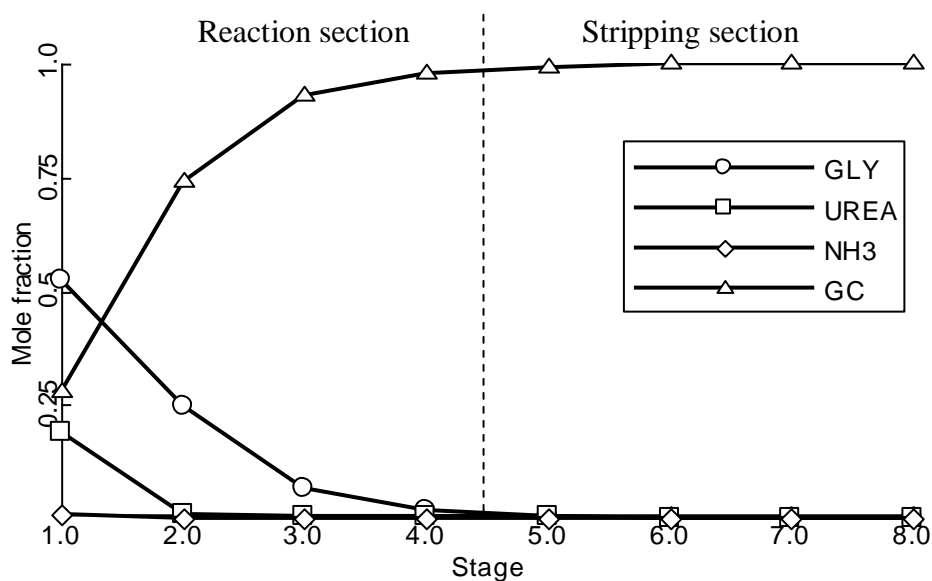


Figure 5.22 Mole fraction profile of the components in the reactive distillation column

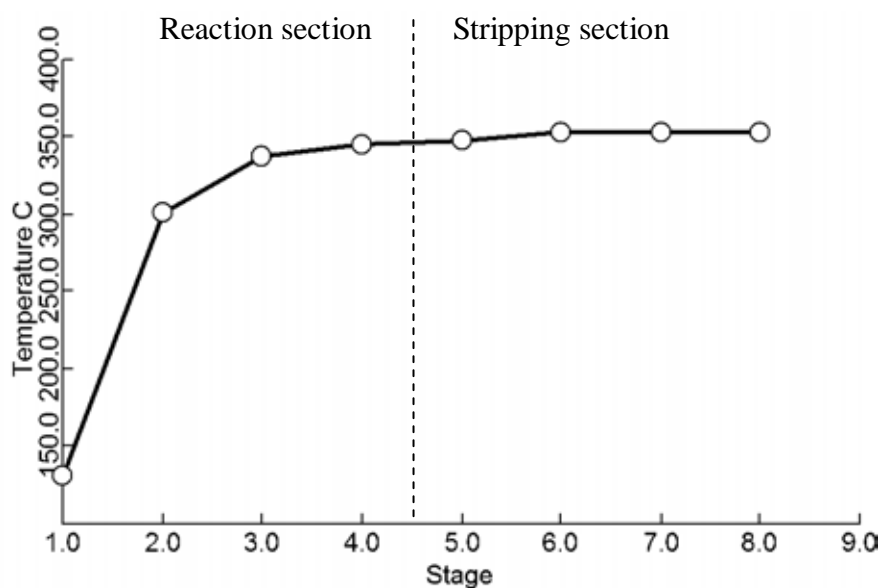


Figure 5.23 Temperature profile in the reactive distillation column

Table 5.5 Mole fraction of reactive distillation streams.

	FEED-G	FEED-U	VAP	DIST	BOTT
Temperature, °C	25.00	25.00	130.99	130.99	353.45
Pressure, bar	1.00	1.00	1.00	1.00	1.00
Vapor Fraction	0.00	0.00	1.00	0.00	0.00
Mole Flow, mol/hr	25.00	25.00	130.99	130.99	353.45
Mole Flow, mol/hr					
Glycerol	100.00	0.00	0.20	6.39	0.01
Urea	0.00	100.00	4.28	2.31	0.00
Ammonia	0.00	0.00	186.71	0.11	0.00
Glycerol carbonate	0.00	0.00	0.01	3.40	89.99
Mole Fraction					
Glycerol	1.00	0.00	0.00	0.52	0.00
Urea	0.00	1.00	0.02	0.19	0.00
Ammonia	0.00	0.00	0.98	0.01	0.00
Glycerol carbonate	0.00	0.00	0.00	0.28	1.00

In this study, the suitable design for synthesis of glycerol carbonate with reactive distillation is no rectifying stages, 3 stripping stages, 3 reaction stages, reflux ratio of 2, and reboiler heat duty of 15 kW. From these operating conditions, 93% conversion of glycerol, 96% yield, and 100% purity of glycerol carbonate could be achieved. The reactive distillation streams are summarized in Table 5.5.

Table 5.6 Comparison of synthesis of glycerol carbonate with reactive distillation and conventional method.

Method	% purity of glycerol carbonate	% conversion of glycerol	Total heat duty consumption (kW)	Total heat duty consumption / Mole GC (kW/mol GC)
Reactive distillation	100	93.41	19.35	0.215
Conventional method	100	72.52	24.56	0.342

The comparison of synthesis of glycerol carbonate with reactive distillation and conventional method using kinetic model at the same feed conditions and outlet purity of glycerol carbonate are summarized in Table 5.6. The results showed that higher conversion of glycerol (93%) could be achieved by using the reactive distillation compared with the conventional method (72.5% conversion of glycerol). This could occur because the reactive distillation shifted effectively equilibrium reaction by combination reaction and separation unit that could remove ammonia in vapor phase to the top of column and introduce glycerol carbonate to the bottom of column by stripping section. Furthermore, the residues of glycerol and urea in the distillate could be recycled to the reactive section by controlling reflux ratio of the column. Compared with reactive distillation, the conventional method shifted equilibrium reaction by operating under vacuum condition or using sweep gas such as nitrogen which lead to increase the operation cost. In addition, total heat duty consumption of reactive distillation is lower than its conventional method as shown in Table 5.6. This could occur because more residue reactant from reactor was feed to

distillation column in conventional method. Consequently, synthesis of glycerol carbonate by using reactive distillation could provide atmospheric continuous operation, reduction of plant cost, and low the energy consumption which lead to increase potential industrial application.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATION

6.1 Conclusions

In this thesis, the synthesis of glycerol carbonate via glycerolysis of urea by using reactive distillation was investigated. The follows are the conclusions drawn from this study.

For estimation of missing parameters of glycerol carbonate, the group contribution methods including Benson's, Joback's and Gani's methods were studied. Gani's method provided the lowest deviation by comparison with experimental results and properties from database of ethylene carbonate and propylene carbonate.

The reaction model parameters were determined from batch experiments. Equilibrium and reaction rate constants are shown in the following equations.

$$\ln K_{eq} = -8,041 + 291,370(1/T) + 1,316.8\ln(T) - 1.4475(T)$$

$$\ln k = -3,834.9/T - 3.0584$$

The suitable design and operating variables for synthesis glycerol carbonate by using reactive distillation are no rectifying stage, 3 reactive stage, 3 stripping stages, reflux ratio of 2 and reboiler heat duty of 15 kW. From this configuration, 93% conversion of glycerol, 96% yield and 100% purity of glycerol carbonate are achieved.

The synthesis of glycerol carbonate from the reaction between glycerol and urea by using reactive distillation was compared with the conventional process. At the same feed conditions, reactive distillation provided higher conversion of glycerol and lower energy consumption than the conventional method. This could occur because the combination of reaction and separation unit by using reactive distillation can shift effectively equilibrium reaction and residue reactant can be recycled to the reactive section by controlling reflux ratio.

6.2 Recommendations

In this research, the recommendations are proposed as follows:

1. An activity coefficient of the components can be applied to the equilibrium reaction model.
2. A rate-based approach for reactive distillation simulation should be considered. This approach takes into account mass and heat transfers of multicomponent, thus being a more accurate and reliable model than the conventional equilibrium stage model.
3. The synthesis of glycerol carbonate from the reaction between glycerol and urea by using reactive distillation should be experimentally performed and the obtained results to be compared with those from simulation.

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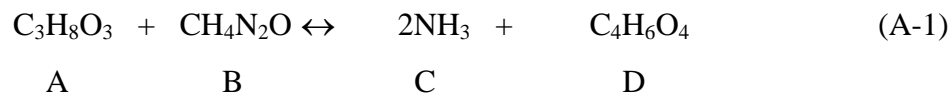
APPENDICES

APPENDIX A

THERMODYNAMIC EQUILIBRIUM CALCULATIONS

In this section, the thermodynamic equilibrium constants at difference temperature were determined. Equilibrium constant is based on mole composition of each component in liquid phase. Therefore, mole composition of each component in liquid phase should be calculated.

The reaction between glycerol and urea and stoichiometry equations of each components are showed as follows:



$$N_A = N_{A0}(1 - X_A) \quad (\text{A-2})$$

$$N_B = N_A \quad (\text{A-3})$$

$$N_C = 2 * N_{A0} * X_A \quad (\text{A-4})$$

$$N_D = N_{A0} * X_A \quad (\text{A-5})$$

For example: determination of equilibrium mole composition of ammonia in liquid phase from the equilibrium conditions at 100°C (32.37% conversion of glycerol)

From vapor-liquid equilibrium equation:

$$y_i P = x_i P_i^{\text{sat}}$$

where P_C^{sat} at 100 °C = 62.37 bar

and $P = 1$ bar

Therefore, the relationship between mole fraction of ammonia in gas phase and liquid is obtained.

$$y_C = (62.37)x_C$$

Total mole compositions of each components at equilibrium could be obtained from stoichiometry equations.

$$\begin{aligned}
N_A &= N_{A0}(1 - X_A) &= 0.5477*(1-0.32) &= 0.3704 \text{ mol} \\
N_B &= N_A &= 0.3704 \text{ mol} \\
N_C &= 2 * N_{A0} * X_A &= 2*0.5477*0.32 &= 0.3546 \text{ mol} \\
N_D &= N_{A0} * X_A &= 0.5477*0.32 &= 0.1773 \text{ mol} \\
N_T &= 0.3704 + 0.3704 + 0.3546 + 0.1773 &= 1.2727 \text{ mol}
\end{aligned}$$

Mole of ammonia in gas phase could be obtained from

$$N_{C,\text{gas}} = y_C N_{T,\text{gas}} = (62.37)x_C N_{T,\text{gas}}$$

$$\begin{aligned}
\text{Where } N_{T,\text{gas}} &= PV/RT &= (1)(0.00005)/(8.314*10^{-5})(373.15) \\
&&= 0.0016 \text{ mol}
\end{aligned}$$

And mole of ammonia in liquid phase could be obtained from

$$N_{C,\text{liq}} = x_C N_{T,\text{liq}}$$

$$\text{Where } N_{T,\text{liq}} = N_T - N_{T,\text{gas}} = 1.2727 - 0.0016 = 1.2711 \text{ mol}$$

Therefore, mole fraction of ammonia in liquid phase at equilibrium could be obtained from mole balance.

$$N_{C,\text{gas}} + N_{C,\text{liq}} = N_{C,\text{total}}$$

$$(62.37)x_C N_{T,\text{gas}} + x_C N_{T,\text{liq}} = 2N_{A0}x_A$$

$$(62.37)(0.0016)x_C + (1.2711)x_C = 2(0.5477)(0.32)$$

$$\text{So, } x_C = 0.2585$$

Accordingly, mole fraction of each components in liquid could be achieved with the same solution. And Equilibrium constant can be calculated from following equation and the results are shown in Table B.1.

$$K_{\text{eq}} = \frac{(x_D) \cdot (x_C)^2}{(x_A) \cdot (x_B)} \quad (\text{A-6})$$

Table A.1 Equilibrium constants at difference temperature.

Temperature ($^{\circ}\text{C}$)	Equilibrium constant
100	0.1249
140	0.1933
160	0.5038
180	1.0884

APPENDIX B

FITTING EQUILIBRIUM CONSTANT MODEL BY USING MATLAB

In this study, MatLab was used to fitting an equilibrium constant model. Equilibrium constants at difference temperature were obtained from experimental mole fraction of components. Equilibrium constants as a function of temperature which can be applied to simulate synthesis of glycerol carbonate in Aspen plus program are in the equation form as shown below:

$$\ln K_{eq} = A + B(1/T) + C\ln(T) + D(T) \quad (B.1)$$

Table B.1 Equilibrium constants at difference temperature.

T	$1/T$	$\ln(T)$	K_{eq}	$\ln K_{eq}$
373.15	0.0027	5.9220	0.1249	-2.0806
413.15	0.0024	6.0238	0.1933	-1.6435
433.15	0.0023	6.0711	0.5038	-0.6855
453.15	0.0022	6.1162	1.0884	0.0847

Equation (B.1) was adjusted in the matrix form as shown below and solved by using MatLab.

$$\begin{pmatrix} 1.0000 & 0.0027 & 5.9220 & 373.15 \\ 1.0000 & 0.0024 & 6.0238 & 413.15 \\ 1.0000 & 0.0023 & 6.0711 & 433.15 \\ 1.0000 & 0.0022 & 6.1162 & 453.15 \end{pmatrix} + \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = \begin{pmatrix} -2.0806 \\ -1.6435 \\ -0.6855 \\ 0.0847 \end{pmatrix}$$

Source code & Results by MATLAB

```
>> X = [1 0.00268 5.92198 373.15; 1 0.00242 6.023811 413.15; 1 0.002309 6.071084
433.15; 1 0.002207 6.116223 453.15];
```

```
Y = [-2.08058; -1.64351; -0.6855; 0.084729];
```

```
Z = X\Y;
```

```
A = Z(1,1), B = Z(2,1)
```

```
C = Z(3,1), D = Z(4,1)
```

```
A =
```

```
-8.0410e+003
```

```
B =
```

```
2.9137e+005
```

```
C =
```

```
1.3168e+003
```

```
D =
```

```
-1.4475
```

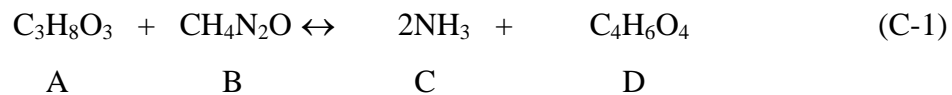
Therefore, equilibrium reaction model could be obtained in the following equations.

$$\ln K_{eq} = -8,041 + 291,370(1/T) + 1,316.8\ln(T) - 1.4475(T) \quad (\text{B.2})$$

APPENDIX C

DETERMINATION THE REACTION RATE CONSTANT BY USING POLYMATH

In this section, the reaction rate constant was determined by using Polymath program. The synthesis of glycerol carbonate via glycerolysis of urea has the following stoichiometry.



The reaction rate of glycerol and stoichiometry equations of each components can be expressed in the form as follows:

$$r_{\text{Gly}} = -k^+ \left(x_{\text{Gly}} x_{\text{Urea}} - \frac{x_{\text{NH}_3}^2 x_{\text{GC}}}{K_{eq}} \right) \quad (\text{C-2})$$

$$r_{\text{Urea}} = r_{\text{Gly}} \quad (\text{C-3})$$

$$r_{\text{NH}_3} = -2^* r_{\text{Gly}} \quad (\text{C-4})$$

$$r_{\text{GC}} = -r_{\text{Gly}} \quad (\text{C-5})$$

The experimental concentration of components as a function of time were inserted in into Polymath Regression (REG) Table. And stoichiometry equations were defined in the table. Then the data was fit into a polynomial equation and differentiated to obtain the dC_A/dt values for each data point as shown in Figure C.1. The obtained data was fitted to the reaction rate model by using the nonlinear regression as shown in Figure C.2. Finally, the reaction rate constant was obtained as shown in Figure C.3.

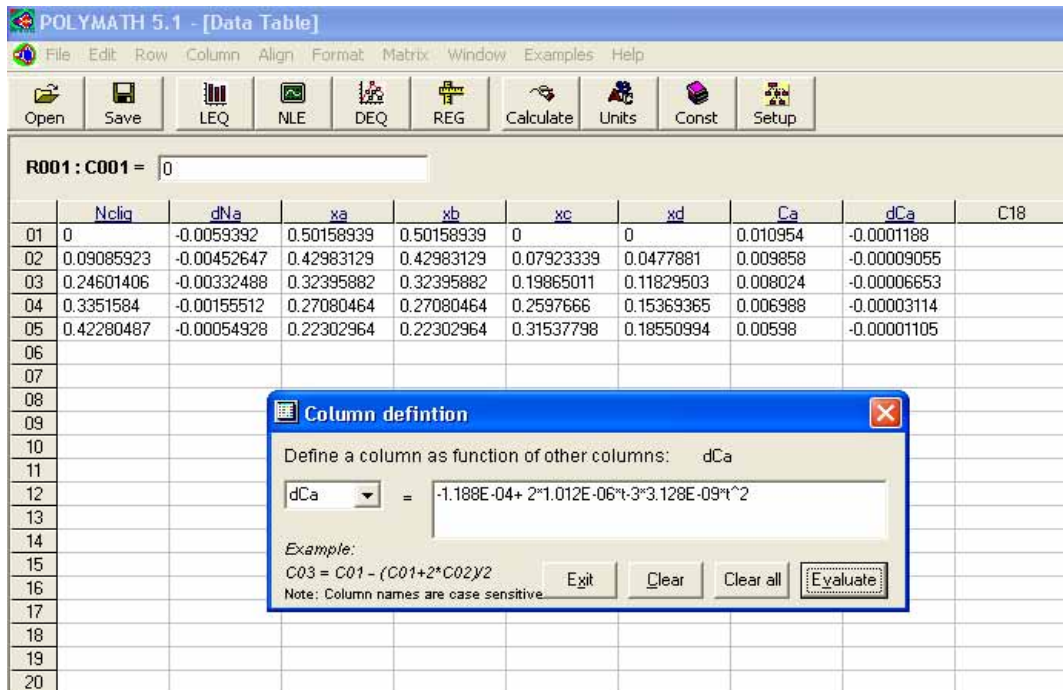
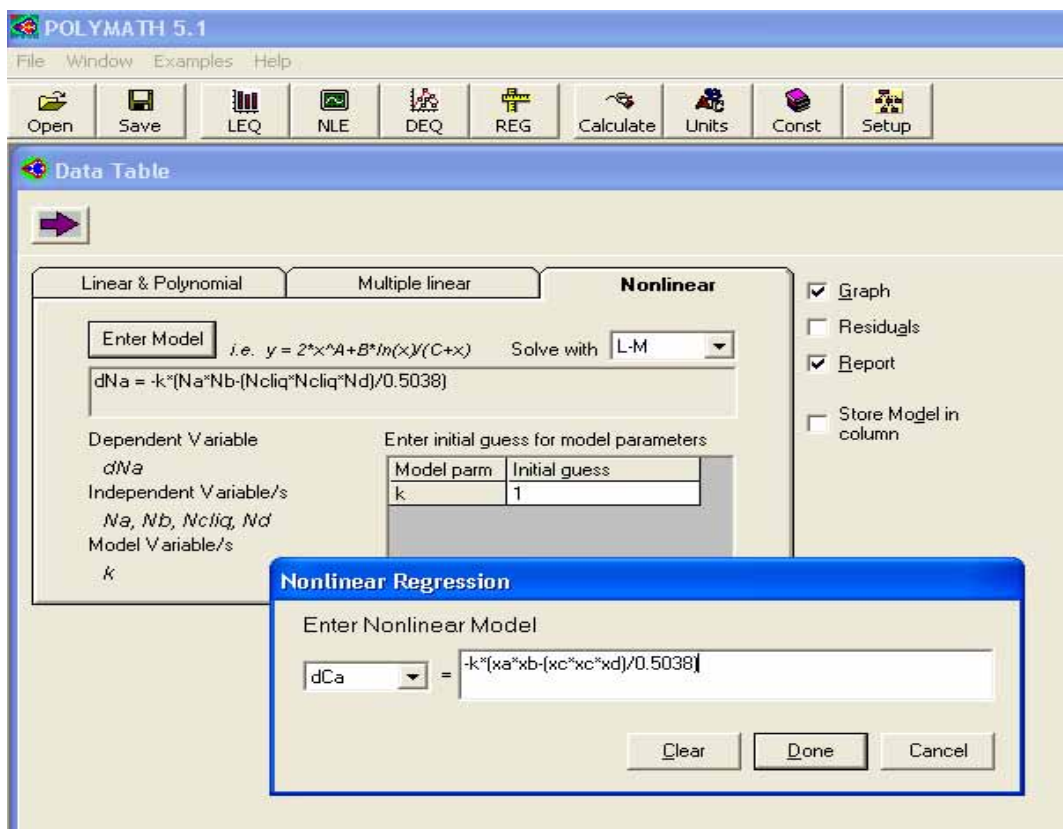
Figure C.1 Determination of the dC_A/dt values by using Polymath.

Figure C.2 The nonlinear regression.

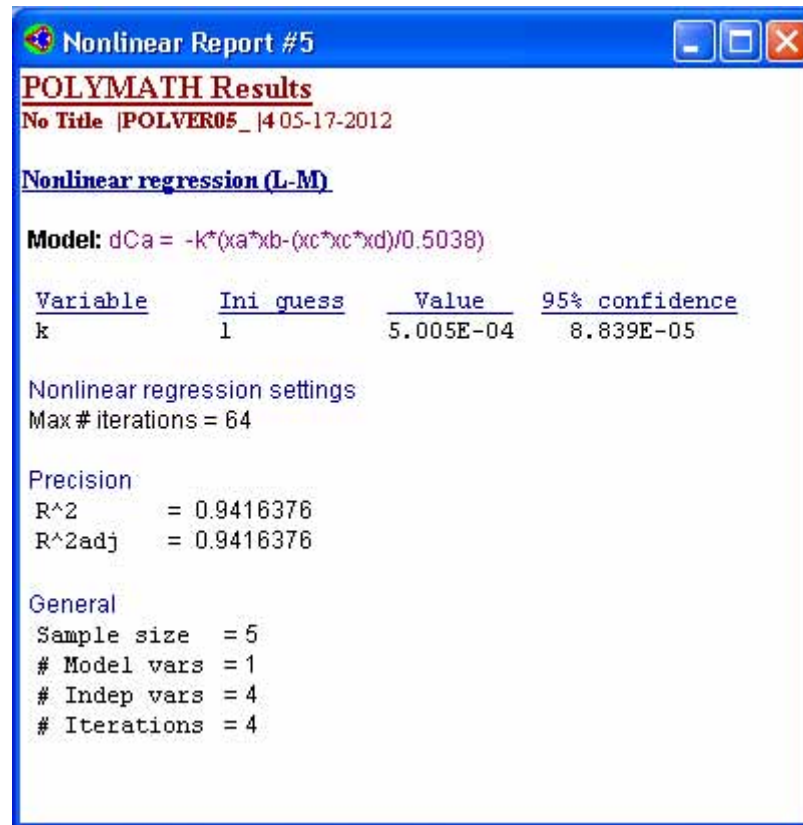


Figure C.3 The reaction rate constant from Polymath results

Therefore, the reaction rate constant at difference temperature can be obtained as shown in Table C.1.

Table C.1 The reaction rate constant at difference temperature.

Temperature (°C)	The reaction rate constant (mol/ml*min)
100	1.065×10^{-4}
140	1.921×10^{-4}
160	5.005×10^{-4}

APPENDIX D

CALIBRATION CURVE

Mole composition of glycerol and glycerol carbonate in the reaction mixture was analyzed by gas chromatography (Shimadzu model 14B) equipped with ZB-5HT capillary column and a flame ionization detector (FID). Table D.1 shows the operating conditions for gas chromatography. The calibration curves of these components are showed in Figure D.1 and D.2, respectively. Those provide the relationship between mole composition of component and peak area of gas chromatography.

Table D.1 Operating conditions for gas chromatography.

Gas Chromatography	Shimadzu GC-14B
Detector	FID
Column	ZB-5HT
- Column material	Phenyl-Dimethylpolysiloxane
- Length (m)	30
- Inner diameter (mm)	0.25
- Film Thickness (um)	0.25
- Maximum temperature (°C)	400
Carrier gas	N ₂ (99.999%)
Carrier gas flow (ml/min)	30
Column temperature	
- initial (°C)	50
- final (°C)	340
Injector temperature (°C)	310
Detector temperature (°C)	340
Analyzed compounds	High molecular weight compounds

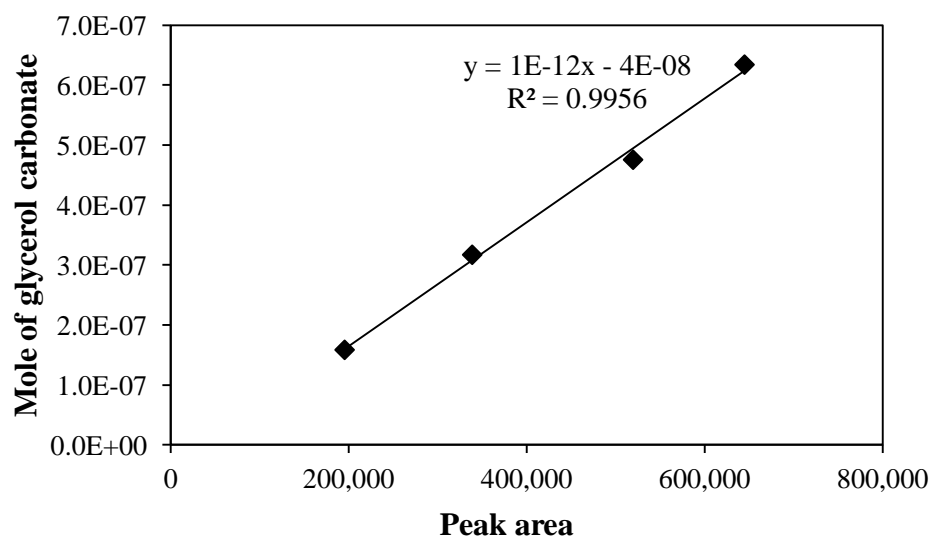


Figure D.1 Calibration curve of glycerol carbonate.

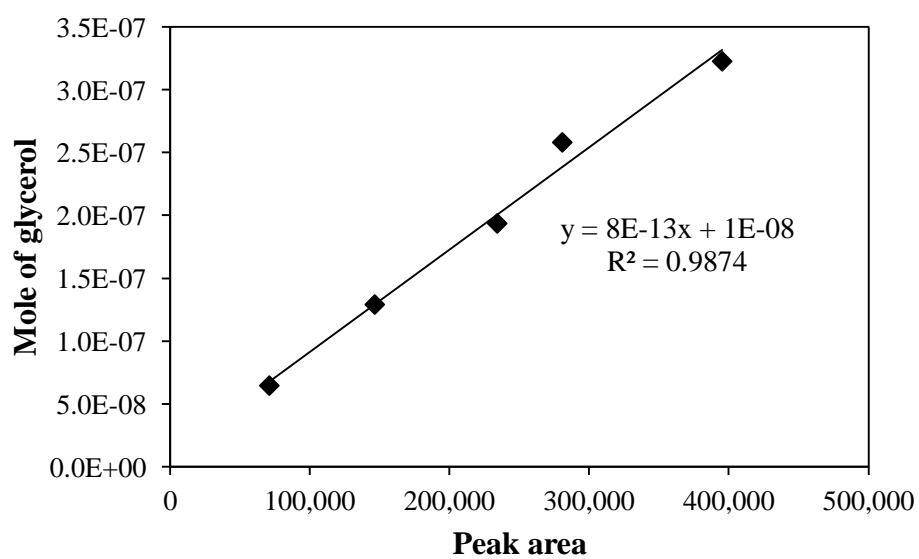


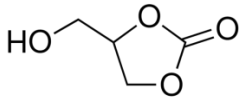
Figure D.2 Calibration curve of glycerol.

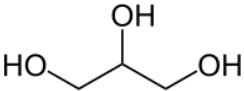
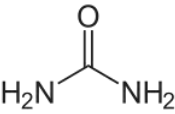
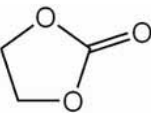
APPENDIX E

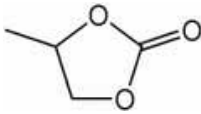
GROUP CONTRIBUTION METHODS

Group contribution methods including Joback's, Gani's and Benson's method were used to determine thermodynamic properties of component (Gibb's free energy). Table E.1 showed the estimation of thermodynamic parameters by three group contribution methods using Aspen plus.

Table E.1 Group contributions of glycerol carbonate.

Components/ Molecular structure	Group contribution method	Type subgroup	No.	Aspen subgroup ID
Glycerol carbonate 	Joback	>CH ₂	1	101
		>CH- in a ring	1	111
		-OH	1	119
		-O- in a ring	2	122
		>CH ₂ in a ring	1	110
		>C=O in a ring	1	124
	Gani	-OH (alcohol)	1	1200
		-COO-	1	3300
		>CH ₂	1	1010
		>CH-	1	1005
		-CH ₂ O- (C-ring)	1	1600
	Benson	O-(C)(H)	1	189
		C-(O)(C)(H) ₂	2	211
		C-(O)(C) ₂ (H)	1	210
		O-(CO)(C)	2	178
		1,3 dioxane ring	1	219
		Optical isomer	1	406

		Total symmetry	1	405
Glycerol 	Joback	>CH2	2	101
		>CH-	1	102
		-OH	3	119
	Gani	-OH (alcohol)	3	1200
		>CH2	2	1010
		>CH-	1	1005
	Benson	O-(C)(H)	3	189
		C-(O)(C)2(H)	1	210
		C-(O)(C)(H)2	2	211
		Optical isomer	1	406
Total symmetry		2	405	
Urea 	Joback	>C=O	1	123
		-NH2	2	129
	Gani	-CONH2	1	3550
	Benson	CO-(N)(H)	1	251
		N-(CO)(H)2	2	253
		Optical isomer	1	406
		Total symmetry	2	405
	Ethylene carbonate 	Joback	-O- in a ring	2
>CH2 in a ring			2	110
>C=O in a ring			1	124
Gani		-COO-	1	3300
		>CH2	1	1010
		-CH2O- (C-ring)	1	1600
Benson		O-(CO)(C)	2	178
		C-(O)(C)(H)2	2	211
		1,3 dioxane ring	1	219
		Optical isomer	1	406
		Total symmetry	2	405
Propylene	Joback	>CH3	1	100

carbonate 		>CH- in a ring	1	111
		-O- in a ring	2	122
		>CH ₂ in a ring	1	110
		>C=O in a ring	1	124
	Gani	-COO-	1	3300
		>CH ₃	1	1015
		>CH-	1	1005
		-CH ₂ O- (C-ring)	1	1600
	Benson	C-(O)(C)(H) ₂	1	211
		C-(O)(C) ₂ ((H))	1	210
		O-(CO)(C)	2	178
		1,3 dioxane ring	1	219
		Optical isomer	1	406
		Total symmetry	2	405

VITA

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