A Study on the Kinetics of Glycerol Carbonate Production from Glycerol and Dimethyl Carbonate Using Calcium Oxide from Cockle Shell as a Catalyst

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การศึกษาจลนพลศาสตร์ของการผลิตกลีเซอรอลคาร์บอเนตจากกลีเซอรอลและไดเมทิลคาร์บอเนต โดยใช้แคลเซียมออกไซด์จากเปลือกหอยแครงเป็นตัวเร่งปฏิกิริยา

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By	Miss Piyathida Srirakij
Field of Study	Petrochemical Engineering
Advisor	Asst. Prof. Dr. Kunlanan Kiatkittipong

Accepted by the Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang in Partial Fulfillment of the Requirements for the Degree of Bachelor of Engineering (Petrochemical Engineering).

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Abstract

This research glycerol is used as a raw material to produce a high value product. The main problem is the increase in the biodiesel plant dramatically leads to the oversupply of its by-product glycerol in biodiesel production. Glycerol carbonate is one of a valuable product from glycerol by transesterification with glycerol and dimethyl carbonate using calcium oxide from cockle shell as a catalyst. There are various reaction conditions, which this research involve kinetics study. Effect of temperature was investigated, which the temperatures were 55, 65 and 75°C at the molar ratio of glycerol/DMC/CaO of 1: 2.5: 0.1. CaO was prepared by chemical method, the calcination temperature is 900°C. CaO has specific surface area (BET) 1.90 m^2/g. The highest conversion of glycerol at 75°C is 97.08% and the highest yield of glycerol carbonate at 75°C is 28.5%. For the kinetic study this reaction has rate constant at 55, 65 and 75°C which are 0.0066, 0.0071, and 0.0099 dm3/mol min respectively. And the activation energy is 19,283 J/mol.

Keywords: Glycerol, Glycerol Carbonate, Kinetics

เรื่อง การศึกษาจลนพลศาสตร์ของการผลิตกลีเซอรอลคาร์บอเนตจากกลีเซอรอลและไดเมทิลคาร์บอเนตโดยใช้แคลเซียมออกไซด์จากเปลือกหอยแครงเป็นตัวเร่งปฏิกิริยา
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บทคัดย่อ

ปริญญานิพนธ์นี้ได้ถูกจัดทำขึ้นโดยมีจุดประสงค์เพื่อที่จะนำกลีเซอรอลมาใช้เป็นวัตถุดิบในการผลิตผลิตภัณฑ์ที่มีมูลค่าเพิ่มขึ้น โดยปัญหาหลักที่จัดทำงานวิจัยนี้ขึ้นเนื่องมาจากว่า ประชากรมีความต้องการในการใช้พลังงานสูงขึ้นทำให้เกิดปัญหาการขาดแคลนพลังงาน จึงมีการนำพลังงานทดแทน เช่น ไบโอดีเซลมาใช้ ในการผลิตไบโอดีเซลจะได้ไบโอดีเซลเป็นผลิตภัณฑ์ และได้กลีเซอรอลเป็นผลพลอยได้ด้วย ซึ่งกลีเซอรอลคาร์บอเนตเป็นหนึ่งในผลิตภัณฑ์ที่มีมูลค่า โดยผลิตจากกลีเซอรอลทำปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชันกับไดเมทิลคาร์บอเนต โดยใช้แคลเซียมออกไซด์จากเปลือกหอยแครงเป็นตัวเร่งปฏิกิริยา ปฏิกิริยาทำภายใต้สภาวะต่างๆ โดยงานวิจัยนี้เกี่ยวข้องกับการศึกษาทางจลนพลศาสตร์ ทำการทดลองที่อุณหภูมิ 55, 65 และ 75 องศาเซลเซียส ที่อัตราส่วนเชิงโมลของกลีเซอรอลต่อไดเมทิลคาร์บอเนตต่อแคลเซียมออกไซด์เท่ากับ 1: 2.5: 0.1 ตัวเร่งปฏิกิริยาถูกเตรียมด้วยวิธีการเผาภายใต้อุณหภูมิสูง ที่อุณหภูมิ 900°C โดยแคลเซียมออกไซด์มีพื้นที่ผิว 1.90 ตารางเมตร/กรัม จากการทดลองที่อุณภูมิ 75 องศา มีอัตราการเปลี่ยนแปลงของกลีเซอรอลสูงสุด 97.08% และให้ผลพลอยได้ของกลีเซอรอลคาร์บอเนตเท่ากับ 28.5% และนอกจากนั้นข้อมูลที่ได้จากการทดลองจะนำมาศึกษาจลนพลศาสตร์ โดยหาค่าคงที่ของปฏิกิริยาที่อุณหภูมิ 55, 65 และ 75 องศาเซลเซียสได้เท่ากับ 0.0066, 0.0071, and 0.0099 ลิตร/ โมล นาที ตามลำดับ และให้ค่าพลังงานก่อกัมมันต์เท่ากับ 19,283 จูล/โมล

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Miss Piyathida Srirakij

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CHAPTER 1
INTRODUCTION

1.1 Background

In recent years, the demand of biodiesel production has been raised every year which the products are biodiesel and glycerol as a by-product. In the term of the world marketing with the growth of biodiesel tend to 11.96 billion gallons in 2020 [1]. Nowadays, biodiesel production is well known which from transesterification process of triglyceride with alcohol. For the increasing of biodiesel production, the accumulate of by-product, crude glycerol has become a problem in the chemical industry. Since the amounts of by-product are produced large which 100 kg of biodiesel produced, there are 10 kg glycerol formed [2]. The unavoidable production of glycerol as a by-product with a low commercial value, due to its impurities and excessive amount. Moreover, there are many ways to convert of glycerol to value-added chemicals which have been developed in recent year.

Glycerol is widely use in the food industry, cosmetic industry, sweetener, pharmaceutical and humectant. For the conversion of glycerol to value-added chemical, there are many glycerol derivatives, which can occur in two pathways; chemical and biochemical pathway [3]. From the biodiesel production, glycerol is rapidly increasing a high volume which relative to the growth of biodiesel production. The value of biodiesel is increasing every year, in contrast glycerol is low prices in the market global because of the high value is dependent on its purity. Therefore, crude glycerol will have purified before used [4].

Moreover, the development for upgrading glycerol to value-added product are needed to provide more efficiency of glycerol usage. Due to the usage of glycerol, the derivatives of glycerol are Epichlorohydrin, Propylene glycol, Lactic acid, Acrolein, and Glycerol carbonate, etc [5]. In this research provide interesting the conversion of glycerol to glycerol carbonate by catalyzed with calcium oxide (CaO) and the study on the kinetics of glycerol carbonate production.

Glycerol Carbonate (GC) is important chemical products which can be obtained from glycerol. Generally, glycerol carbonate is stable and colorless liquid that widely used as solvent, monomer, additive, and chemical intermediate, etc [6]. Glycerol carbonate can be obtained from several routes such as the reaction between glycerol and CO_2 in the presence of metallic catalyst [7], the phosgenation between glycerol and phosgene [8]. the glycerolysis of urea. However, these routes have some problematic. For example, some of starting raw materials are toxic and corrosive, starting from CO_2 must be required high pressure [9], and glycerolysis of urea must be performed under vacuum experiment [10].

One alternative route is use the organic carbonate (ethylene carbonate and dimethyl carbonate) as a carbonate source [11]. The transesterification between ethylene carbonate or dimethyl carbonate were carried out under mild conditions with various catalysts such as the homogeneous catalyst K_2CO_3 [12], the enzymatic catalyst lipase [13], and the heterogeneous solid base catalyst CaO [14]. The heterogeneous catalyst is suitable for this reaction than homogeneous catalyst because it is easy to separate catalyst from product. In the part of green chemistry, this reaction is not required any solvent, and this is eco-friendly process.

This work presents a study of the kinetics of glycerol carbonate with dimethyl carbonate and calcium oxide as catalyst for glycerol carbonate production. The transesterification is reversible reaction and kinetic model was assumed in the determination of the kinetic parameters for the reaction. From the experimental data, can be calculated the rate constant and chemical equilibrium. It was necessary to study the effect of different temperature to investigate the activation energy(Ea) which using Arrhenius equation to predict the kinetic parameters.

1.2 Objectives

1.2.1 To study the value-added product of glycerol from biodiesel production.

1.2.2 To study on the glycerol conversion to glycerol carbonate using calcium oxide from cockleshell as a catalyst under typical condition.

1.2.3 To determine the kinetic model based on experimental data for glycerol conversion to glycerol carbonate.

1.3 Scopes of Work

1.3.1 To prepare CaO, calcinated at 1,000°C

1.3.2 To study the reaction in the lab scale and study the effect of temperature on the kinetic parameters of glycerol carbonate production. Rate constant at temperature 55°C, 65°C, and 75°C.

1.4 Expected Outputs

1.4.1 Minimize the by-product of biodiesel production, which can be convert to a valuable product and reduce cost of the biodiesel production

1.4.2 Understanding of how the variable have the effect on transesterification of glycerol and dimethyl carbonate.

1.5 Work plan

Table 1. Work plan

No.	Task	2017						2018				
		Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May.
1	Identify topic and scope of project	◄	─	►								
2	Study the literature	◄	─	─	─	►						
3	Experimental Laboratory: catalyst preparation						◄	►				
4	Experimental Laboratory: Glycerol carbonate production								◄	►		
5	Product analysis									◄►		
6	Data analysis									◄	►	
7	Report										◄	►

CHAPTER 2
LITERATURE REVIEW

2.1 Glycerol [15]

Glycerol is a chemical compound, also known as glycerin or propane-1,2,3-triol. The chemical formula is $CH_2OHCHOHCH_2OH$ and the chemical structure shown in Figure 1. Glycerol consists of three carbon atoms and two hydroxyl groups that represent to the solubility in water and hydroscopic. Glycerol is one of the important chemicals because it widely used in many industries such as food as a sweetener, cosmetic, and pharmaceutical. Glycerol can be generated from transesterification of fat and oil in biodiesel production which transesterification is the reaction between triglyceride react with alcohol in the presence of a catalyst to produce the product, fatty acid methyl ester (FAME) and glycerol as a byproduct. The glycerol, which obtained from biodiesel plant is called crude glycerol and this byproduct consists of glycerol, water, organic and inorganic salts, soap, alcohol.

The general characteristic of glycerol is a colorless, odorless, non- toxic, hydroscopic, viscous and sweet taste liquid. Glycerol is soluble in water and slightly in alcohol and soluble in many solvents such as ether, ethyl acetate, and dioxane. Glycerol can be used as a renewable source for biodegradable products and can be developed in the green process and technology.

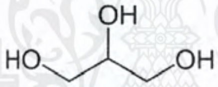


Figure 2.1 Structure of glycerol

2.1.1 Physical properties of glycerol

Glycerol is a colorless, odorless, non-toxic, hydroscopic, vicious and sweet taste of liquid. For the important properties of glycerol is shown in Table 2.1

Table 2.1 The physical properties of glycerol

Properties	Values
Molecular weight	92.09 g/mol
Melting point	17.8 °C
Boiling point (760 mmHg)	290 °C
Density (20 °C)	1.261 g/ cm^3
Flash point	177 °C
Refractive index (n_D)	1.474
Viscosity	1.2 Pa.s
Surface tension (20°C)	64.0 mN/m

2.1.2 Chemical properties of glycerol

Glycerol is a reactive molecule which chemical nature is alcohol. The primary hydroxyls are more reactive than the secondary hydroxyl group, and the first one to react does so more readily than the second. Glycerol can be heated to 250°C without a formation of acrolein.

2.1.3 Applications of glycerol

Glycerol has important industrial applications such as food industry, a chemical building block in a production of alkyd resins and polyurethanes for paint, ink and coating industry. In addition, glycerol is also a raw material for the manufacture of many different types of chemical intermediate, including solvents, plasticizers, and surfactants.

2.1.3.1 Food and beverages

Glycerol is non-toxic chemical which used in food industry or related food industry such as the manufacture of mono- and di-glycerides for use as emulsifiers, Solvent for flavors and food coloring, the filler in low-fat food products – cookies, the sweetener in the sugar, humectants and softening agent in a wide range of products – candy and cake.

2.1.3.2 Pharmaceutical and personal care

Glycerol is a chemical that used in pharmaceutical and personal care fields such as a smoothness, lubrication, and humectant. Furthermore, it was found in skin care and hair care products. A glycerol soap can be produced from glycerol, which moisture and lubricants additive.

2.1.3.3 Feedstock

Glycerol is one of the important raw material and a feedstock for the manufacture of polyol-based flexible, polyurethane foams, and nitroglycerin.

2.1.3.4 Lubricant

As known as the characteristic of glycerol, a non-toxic chemical which can be used in lubricant for food or machinery industry.

2.1.3.5 Surface coating

Due to the chemical properties of glycerol, these provide the use of glycerol to the alkyd resins production. And in the surface coating field, the alkyd resin—based was used in surface coating technology.

2.2 Biodiesel production [16]

2.2.1 Definition of biodiesel production

Biodiesel production is a chemical process, which is an alternative route for renewable energy. In general, biodiesel can be produced from vegetable oil, animal fat, and waste cooking oil. Biodiesel was made through a chemical process called transesterification. Transesterification is the reaction of triglyceride with alcohol to form fatty ester and glycerol is a by-product as shown in Figure 2.2. Normally, this process can be catalyzed by an acid or base.

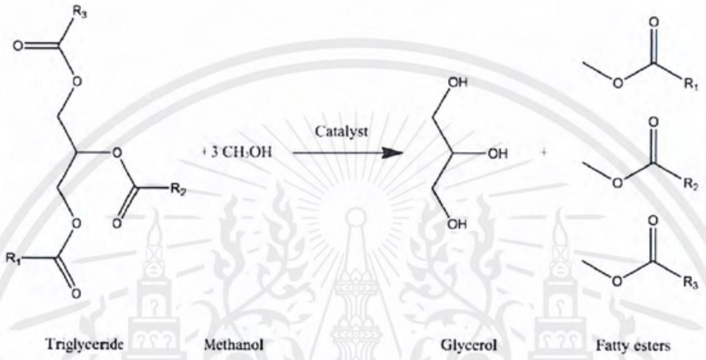


Figure 2.2 Transesterification reaction for glycerol production.

2.3 Calcium oxide [17]

Calcium oxide (CaO) is known as quicklime which is widely used in insecticides and fertilizers. The characteristic of CaO is white powder and crystalline solid at room temperature. CaO can be produced from the thermal decomposition of limestone or seashells, which contain calcium carbonate ($CaCO_3$). So, the process of the transformation of calcium carbonate to calcium oxide is called calcination. The reaction occurs at the temperature above 800°C. And this process will be generating CO_2 so, the equation for the reaction of calcium carbonate calcinated is shown in equation (2.1).

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \tag{2.1}$$

The quicklime is not stable and, when cooled it will react with CO_2 from the air until enough time, it will be completely converted back to calcium carbonate. For the physical properties of calcium oxide shown in Table 2.2.

Table 2.2 The properties of calcium oxide

Properties	Values
Molecular weight	56.077 g/mol
Density	3.35 g/cm^3
Melting point	2572°C
Boiling point	2850°C
Appearance	White powder
Solubility in water	Reacts
Solubility in methanol, diethyl ether, n-octanol	Insoluble
Solubility in acids, glycerol, sugar solution	Soluble

2.4 Dimethyl carbonate [18]

Dimethyl carbonate(DMC) is an organic compound which has a chemical formula $OC(OCH_3)_2$ in Figure 2.3. For the applications of DMC, it was widely used in various industries such as pharmaceutical, agricultural, and additive. DMC is a versatile, non-toxic, and biodegradable chemical which an environmentally sustainable compound and can be used for upgrading chemicals. Normally, DMC is a colorless, flammable with clear liquid and pungent odor material at room temperature.

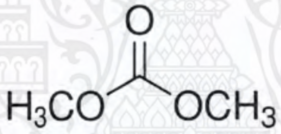


Figure 2.3 Structure of dimethyl carbonate

2.5 Glycerol Carbonate [19]

Glycerol Carbonate is a high-value product with several applications. The market price of glycerol carbonate is high which it can be obtained at low cost and high volume from glycerol. Glycerol Carbonate (GC) is important chemical products that can be obtained from glycerol. Generally, glycerol carbonate is stable, non-toxic chemical and colorless liquid which widely used as solvent, monomer, additive, and chemical intermediate, etc.

Glycerol carbonate can be obtained from several routes such as the reaction between glycerol and CO2 in the presence of metallic catalyst [7], the phosgenation between glycerol and phosgene [8]. The glycerolysis of urea. However, these routes have some problematic. For example, some of starting raw materials are toxic and corrosive, starting from CO2 must be required high pressure [9], and glycerolysis of urea must be performed under vacuum experiment [10].

One alternative route uses the organic carbonate (ethylene carbonate and dimethyl carbonate) as a carbonate source [11]. The transesterification between ethylene carbonate or dimethyl carbonate were carried out under mild conditions with various catalysts such as the homogeneous catalyst K_2CO_3 [12], the enzymatic catalyst lipase [13], and the heterogeneous solid base catalyst CaO [14]. The heterogeneous catalyst is suitable for this reaction than homogeneous catalyst because it is easy to separate catalyst from the product.

In the part of green chemistry, this reaction has not required for any solvent, and this is eco-friendly process.

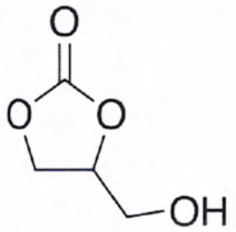


Figure 2.4 Structure of glycerol carbonate

2.6.1 Physical properties of glycerol carbonate

Table 2.3 The Physical properties of glycerol carbonate

Properties	Values
Molecular weight	118.09
Boiling point (760 mmHg)	353.9 °C
Density (25 °C)	1.4 g/cm^3
Flash point	212°C
Refractive index (n_D)	1.469
Viscosity	61 Pa.s
Surface tension (20°C)	44.2 mN/m

2.6 General mole balance [20]

General mole balance equation of any system, the boundaries system must be specified. The volume enclosed by the boundaries is the system volume. A mole balance was performed on species *j* in a system volume, where species *j* is the chemical species of interest in the system.

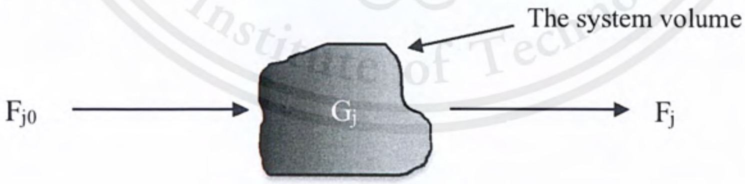


Figure 2.5 Balance on the system volume

For mole balance on species j at any time,

$$\begin{bmatrix}\text{The rate of flow of } j\\ \text{into the system}\\ \text{(moles/time)}\end{bmatrix} - \begin{bmatrix}\text{Rate of flow of } j\\ \text{out of the system}\\ \text{(moles/time)}\end{bmatrix} + \begin{bmatrix}\text{Rate of generation of } j\\ \text{by a chemical reaction within}\\ \text{the system}\\ \text{(moles/time)}\end{bmatrix} = \begin{bmatrix}\text{Rate of accumulation of } j\\ \text{within the system}\\ \text{(moles/time)}\end{bmatrix}$$

$$F_{j0} - F_j + G_j = \frac{d_{N_j}}{dt} \qquad (2.2)$$

Where N_j is the number of moles of species *j* in the system at time t.

If all variables (e.g., temperature, concentration of the chemical species, catalytic activity) are constant in the system, the rate of generation of species *j* (G_j), is the product of the reaction volume (V), and the rate of formation of species *j* (r_j)

$$G_j = r_j V \qquad (2.3)$$

When the rate of formation of species *j* for the reaction varies with the position in the system volume. The value of the rate of formation j in the system (G_j) can be calculated by dividing the surround to a small volume (ΔV) until the rate of formation of species j within these small volumes at i (ΔV_i) in figure 2.6.

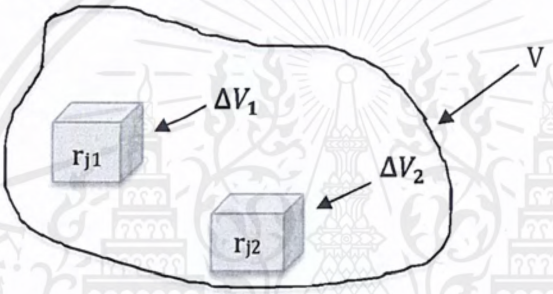


Figure 2.6 Dividing up the system volume.

Therefore,

$$\Delta G_{j,i} = r_{j,i}\,\Delta V_i \qquad (2.4)$$

The rate of information of species *j* in the system which the total volume of the system is divided into M subvolumes, the total rate of generation is

$$G_i = \sum_{i=1}^{M} \Delta G_{j,i} = \sum_{i=1}^{M} r_{j,i}\,\Delta V_i \qquad (2.5)$$

When M → ∞ and $\Delta V \rightarrow 0$, the equation will be

$$Gj = v_{\int r_j dV} \qquad (2.6)$$

Then, replace G*j* in equation 2.2

$$F_{j0} - F_j + v_{\int r_j dV} = \frac{d_{N_j}}{dt} \qquad (2.7)$$

Equation 2.7 is general mol balance which uses for developing the design equation for various type of reactor.

2.7 Batch Reactor

A batch reactor is used for a small-scale operation. It has no flow in and flow out of reactants or products while the reactor is operating. So, $F_{j0} = F_j = 0$ the general mole balance equation 2.7 will be the form

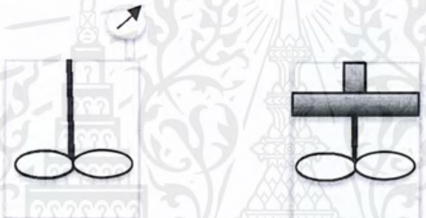
$$V\int r_j dV = \frac{dN_j}{dt} \qquad (2.8)$$

Where $F_{j0} = 0$ and $F_j = 0$

Assume the reactor is an ideal batch reactor, the reaction is well mixing so there is no variation in the rate of generation of species *j* is constant, integrate into the form

$$\frac{dN_j}{dt} = r_j V \qquad (2.9)$$

For gas phase, the batch reactor has 2 types which are a constant-volume batch reactor and constant-pressure batch reactor which is shown in Figure 2.7



(a) (b)

Figure 2.7 (a) constant-volume batch reactor **(b)** constant-pressure batch reactor

The mole balance of constant-volume batch reactor can be expressed as a function of a concentration of species *j* as shown in equation 2.10

$$\frac{1}{V}\frac{dN_j}{dt} = \frac{d(N_j/V)}{dt} = \frac{dC_j}{dt} = r_j \quad \text{(constant-volume)} \qquad (2.10)$$

And the mole balance of constant-pressure batch reactor can be expressed as a function of a concentration of species *j* as shown in equation 2.11

$$\frac{1}{V}\frac{dN_j}{dt} = \frac{1}{V}\frac{d(C_j/V)}{dt} = \frac{dC_j}{dt} + \frac{C_j}{V}\frac{dV}{dt} = r_j \quad \text{(constant-pressure)} \qquad (2.11)$$

or

$$r_j = \frac{dC_j}{dt} + C_j\frac{d\ln V}{dt}$$

The different mole balance equation, the different behavior of batch reactor.

2.8 Determination of kinetic parameters

There are several techniques for determine the kinetic parameters, which are

1. Differential method

For the power law;

$$-\frac{dC_A}{dt} = -r_A = kC_A^{(\alpha+\beta)}$$

From linear equation; y = mx + c

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k_A + (\alpha+\beta)\ln C_A$$

From the experimental data plot graph between $\ln\left(-\frac{dC_A}{dt}\right)$ and $\ln C_A$ to find k and $\alpha + \beta$ from intercept and slope of graph. Then use excess B to plot the graph.
From

$$-\frac{dC_A}{dt} = -r_A k' C_A^{\alpha}$$

From linear equation; y = mx + c

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k'_A + \alpha \ln C_A$$

Then plot graph between $\ln\left(-\frac{dC_A}{dt}\right)$ and $\ln C_A$ to find k' and α from intercept and slope of graph. When $k' = k_A \times C_B^{\beta}$, which C_B^{β} is constant.

2. Integral method

This method must be assumed the order of reaction, then write the rate equation in the form of design equation of reactor. And integrate the equation.
For the power law;

$$-\frac{dC_A}{dt} = kC_A^{(\alpha+\beta)} \quad ; \alpha + \beta = x$$

$$-\frac{dC_A}{dt} = kC_A^{(x)}$$

$$-kdt = \frac{dC_A}{C_A^x}$$

$$-k\int_0^t dt = \int_{C_{A0}}^{C_A} \frac{1}{C_A^x} dC_A$$

$$-kt = \frac{1}{(-x+1)} C_A^{(-x+1)}\Big|_{C_{A0}}^{C_A}$$

$$C_A^{(-x+1)} = C_A^{(-x+1)} - kt(-x+1)$$

When plot graph between $C_A^{(-x+1)}$ and $t(-x+1)$, it is straight line which slope is -k

3. Initial Rate method

This method is used for reversible reaction which reactant concentrations are changed. For the determine the rate of reaction at initial time can be calculated from the relationship between concentration and rate of reaction to find the order and rate constant.

$$\ln\left(-\frac{dC_A}{dt}\right)_{initial} = \ln k_A + \alpha ln C_{A,initial}$$

4. Half-Life method

The half-life of a reaction, $t_{1/2}$, is the amount of time required for a reactant concentration to decrease by half compared with its initial concentration.

$$\ln(t_{1/2}) = \ln\left(\frac{0.5^{(1-\alpha)} - 1}{k(1-\alpha)}\right) + (1-\alpha)\ln C_{A0}$$

Then, plot graph between ln $t_{1/2}$ and $\ln C_{A0}$

2.9 Conversion

In term of conversion, one of the reactants used as the basis of calculation and then relate the other species involved in the reaction to this basis. In general, choose the limiting reagent as the basis of calculation. The stoichiometry was considering the relationship and the general equation is

$$aA + bB \longrightarrow cC + dD \tag{2.12}$$

The conversion is, how much of the reactants are consumed or converted into products. So, the conversion X_A is the number of moles of A reacted per mole of A fed to the reactor.

$$X_A = \frac{\text{Mole of A reacted}}{\text{Moles of A fed}}$$

For the irreversible reaction, the maximum conversion is 1.0, i.e., complete conversion.

For the reversible reaction, the maximum conversion is the equilibrium conversion X_e, i.e., $X_{max} = X_e$

2.10 Literature review

Bell et al, studied the synthesis of glycerol carbonate from ethylene as shown in Figure 2.8 First, ethylene must be preparing to be an ethylene carbonate which the condition is 125°C and Sodium Bicarbonate used as a catalyst. Then, ethylene carbonate reacts with glycerol, the product glycerol carbonate and ethylene glycol were obtained. This experiment found which yield is 88%. [21]

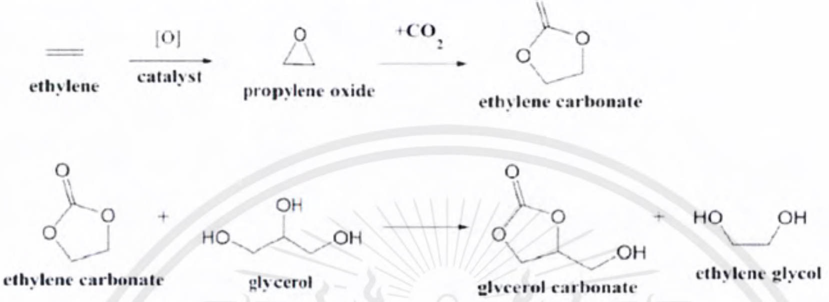


Figure 2.8 Glycerol carbonate from ethylene

Claude et al, studied the glycerol synthesis from urea which urea is low price. The reaction between glycerol and urea use sulfate metal as a catalyst ($MnSO_4$, $ZnSO_4$, $MgSO_4$, $NiSO_4$, and $FeSO_4$). The molar ratio 1 to 8 %W/W. For the optimum condition should use molar ratio urea and glycerol 0.65 to 1.2. This experiment has shown that the most effective catalyst is $ZnSO_4$ which give the highest yield 80%. [22]

Zul et al, studied the glycerol carbonate via supercritical dimethyl carbonate. For the reaction scheme was shown in Figure 2.9 condition at 300°C/20MPa, the highest yield of glycerol carbonate is 98 %. [23]

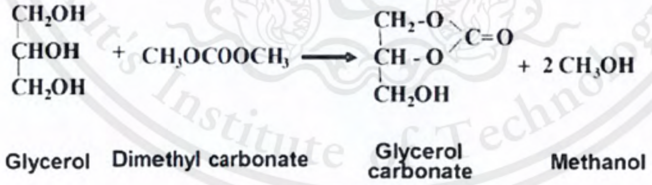


Figure 2.9 the reaction scheme of glycerol carbonate via supercritical dimethyl carbonate

CHAPTER 3
RESEARCH METHODOLOGY

3.1 Apparatus and instruments

1. X-ray fluorescence (XRF)
2. Gas chromatography-mass spectrometry (GC-MS)
3. Three-neck round bottom flask
4. Magnetic stir bar
5. Condenser
6. Thermometer
7. Separatory funnel
8. Hotplate
9. Burette
10. Pipette
11. Clamp and clamp holder
12. Stand
13. Laboratory glassware
14. Graduate cylinder
15. Sampling bottle
16. Glass rod
17. Desiccator
18. Universal indicator paper
19. Sieve and sieve shakers
20. Furnace
21. Stainless Pot
22. Glass stopper

3.2 Chemicals

1. Commercial glycerol
2. Dimethyl carbonate
3. Calcium oxide from cockle shell
4. Distilled water
5. Oil

3.3 Experimental procedure

3.3.1 Preparation and characterization of calcium oxide

3.3.1.1 Preparation of CaO from cockle

1. Wash cockle shell with tap water to remove sand, seaweeds deposited on a surface of the shell.
2. Crush shell by hammer (roughly crush)
3. Died crush shell at 105°C for 30 min in the oven and crush into powder, then use the sieve and sieve shaker to separate particle size of cockle powder.
4. Calcined cockle powder at 1000 °C with the heating rate 10°C/min for 8 h to transformation $CaCO_3$ into CaO catalyst
5. Catalyst keeps in the desiccator

3.3.1.2 Characterization of calcium oxide catalyst

The catalyst analyzes by using;

1. Determine the structure using X-ray diffraction (XRD)
2. Determine of the surface area using BET

3.3.2 Synthesis of glycerol carbonate by using calcium oxide(CaO) as the catalyst

3.3.2.1 Reaction procedure

1. Glycerol (20.61 mL), dimethyl carbonate (59.39 mL) which glycerol: dimethyl carbonate of 1: 2.5, and CaO (1.508 g) were added into a three-neck round bottom flask.

2. Afterward place the hot bath on a hot plate, which hot bath contain the oil as a heating media and temperature in this experiment were 55°C, 65°C, and 75°C.

3. Then the three-neck round bottom flask put into the hot oil bath and place on a hot plate at a specific temperature. After the reaction, sampling the product and collect into sampling bottle.

4. The sample of the product was collected in a bottle and characterized by using Gas chromatography-mass spectrometry (GC-MS)

3.3.2.2 Sample analysis

The product was analyzed on GC-MS (Agilent technologies, 6890N) equipped with the capillary column (DB-WAX 122-7032). The column temperature range 20-250°C, the column has length 30 cm, the inside diameter of 0.25 cm.

3.4 Data analysis

Use a differential method to find the order of reaction and Arrhenius equation to find activation energy.

CHAPTER 4
RESULTS AND DISCUSSION

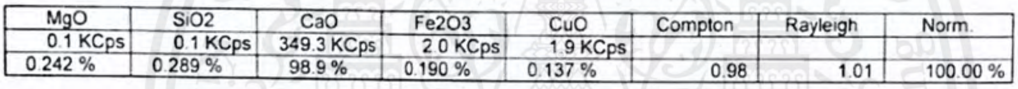
4.1 Physical and chemical of Calcium oxide calcined

Calcium oxide (CaO) used as a catalyst in the synthesis of glycerol carbonate by transesterification between glycerol and glycerol carbonate. CaO was synthesized by the calcination process. The structure of CaO was determined by using 1. X-ray fluorescence (XRF), the surface area using BET. The physical component of CaO as shown in table 4.1 and chemical component of CaO in table 4.2.

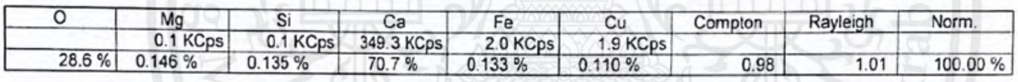
Table 4.1 The Physical component of CaO

Physical	Measurable
Specific surface area (BET)	1.90 m^2/g
Average pore diameter	11.89 nm
Total pore volume	0.0057 cm^3/g

Table 4.2 The Chemical component of CaO



MgO	SiO2	CaO	Fe2O3	CuO	Compton	Rayleigh	Norm.
0.1 KCps	0.1 KCps	349.3 KCps	2.0 KCps	1.9 KCps			
0.242 %	0.289 %	98.9 %	0.190 %	0.137 %	0.98	1.01	100.00 %



O	Mg	Si	Ca	Fe	Cu	Compton	Rayleigh	Norm.
	0.1 KCps	0.1 KCps	349.3 KCps	2.0 KCps	1.9 KCps			
28.6 %	0.146 %	0.135 %	70.7 %	0.133 %	0.110 %	0.98	1.01	100.00 %

CaO is a white powder which can be obtained from natural sources such as carbonate rock production, waste shell i.e cockle, scallop and mussel shell. From BET analysis, was investigated that CaO have the specific surface area (BET) 1.90 m^2/g, average pore diameter 11.89 nm, total pore volume 0.0057 cm^3/g.

4.2 The effect of reaction temperature

4.2.1 Conversion of glycerol and Yield of glycerol carbonate

The temperature effect was studied, and the result was shown in Figure 4.1. In this experiment, the reaction temperature was verified at 55°C, 65°C, and 75°C The result shows that with time goes on, the conversion of glycerol increases when the reaction temperature increase, and give the highest conversion of glycerol 97.08% at 75°C. This result can be used Arrhenius equation to conclude that why an increase in reaction temperature also increase conversion. From Arrhenius equation, where $k = Ae^{\frac{-E_a}{RT}}$, k is reaction rate, R is gas constant, E_a is activation energy and T is absolute temperature, when the reaction temperature (T) is increased, the reaction rate (k) will also be increased. Therefore, the reaction rate increase and conversion will increase.

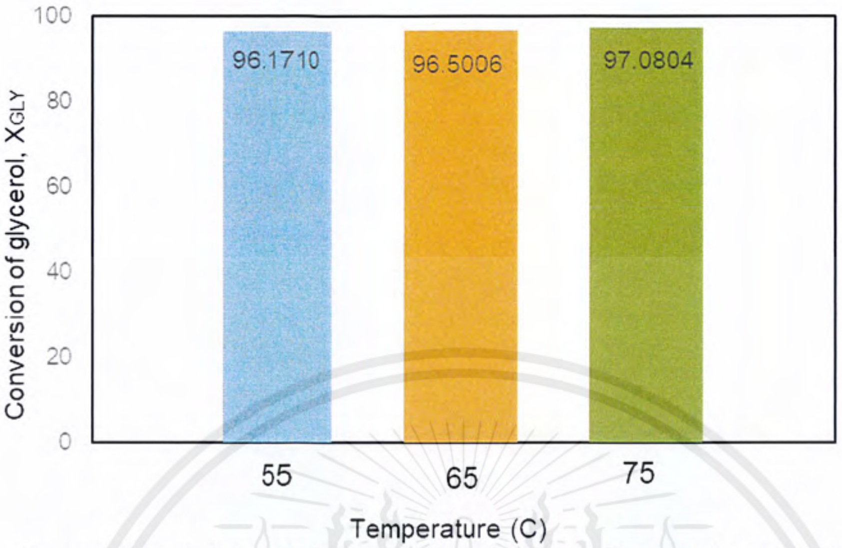


Figure 4.1 Conversion of glycerol at different temperature using a molar ratio of 0.1:1 (CaO: Glycerol)

For the Figure 4.2 show yield of glycerol carbonate at different temperature 55°C, 65°C, and 75°C. The result shows that when the temperature increase then yields also increase. Since the highest temperature was 75°C which can give the highest yield 28.5%. But the tendency of yield increases not relate with the conversion of glycerol. So, the reasons for low yield are the formation of another product formed it might be formed glycidol as another product because glycidol can be derived from glycerol carbonate decomposition due to high basicity of base catalyst, CaO is a strong base and another reason is this reaction is reversible reaction, a high molar ratio of dimethyl carbonate can shift the chemical equilibrium but Glycerol: DMC was used just 1:2.5 it might be enough.

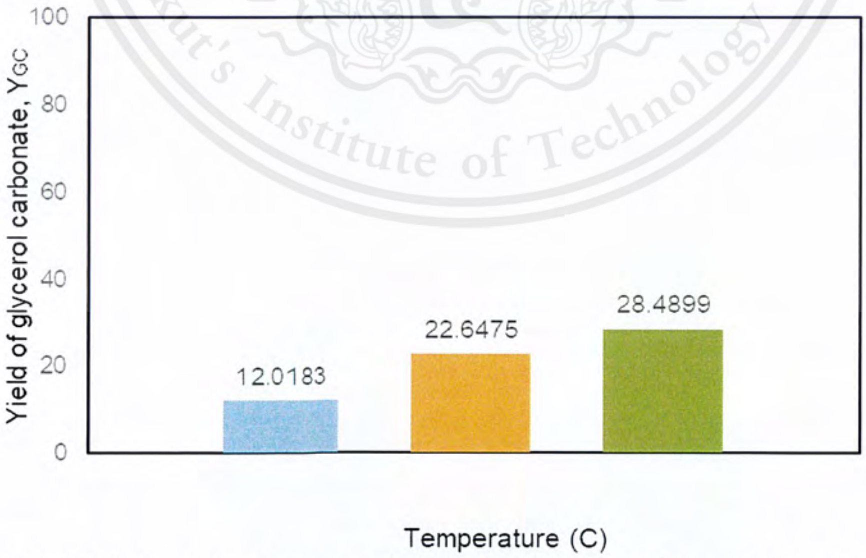


Figure 4.2 Yield of glycerol carbonate at different temperature using a molar ratio of 0.1:1 (CaO: Glycerol)

4.3 Determination of kinetic parameters

To find the kinetic parameter in transesterification reaction which in this reaction is a reversible reaction.

$$\underset{\text{Glycerol}}{C_3H_8O_3} + \underset{\text{DMC}}{H_3COCOOCH_3} \rightleftharpoons \underset{\text{Glycerol carbonate}}{C_4H_6O_4} + \underset{\text{Methanol}}{2CH_3OH}$$

$$A + B \rightleftharpoons C + 2D$$

$$-\frac{r_A}{1} = -\frac{r_B}{1} = \frac{r_C}{1} = \frac{r_D}{2}$$

From the general mole balance of batch reactor (constant-volume batch reactor) with the function of concentration was shown in equation:

$$\frac{1}{V}\frac{dN}{dt} = \frac{d(N/V)}{dt} = \frac{dC}{dt}$$

$$r_A = -\frac{dC_A}{dt} = k_1 C_A^{\alpha} C_B^{\beta} - k_{-1} C_C^{\delta} C_D^{\theta}$$

$$r_B = -\frac{dC_B}{dt} = r_A$$

$$r_C = -\frac{dC_C}{dt} = -r_A$$

$$r_D = -\frac{dC_D}{dt} = -2r_A$$

Based on Arrhenius equation (Equation 4.4)
Rate constant (k) from Arrhenius equation

$$k(T) = Ae^{\frac{-E_a}{RT}} \qquad (4.4)$$

Where, k is reaction rate constant in 1/min
Ea is the activation energy of the reaction in kJ/mol
A is the pre-exponential factor in 1/min
R is gas constant in kJ/mol K

For equilibrium rate constant (K_{eq})

This reaction is a reversible reaction, the reaction rate can be expressed in the function of a concentration of the relevant substant (i.e., reactant, product) at equilibrium. The equilibrium rate constant (K_{eq}) is

$$A + B \underset{k_-}{\overset{k_1}{\rightleftharpoons}} C + 2D$$

$$K_{eq} = \frac{k_1}{k_{-1}}$$

$$K_{eq} = \frac{C_C C_D^2}{C_A C_B} \qquad (4.5)$$

In this experiment DMC is excess, assume that the reaction will be irreversible. The integral method was used to find the kinetic parameter of the reaction

$$A + B \longrightarrow C + 2D$$

The rate equation is

$$-r_A = -\frac{dC_A}{dt} = kC_A^{\alpha}C_B^{\beta} \quad \text{-----------------------(1)}$$

Integral method

Gly:DMC = 1: 2.5
Assume, excess DMC

$$C_B = C_{B0}$$

$$-r_A = kC_{B0}^{\beta}\, C_A^{\alpha} \quad ; k' = kC_{B0}^{\beta}$$

$$-r_A = k'C_A^{\alpha}$$

$$-\frac{dC_A}{dt} = k'C_A^{\alpha}.$$

$\alpha = 0,1, 2$

From Integral method
For zero-order assume $\alpha = 0$

$$-\frac{dC_A}{dt} = k'C_A^{\alpha}$$

If $\alpha = 0$

$$-\frac{dC_A}{dt} = k'$$

Integrate both side with $C_A = C_{A0}$ at t = 0

$$dC_A = -k'dt$$

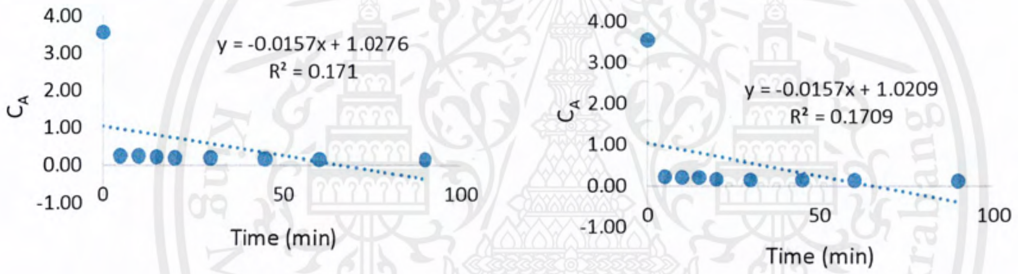
$$-k'\int_0^t dt = \int_{C_{A0}}^{C_A} dC_A$$

$$-k't = C_A - C_{A0}$$

$$C_A = C_{A0} - k't$$

Plot the experimental data for the relationship between C_A and t when a graph is linear and intercept at the origin, which is zero-order reaction and - k′ is a slope of the graph.

55°C zero-order 65°C zero-order



75°C zero-order

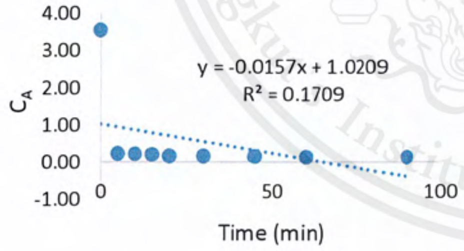


Figure 4.3 The relationship between C_A and Time (min) at different temperature using a molar ratio of 0.1:1 (CaO: Glycerol)

From Figure 4.3 the data was not fit with zero-order because when plot C_A and time, the linear in not through origin and it is a small R^2 values. Therefore, it can conclude that this assumption is not true. Then assume (α = 1, 2) and calculation follows these steps.

For first-order, assume α= 1

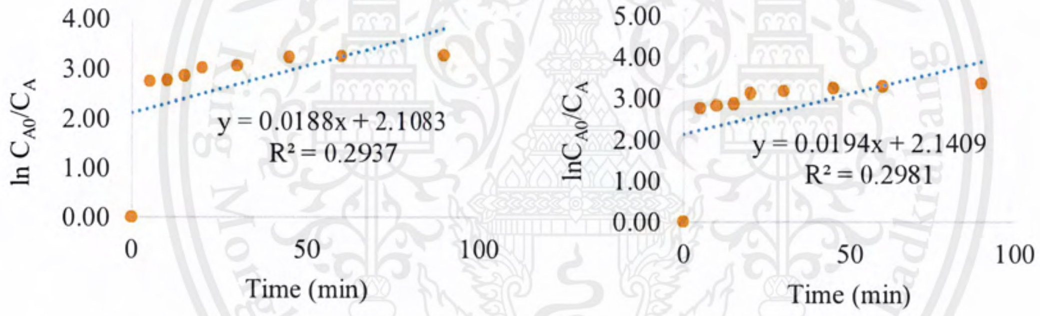
If $\alpha = 1$

$$\frac{dC_A}{C_A} = -\mathrm{k}'\mathrm{dt}$$

$$-k'\int_0^t dt = \int_{C_{A0}}^{C_A} \frac{1}{C_A}\mathrm{d}C_A$$

$$\mathrm{k}'\mathrm{t} = \ln\left(\frac{C_{A0}}{C_A}\right)$$

Plot the experimental data for the relationship between $\ln\left(\frac{C_{A0}}{C_A}\right)$ and t when a graph is linear and intercept at the origin, which is first-order reaction and k is a slope of the graph.



55°C first-order

65°C first-order

75°C first-order

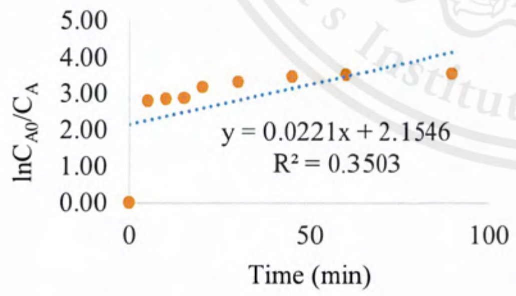


Figure 4.4 The relationship between lnC_{A0}/C_A and Time (min) at different temperature using a molar ratio of 0.1:1 (CaO: Glycerol)

From the 4.4 the data was not fit with the first-order reaction because when plot between lnC_{A0}/C_A and Time (min), the linear in not through origin and small R^2 values. So, it can be concluded that this assumption is not true.

For second-order, assume α= 2
If α = 2

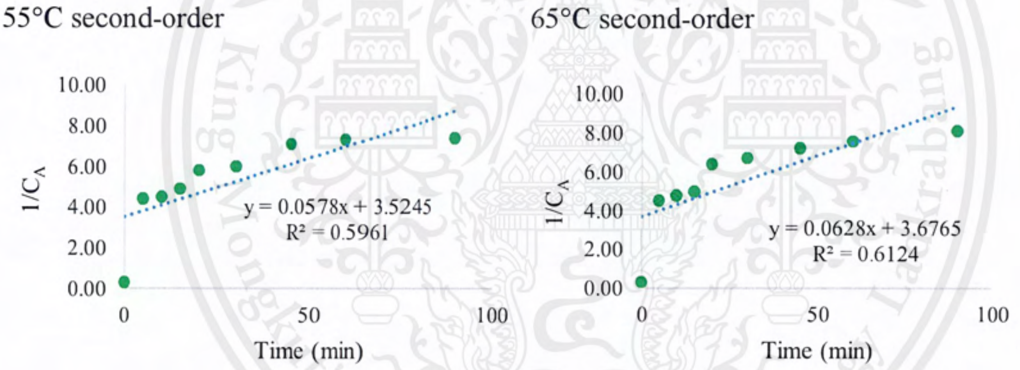
$$\frac{dC_A}{C_A} = -\mathrm{k}'\mathrm{dt}$$

$$-k'\int_0^t dt = \int_{C_{A0}}^{C_A} \frac{1}{C_A^2}\mathrm{d}C_A$$

$$\mathrm{k}'\mathrm{t} = \frac{1}{C_A} - \frac{1}{C_{A0}}$$

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + k't$$

Plot the experimental data for the relationship between $\frac{1}{C_A}$ and t when a graph is linear and intercept at the origin, which is first-order reaction and k is a slope of the graph.


55°C second-order

65°C second-order

75°C second-order

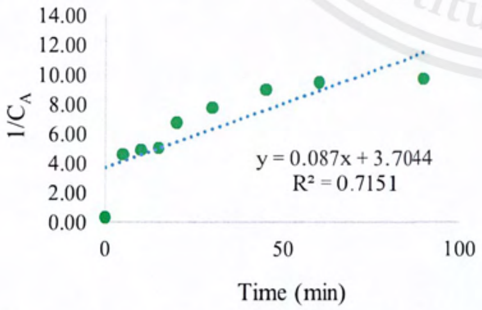


Figure 4.5 The relationship between $1/C_A$ and Time (min) at different temperature using a molar ratio of 0.1:1 (CaO: Glycerol)

In Figure 4.5 the experimental data show the relationship between $1/C_A$ and Time (min) at different temperature using a molar ratio of 0.1:1 (CaO: Glycerol). The tendency of data is linear and intercept at the origin. Therefore, the overall order of this reaction is a second-order reaction which have the k′ from slope of graph 0.0578, 0.0628, and 0.087 at 55°C, 65°C, and 75°C respectively. But for the rate constant can be calculated from $k' = kC_{B0}^{\beta}$ Therefore, k will be 0.0066, 0.0071, and 0.0099 dm^3/mol min at 55°C, 65°C, and 75°C, respectively.

Activation energy (Ea) and k_0

The rate constant is depending on temperature which follow the Arrhenius equation.

$$k(\mathrm{T}) = \mathrm{k_0} \mathrm{e}^{\frac{-\mathrm{E_a}}{\mathrm{RT}}}$$

$$\ln k = \ln \mathrm{k_0} - \frac{\mathrm{E_a}}{\mathrm{R}} \frac{1}{\mathrm{T}}$$

k_0 and Ea can be calculated from the experimental data plot between lnk and 1/T when, lnk is y-intercept and -Ea/R is a slope of graph.

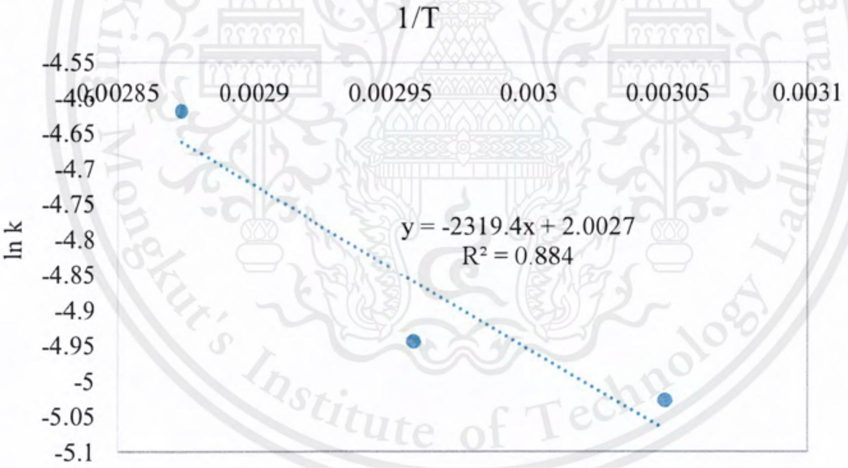


Figure 4.6 The relationship between lnk and 1/T

From Figure 4.6 y-intercept is 2.0027, slope is -2319.4

$\ln k_0$ (y-intercept) =2.0027

k_0 = 7.409

Therefore, $k = 7.409 \times e^{-\frac{19{,}283}{RT}}$

$\frac{E_a}{R} = -2319.4$

Ea = 2319.4 × 8.314 = 19,283 J/mol

CHAPTER 5
CONCLUSION

5.1 Conclusion

5.1.1 Synthesis of CaO

Calcium oxide (CaO) used as a catalyst in the synthesis of glycerol carbonate by transesterification between glycerol and glycerol carbonate. From XRD analysis, was investigated that CaO have mainly compound CaO and BET analysis, have the specific surface area (BET) 1.90 m2/g, average pore diameter 11.89 nm, total pore volume 0.0057 cm^3/g

5.1.2 Effect of temperature

The highest temperature in this experiment was observed at 75°C which can give the highest conversion of glycerol and yield of glycerol carbonate 97.08% and 28.5%. respectively.

5.1.2.3 Kinetic parameter

The kinetics of transesterification of glycerol and dimethyl carbonate to produce glycerol carbonate, this reaction is second-order. And can calculate the kinetic parameter, rate constant at 55°C, 65°C, and 75°C which 0.0066, 0.0071, and 0.0099 dm3/mol min respectively. For the activation energy and rate constant which follow Arrhenius equation is 19,283 J/mol and $k = 7.409 \times e^{-\frac{19,283}{RT}}$ respectively.

5.2 Recommendations

5.2.1 The reaction must use a molar ratio of glycerol: DMC more than 1:2.5 to shift the reaction forward and to get a high yield of glycerol carbonate.

5.2.2 The temperature should be high than this experiment because the rate of reaction is depending on temperature.

5.2.3 Determination of kinetic parameter such as rate constant, for the high accuracy should be used activity-based to calculate the rate constant.

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APPENDIX A.
Raw Data and Calculation

The condition of Gas chromatography-mass spectrometry GC G1530 N MS G2573A

Samples:

Name: Glycerol carbonate at 55, 65, and 75 C°
Volume: 1 microliters

Standard compounds:

Name: Glycerol, Dimethyl carbonate, Glycerol Carbonate, and Methanol

Condition of GC G1530 N MS G2573A

Oven:

- Inlet temperature = 45 C°
- Maximum temperature = 250 C°
- Post temperature = 45 C°
- Run time = 20.17 min
- Ramps

run	Rate (C°/min)	Final temperature (C°)
1	10	100
2	30	250

- Mode: Split	
- Initial temperature	250 C°
- Pressure	7.11 psi
- Split ratio	100:1
- Split flow	101mL/min
- Total flow	101 mL/min
- Gas Type	Helium

Capillary column:

- Model number	122-7032
- DB-WAX	
- Maximum temperature	250 C°
- Nominal length	30 m
- Nominal diameter	0.250 mm
- Nominal film thickness	0.25µm
- Mode	Constant flow
- Initial flow	1mL/min

Detector

- Mass spectrometer detector

Calibration curve

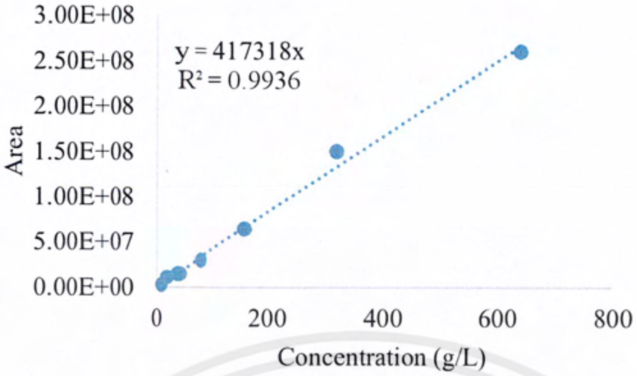

Figure A.1 Calibration curve for standard glycerol

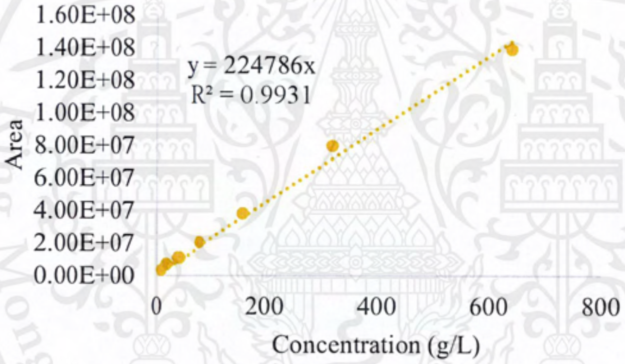

Figure A.2 Calibration curve for standard dimethyl carbonate

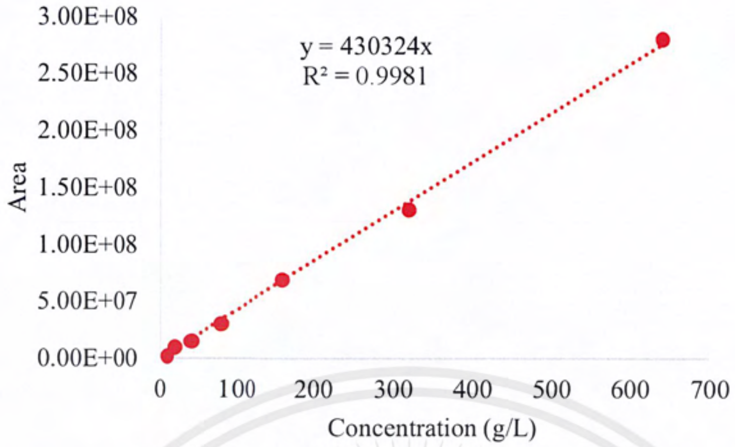

Figure A.3 Calibration curve for standard glycerol carbonate

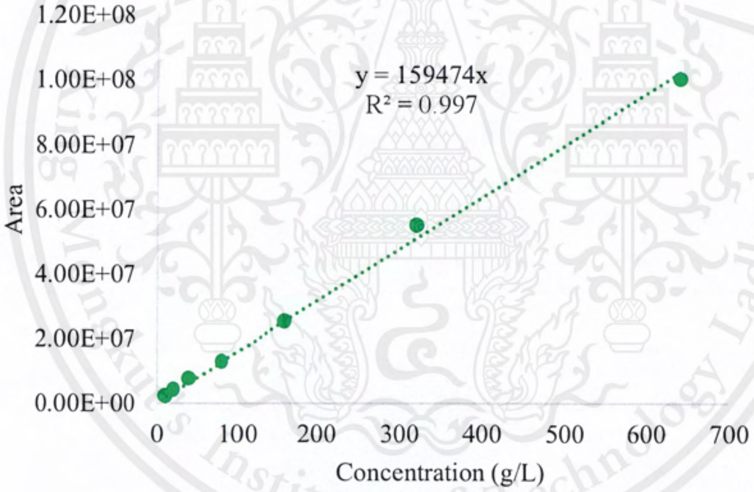

Figure A.3 Calibration curve for standard methanol

Table A1. The experimental data at 55°C

Time (min)	Glycerol Conc. out (mol/L)	Glycerol Conc. In (mol/L)	%Conversion of Glycerol	GC Conc. (mol/L)	%Yield of GC
0	0	3.5311	0	0	0
5	0.2273	3.5311	93.5641	0.0318	0.9637
10	0.2229	3.5311	93.6874	0.0568	1.7176
15	0.2043	3.5311	94.2134	0.0917	2.7561
20	0.1729	3.5311	95.1022	0.1090	3.2462
30	0.1669	3.5311	95.2728	0.1485	4.4145
45	0.1410	3.5311	96.0072	0.2018	5.9530
60	0.1370	3.5311	96.1206	0.2468	7.2701
90	0.1352	3.5311	96.1710	0.4089	12.0414

Table A2. The experimental data at 65°C

Time (min)	Glycerol Conc. out (mol/L)	Glycerol Conc. In (mol/L)	%Conversion of Glycerol	GC Conc. (mol/L)	%Yield of GC
0	0	3.5311	0	0	0
5	0.2226	3.5311	93.6948	0.0617	1.8661
10	0.2102	3.5311	94.0475	0.1145	3.4475
15	0.2021	3.5311	94.2776	0.1255	3.7699
20	0.1570	3.5311	95.5533	0.1590	4.7110
30	0.1497	3.5311	95.7619	0.1649	4.8757
45	0.1390	3.5311	96.0635	0.2142	6.3133
60	0.1325	3.5311	96.2463	0.2826	8.3143
90	0.1236	3.5311	96.5006	0.7521	22.0700

Table A3. The experimental data at 75°C

Time (min)	Glycerol Conc. out (mol/L)	Glycerol Conc. In (mol/L)	%Conversion of Glycerol	GC Conc. (mol/L)	%Yield of GC
0	0	3.5311	0	0	0
5	0.2189	3.5311	93.8022	0.1161	3.5061
10	0.2062	3.5311	94.1613	0.1273	3.8277
15	0.2003	3.5311	94.3274	0.1375	4.1270
20	0.1486	3.5311	95.7915	0.1611	4.7622
30	0.1295	3.5311	96.3323	0.1693	4.9771
45	0.1117	3.5311	96.8363	0.2223	6.5023
60	0.1056	3.5311	97.0098	0.3358	9.8017
90	0.1031	3.5311	97.0804	0.9766	28.4899

Calculation

1. Find conversion of glycerol

$$\%\text{Conversion} = \frac{\text{Concentration}_{\text{Glycerol, in}} - \text{Concentration}_{\text{Glycerol, out}}}{\text{Concentration}_{\text{Glycerol, in}}} \times 100\%$$

2. Find yield of glycerol carbonate

$$\%\text{Yield} = \frac{\text{Concentration}_{\text{Glycerol carbonate, out}}}{\text{Concentration}_{\text{Glycerol, in}} - Concentration_{Glycerol,out}} \times 100\%$$

BIBLIOGRAPHY

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