Esterification of Oleic acid in a Microreactor

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การศึกษาปฏิกิริยาเอสเทอริฟิเคชันของกรดโอเลอิกในเครื่องปฏิกรณ์ระดับไมโคร

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Abstract

This work studied the esterification reaction of oleic acid in soybean oil with methanol in a microreactor by using sulfuric acid as a catalyst. The effect of reaction temperature in the range of 60 - 100 °C, methanol to oleic acid molar ratio 10:1 - 50:1 and catalyst concentration 2 - 10 wt% of oleic acid on oleic acid conversion was studied. The results show that oleic acid conversion increased when increase reaction temperature and molar ratio of methanol to oleic acid while catalyst concentration was not significant on increasing of oleic acid conversion. The highest oleic conversion that obtained from this work is 71.38% at reaction temperature 100 °C, methanol to oleic acid molar ratio 30:1 and catalyst concentration 6 wt% of oleic acid

Keywords: Oleic acid, Esterification, Microreactor

ปริญญานิพนธ์เรื่อง	การศึกษาปฏิกิริยาเอสเทอริฟิเคชันของกรดโอเลอิกในเครื่องปฏิกรณ์ระดับไมโคร
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บทคัดย่อ

ปริญญานิพนธ์นี้มีวัตถุประสงค์ศึกษาปฏิกิริยาเอสเทอริฟิเคชันระหว่างกรดโอเลอิกในน้ำมันถั่วเหลืองกับเมทานอลในเครื่องปฏิกรณ์ระดับไมโครโดยใช้กรดซัลฟิวริกเป็นตัวเร่งปฏิกิริยา และศึกษาอิทธิพลของอุณหภูมิทำปฏิกิริยา สัดส่วนโดยโมลของเมทานอลต่อกรดโอเลอิก และความเข้มข้นของตัวเร่งปฏิกิริยาที่ส่งผลต่อค่าการแปลงผันทางเคมีของกรดโอเลอิก โดยศึกษาอุณหภูมิทำปฏิกิริยาอยู่ในช่วง 60 - 100°C สัดส่วนโดยโมลของเมทานอลต่อกรดโอเลอิกระหว่าง 10:1 - 50:1 และความเข้มข้นของกรดซัลฟิวริกร้อยละ 2 - 10 โดยมวลเมื่อเทียบกับความเข้มข้มของกรดโอเลอิก ผลการทดลองแสดงให้เห็นว่าการเพิ่มอุณหภูมิทำปฏิกิริยาและการเพิ่มสัดส่วนโดยโมลของเมทานอลต่อกรดโอเลอิกจะส่งผลให้ค่าการแปลงผันทางเคมีของกรดโอเลอิกเพิ่มขึ้น ในขณะที่การเพิ่มปริมาณตัวเร่งปฏิกิริยาจะไม่ส่งผลอย่างมีนัยสำคัญต่อการเพิ่มขึ้นของค่าการแปลงผันทางเคมี และจากการศึกษาทำให้พบว่าค่าการแปลงผันของกรดโอเลอิกที่สูงที่สุดในช่วงที่ทำการทดลองคือร้อยละ 71.38 ณ สภาวะอุณหภูมิทำปฏิกิริยา 100°C สัดส่วนโดยโมลของเมทานอลต่อกรดโอเลอิก 30:1 และปริมาณตัวเร่งปฏิกิริยาร้อยละ 6 โดยมวลเมื่อเทียบกับความเข้มข้นของกรดโอเลอิก

คำสำคัญ: กรดโอเลอิก, ปฏิกิริยาเอสเทอริฟิเคชัน, เครื่องปฏิกรณ์ระดับไมโคร

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Saran Saysuwan

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NOMENCLATURE

AV	Acid value of sample	mg KOH/g oil
AV_{in}	Initial acid value of the soybean oil	mg KOH/g oil
AV_{out}	Acid value of product sample	mg KOH/g oil
X	Oleic acid conversion	%
C	Molarity of KOH solution	mol/L
V	Volume of the KOH solution required for titration	mL
m	Weight of sample	g

CHAPTER I
INTRODUCTION

1.1 Background

Biodiesel is alternative energy that is environmentally friendly and plays an important role in Thai society. Because of the current state of public awareness of future energy trends, trying to reduce energy consumption and turn to alternative energy is important to increase energy security in the country. Due to the environment and geography of Thailand, it is suitable for plants growth, which can be extracted and processed into biodiesel. Therefore, the production of these agricultural products to biodiesel is another way to increase the stability energy for the country. It is also a way of transforming agricultural products into value-added products.

Biodiesel production generally involves the production of crude oil from plants through the transesterification reaction. To obtain a good quality biodiesel, vegetable oils used in biodiesel production should be oils with low free fatty acids, to reduce the reaction of soap which occurs from saponification reaction. A one of the ways to reduce the amount of free fatty acid is to use vegetable oil to perform through the esterification reaction, to convert free fatty acids from vegetable oils into FAAE (fatty acid alkyl ester) which is an important component in biodiesel.

Generally, the reactor for biodiesel production is the batch reactor, and it has been found that the production of biodiesel from conventional reactor is limited in many ways, such as non-uniform mixing, occur vertex and dead zone, low mass transfer and heat transfer rate, non-uniform mass and heat distribution within the reactor which all of these also affect the kinetics study of the reaction and influence to resulting product has a conversion value, selectivity, and yield that does not meet the expected goal.

From these restrictions, lead to more study and several research to find the ways that overcome the problems. One of the technologies that have been referred to is the microreactor technology, which is a micrometer reactor that has reported advantage and benefits in many areas such as good mass and heat transfer rates, segment flow characteristic that makes the substances well mixing, provide high conversion, selectivity and yield under very short residence time. Lead to this research to bring microreactor to produce biodiesel through esterification reaction for transform agricultural products into the most efficient biodiesel.

1.2 Objective

Study esterification reaction in a microreactor and investigate influences of reaction temperature, molar ratio of methanol to oleic acid and H_2SO_4 concentration on conversion of oleic acid

1.3 Scopes of Work

1.3.1 Study the homogeneous esterification reaction by using H_2SO_4 as catalyst

1.3.2 The operating conditions in the study is reaction temperature, molar ratio of methanol to oleic acid and H_2SO_4 concentration

1.3.3 The operating conditions used in this study is temperature ranges from 60-100°C, molar ratio of methanol to oleic acid 10:1-50:1 and H_2SO_4 concentration 2 - 10 wt% of oleic acid

1.4 Work Procedures

1.4.1 Studies general characteristic of Microreactor

1.4.2 Study operating conditions of the esterification reaction

1.4.3 Design reactor and conduct experiment to observe influence of operating conditions on performance of reactor

1.5 Expected Outputs

1.5.1 Increase the choice of reactor to perform esterification reaction

1.5.2 Observe influences of temperature, molar ratio of methanol to oleic acid and H_2SO_4 concentration on performances of microreactor

CHAPTER II
LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is an alternative fuel that produced from agricultural products to replace or mixed with normal diesel fuel, the key component of biodiesel is alkyl ester. [1] Production and synthesis of biofuels can be made from a variety of processes, such as pyrolysis, dilution, micro emulsion, tranesterification and esterification. The raw materials can be used in biodiesel production divided into 3 groups includes oil-yielding plants, animal fats, and recycled cooking oil. Biodiesel produced from each substance or different processes will vary in quality depending on the amount of free fatty acid, moisture content, catalyst concentration, molar ratio of reactants, reaction time and reaction temperature. The benefits of biodiesel are that it can be used instead of diesel without reducing engine performance, low air pollution because of the lower CO_2 emissions than conventional fuel, no element of sulfur then it does not cause SO_2 when burned which is the main cause of acid rain, safe due to lower flammable than conventional fuel, biodegradable, reduce the accumulation of toxic residues in the environment and environmentally friendly. [2]

Biodiesel production is most commonly produced by transesterification reactions or esterification reactions to convert triglycerides and free fatty acid respectively to obtain fatty acid alkyl ester (FAAE). [1] Side reaction can be occurred if the raw material that used to produce biodiesel consists of amount of free fatty acid more than 2% which called Saponification reaction that results in lower quality of biodiesel. This problem can be solved by trying to reduce the amount of free fatty acid in the raw material, which can be achieved by physical treatment and chemical treatment, one of which is perform esterification reaction. [3]

2.2 Esterification Reaction

Esterification is a reaction commonly used to reduce the amount of free fatty acid that is present in the raw material to be used in biodiesel production. The reactants is a free fatty acid which is contained in vegetable oil, reacts with alcohol in combination with acidic catalysts to produce biodiesel or fatty acid alkyl ester (FAAE) and water according to the chemical equation in figure 2.1.

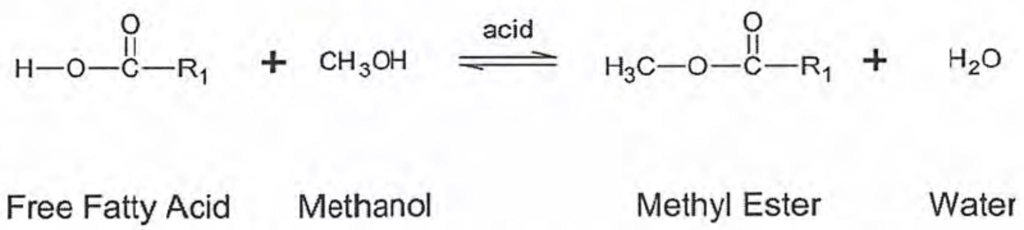

Figure 2.1 Chemical equation of esterification reaction [4]

From the esterification reaction of free fatty acids shown in Figure 2.1, a variety of alcohol can be used in the reaction such as methanol, ethanol, propanol and butanol. Most commonly used methanol and ethanol because of relatively cheap and has many chemical propertie, such as polarity and short chain alcohol which can react quickly with triglycerides and can dissolve with catalysts as H_2SO_4. [1]

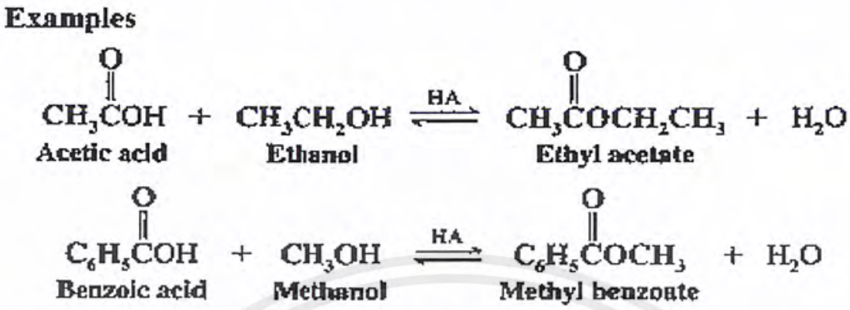

Figure 2.2 Subtype of esterification reaction [5]

Figure 2.2 observed the pattern of esterification and shows that the composition of the product or type of ester compound obtained at the end of the reaction is dependent on the type of fatty acid and type of alcohols that react in the same amount of moles. Most often excess alcohol is added to ensure that the substance is produced as an ester compound. Since the esterification is reversible reaction, adding excess alcohol increases the concentration of the reactant to push the reaction forward and obtain more products.

After the reaction has been completed, two products of ester and water are formed. Water is more density than fatty acid alkyl ester and due to both products has different polarity; the products are separated automatically when reaction complete. After that, the products can be separated for further purification by passing through the centrifuge machine and rotary evaporator to remove amount of water that contain in the fatty acid alkyl ester to obtain purified biodiesel.

2.3 Microreactor [6]

2.3.1 Introduction

Microreactor is a newly developed reactor with significant flow characteristics, mass and heat transfer and chemical kinetics behavior. With these properties, microreactors can be applied to a wide range of reactions and systems [7-9]. The advantage of this technology is a small system with short diffusion times, thus increasing the rate of mass transfer and heat transfer, the amount of reactants used in the reaction is low but the product has high conversion and yield, [6, 10] capability to operate at high temperature and pressure conditions, can be used to reduce the use of chemicals. The system is designed to continuously synthesize chemicals. [11]

2.3.2 Size

Microreactors are designed to provide a structure for the reactant to flow through several phases as liquid phase, gas phase, liquid-gas mixture, and mixture of liquid, solid and gas phase. The size of microreactor ranged from micrometer to millimeter. The arrangement can be arranged in a single tube and multi-tube by numbering technique, which is a technique that helps in increasing the production rate. [6]

2.3.3 Geometric

The internal surface and shape of the reactor depends on the purpose of the design and the invention to be applied to the reaction which variety from the conventional spiral to sophisticated systems, with the addition of reagents injection, mixing incubation, quench addition, solvent exchange, crystallization, thermal management, extraction, encapsulation and phase separation.

2.3.4 Construction material

Materials used in the design of microreactors include several types [12] such as glass [6], elastomer [13], silicon [14], quartz, polymer, metal, and ceramics. The selection criteria for the microreactor fabrication depend on the operating condition and characteristics of the reaction because each material can withstand different operating conditions. The microreactor fabrication can be invented in several ways, such as laser ablation, wet chemical etching, abrasive micromachining, deep reactive ion etching, molding, embossing, casting and milling.

2.3.5 Fluid flow

Because of the small size of the microreactor, the flow pattern resulting from the feeding of the reactants into the reactor occurs in form of a droplet which this flow pattern called the segmental flow. [6] It is found that this type of flow that results in better mass transfer because of increase interface area between the substance and the internal vertex within the flow segment causes better mixing. [6, 16]

2.3.6 Mixing Mechanism

Fluid flow patterns in microreactors are considered by Reynolds Number (Re), and generally flow is in the laminar region. In order to analysis of the mass transfer phenomena occurring within the reactor is usually analyzed using a diffusion model, which is proved by Fick's law. Except in the case that disturbances caused by split and recombine stream to decrease diffusion time, interior surface design is more rugged or complicated, the effect of these disturbances can affect the flow region becoming turbulent. [6, 18-19]

2.3.7 Multifunctional Integration

Some microreactors have improved capability by providing more functionality for the reactors, [6] examples of such functions include installation of mixer, separator, heat exchanger, heater, cooler [20] With these functions, the reactor can be applied to a complex process or unit operations. Various type of operations, such as extractions, crystallizations, purifications, conversions, phase changes, phase separations and identification.

2.4 Literature Review

Sunitha T. et al. [21, 22] reported on the problem of the kinetics studies in a batch reactor. They found that the reactors were characterized by low mass transfer, making difficult to study kinetics. They know that microreactor has an ability to transfer mass. Therefore they turned to studying the kinetics of the reaction in microreactor and bring the results back to the comparison with batch reactor for compare the performance of both reactors by using a 3-phase reaction as a model for the study. The major conclusions were mass transfer coefficient in the microreactor was about 100 times higher than batch reactor. After that, the microreactor technology continued to evolve and applied to study various reactions.

Nut C. et al. [23] perceive the important role of biodiesel and have studied the synthesis of biodiesel through the transesterification reaction in microreactor using CaO, which is a heterogeneous catalyst. They investigated the effect of temperature, molar ratio of reactants, catalyst stability, and residence time on the biodiesel yield and compared the results with the conventional reactor. The results show that catalytic microreactor can synthesize biodiesel with quality under standards and significant shorter residence time than other types of reactors.

Similarly, Peiyong S. et al. [24] studied the influence of factors affecting yield of biodiesel and the find optimal conditions for the synthesis of biodiesel through the homogeneous esterification reaction and homogeneous transesterification reaction in microreactor. Subsequently, they used optimal condition to study the continuous two-step reaction of high acid value esterification and transesterification for biodiesel synthesis. The results show that biodiesel produced from this continuous reaction has 99% yields in just a few minutes, which demonstrates the very well efficiency of microreactor.

CHAPTER III
RESEARCH METHODOLOGY

These works design the continuous microreactor to reduce amount of oleic acid that contain in the soybean oil by perform esterification reaction. The effect of reaction temperature, methanol to oleic acid and H_2SO_4 concentration was studied. The experiment details are as followed.

3.1 Chemicals

1. Methanol
2. Sulfuric acid
3. oleic acid
4. Vegetable oil
5. Isopropanol
6. Toluene
7. Potassium hydrogen phthalate
8. Potassium hydroxide
9. Barium hydroxide
10. Phenolphthalein
11. Acetone
12. Hexane
13. Silicone oil
14. Distilled water

3.2 Equipment and Apparatus

1. Pump
2. Microreactor tube
3. Micro mixer
4. Rotary evaporator
5. Centrifuge machine
6. Heat plate
7. Oil bath
8. Thermometers
9. Thermocouple
10. Micropipette
11. Sample bottle
12. Beaker
13. Volumetric flask
14. Syringes

3.3 Experimental Procedures

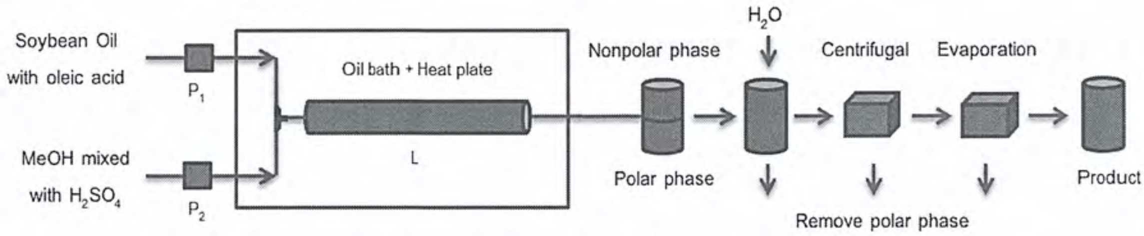

Figure 3.1 Schematic of experimental setup

1. Experimental apparatus installation and setup following Figure 3.1
2. Prepare the reactants and catalyst to be used in the reaction
3. Feed the reactants into the reactors according to the conditions set in Table 3.1 and control the reaction temperature as well as conditions to the specified level.
4. After the reaction was complete, the product samples from reactor were washed to remove the water, remaining methanol and sulfuric acid.
5. Bring the treated product samples to evaporate the water and methanol within a rotary evaporator to increase the purity of the product samples
6. Titrate purified product samples with potassium hydroxide solution and calculate the conversion percentage of oleic acid

3.4 Operating Conditions

Table 3.1 Operating conditions used to study esterification reaction in microreactor

Molar ratio of methanol to oleic acid	10 – 50
Reaction temperature (°C)	60 – 100
H_2SO_4 concentration (wt%)	2 – 10
Residence time (min)	10

3.5 Product Analysis

3.5.1 Acid value Calculation [25]

According to ASTM D974, the product samples is taken from the reaction and weighed, mix the product samples with titration solvent and phenolphthalein indicator to prepare product sample before titration. The product samples was titrated with potassium hydroxide solution which dissolved in isopropanol and the acid value of the oleic acid was determined by using equation (3-1).

$$AV = \frac{V \times C \times 56.1}{m} \tag{3-1}$$

3.5.2 Conversion Calculation [24]

The conversion of oleic acids can be analyzed by measuring the acid value of the initial soybean oil and product sample from esterification reaction. Then calculate the conversion by using the equation (3-2)

$$X = \left(1 - \frac{AV_{out}}{AV_{in}}\right) \times 100 \tag{3-2}$$

CHAPTER IV
RESULTS AND DISCUSSION

Experimental results from this work divided into 3 part which including effect of reaction temperature, effect of methanol to oleic acid molar ratio and effect of sulfuric acid concentration on conversion of oleic acid

4.1 Effect of Reaction Temperature

This work studied effect of reaction temperature on oleic acid conversion at the reaction temperature range of 60 - 110°C while the methanol to oleic acid molar ratio 30:1, sulfuric acid concentration 6 wt% and residence time 10 minutes

The experimental results from Figure 4.1 found that at temperature about 60 to 80°C, the result observe small effect of temperature on oleic acid conversion. The conversion of oleic acid in this range is not significant changing when increase reaction temperature due to slow reaction rate at low reaction temperature.

At reaction temperature higher than 80°C, the result found that strong effect of oleic acid conversion changing when increase reaction temperature because of reaction rate increased when increase temperature.

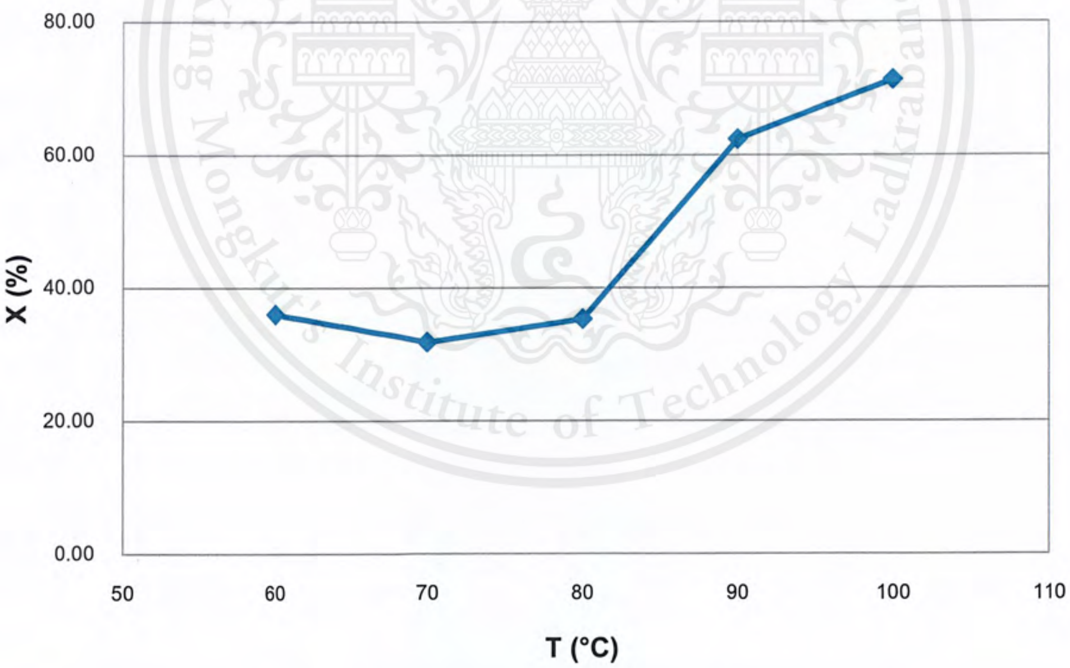

Figure 4.1 Effect of reaction temperature on oleic acid conversion at reaction condition: MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% and τ = 10 min

Increasing of reaction temperature influences on positive physical effect of physical properties such as increase miscibility and diffusion rate between methanol in aqueous phase and oleic acid in oil phase and reduce viscosity of soybean oil which these properties influences on increasing of mass transfer rate which is the reason that increase oleic acid conversion at high reaction temperature

4.2 Effect of Methanol to Oleic acid Molar ratio

The experimental results from Figure 4.2 show influences of methanol to oleic acid molar ratio in range of 10-50 while reaction temperature 80°C, H_2SO_4 concentration 6 wt% and residence time 10 minutes.

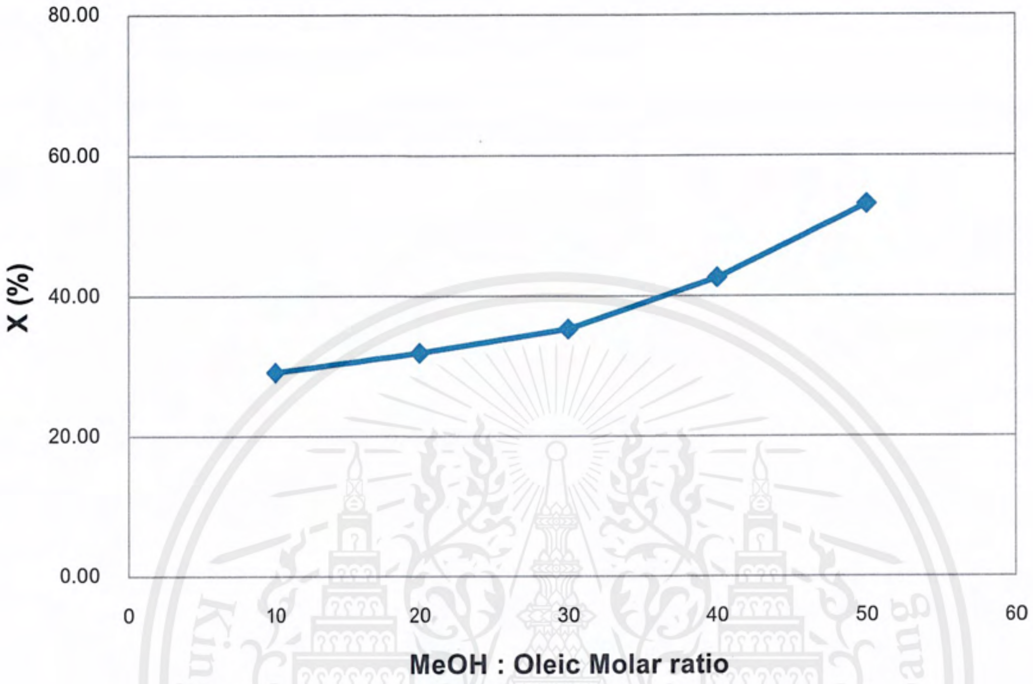

Figure 4.2 Effect of methanol to oleic acid molar ratio on oleic acid conversion at reaction condition: T = 80°C, H_2SO_4 = 6 wt% and τ = 10 min

The results found that oleic acid conversion increased when increase methanol to oleic acid molar ratio because of increased molar ratio will shift the reaction forward to product side and also enhanced interfacial area between methanol and oleic acid in soybean oil.

4.3 Effect of Catalyst Concentration

The effect of sulfuric acid was varied within the range of 2-10 wt% at reaction temperature 80°C, methanol to oleic acid conversion 30:1 and residence time 10 minutes. The result found that not significant of catalyst concentration on oleic acid conversion.

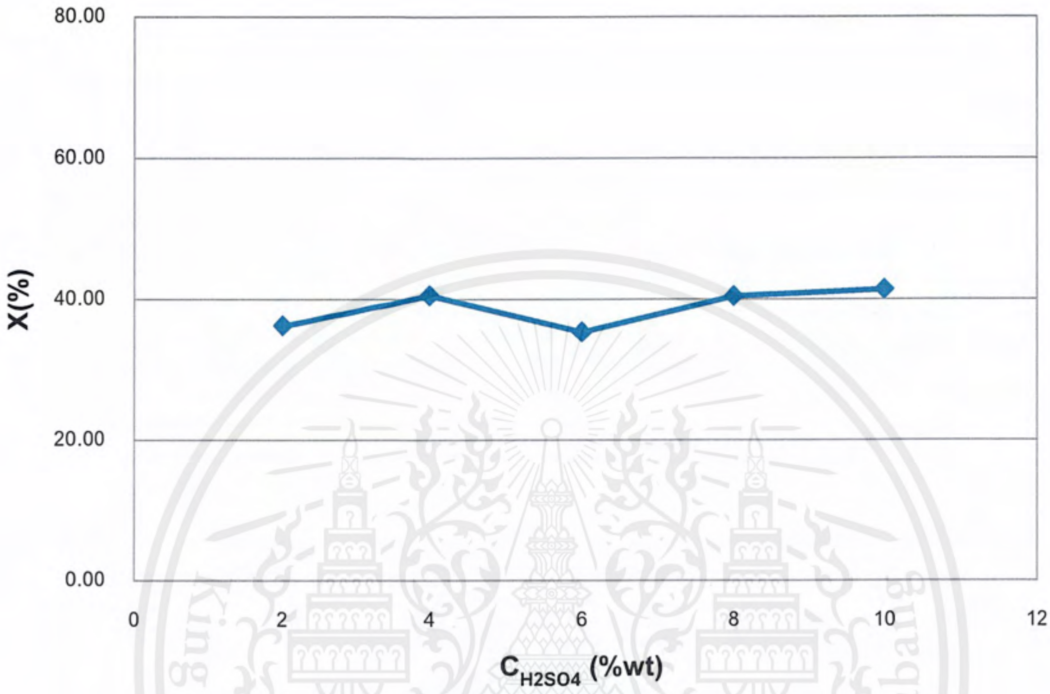

Figure 4.3 Effect of catalyst concentration on oleic acid conversion at reaction condition: T = 80°C, MeOH:Oleic = 30:1 and τ = 10 min

The results found that at catalyst concentration 2 wt% provide oleic acid conversion 36.7% while at catalyst concentration 10 wt%, the conversion small increase to 41.3%. The different of minimum oleic acid conversion and maximum oleic acid conversion is approximate 5%. From this reason, indicated that catalyst concentration is not significant effect on increasing of oleic acid conversion.

CHAPTER V
CONCLUSION

These works studied esterification reaction of oleic acid in soybean oil with methanol in a microreactor by using H_2SO_4 as a catalyst. Effect reaction temperature, methanol to oleic acid molar ratio and catalyst concentration was studied. The experimental results found that oleic acid conversion increased when increase reaction temperature and methanol to oleic acid molar ratio while catalyst concentration was not significant on oleic acid conversion. The highest oleic acid conversion from this work is approximate 71% at reaction temperature 100°C, methanol to oleic acid 30:1 and H_2SO_4 concentration 6 wt% of oleic acid

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APPENDIX

APPENDIX A
CALCULATION METHOD

A.1 Example of calculation the acid value of soybean oil

Acid value calculation of initial soybean oil and the sample at various conditions can be done by incorporating the substance into titrate with potassium hydroxide solution which known concentration.

For this calculation example, shows the method of calculating the acid value of the initial soybean oil and the sample from esterification reaction under conditions of molar ratio of oleic acid to methanol 1:30, react at 100 °C and use 6 %wt of catalyst.

1. Calculate the initial acid value of soybean oil

Initial soybean oil weight	1.00 g
Volume of KOH used for titrate with a sample	2.81 ml.
Concentration of KOH solution	0.1087 M

Calculate the acid value from equation (3.1)

$$AV_{in} = \frac{V \times C \times 56.1}{m} \quad (3\text{-}1)$$

$$AV_{in} = \frac{2.81 \times 0.1087 \times 56.1}{1.00} = 17.14 \text{ mg KOH/g Oil}$$

2. Calculate the final acid value of product samples

Product samples weight	1.00 g
Volume of KOH used for titrate with a sample	0.66 ml.
Concentration of KOH solution	0.1087 M

Calculate the acid value from equation (3.1)

$$AV_{out} = \frac{V \times C \times 56.1}{m} \quad (3\text{-}1)$$

$$AV_{out} = \frac{0.66 \times 0.1087 \times 56.1}{1.00} = 4.03 \text{ mg KOH/g Oil}$$

A.2 Example of calculation the conversion of oleic acid

Calculation of oleic acid conversion was done by using the initial acid value of the soybean oil and the final acid value of the reacted sample to substitute in equation (3-2).

$$X\,(\%) = \left(1 - \frac{AV_{out}}{AV_{in}}\right) \times 100 \qquad (3\text{-}2)$$

For this calculation example, shows the method of calculating the conversion of the initial soybean oil from esterification reaction under conditions of molar ratio of oleic acid to methanol 1:30, react at 100 °C and use 6 %wt of catalyst.

Soybean oil has an initial acid value	17.14 mg KOH / g Oil.
Product samples had a final acid value	4.03 mg KOH / g Oil.

The initial and final acid value in equation (3.2) is

$$X\,(\%) = \left(1 - \frac{4.03}{17.14}\right) \times 100$$
$$= 76.48\ \%$$

APPENDIX B
EXPERIMENTAL DATA

Table B.1 Oleic acid conversion at T = 60°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	12.64	0
0	8.73	30.96
40	8.34	34.02
80	8.34	34.02
120	8.73	30.89
160	8.26	34.65
200	8.26	34.67
240	8.38	33.71
280	8.22	34.96
320	8.38	33.71
360	8.34	34.02
Average conversion (%)		33.56

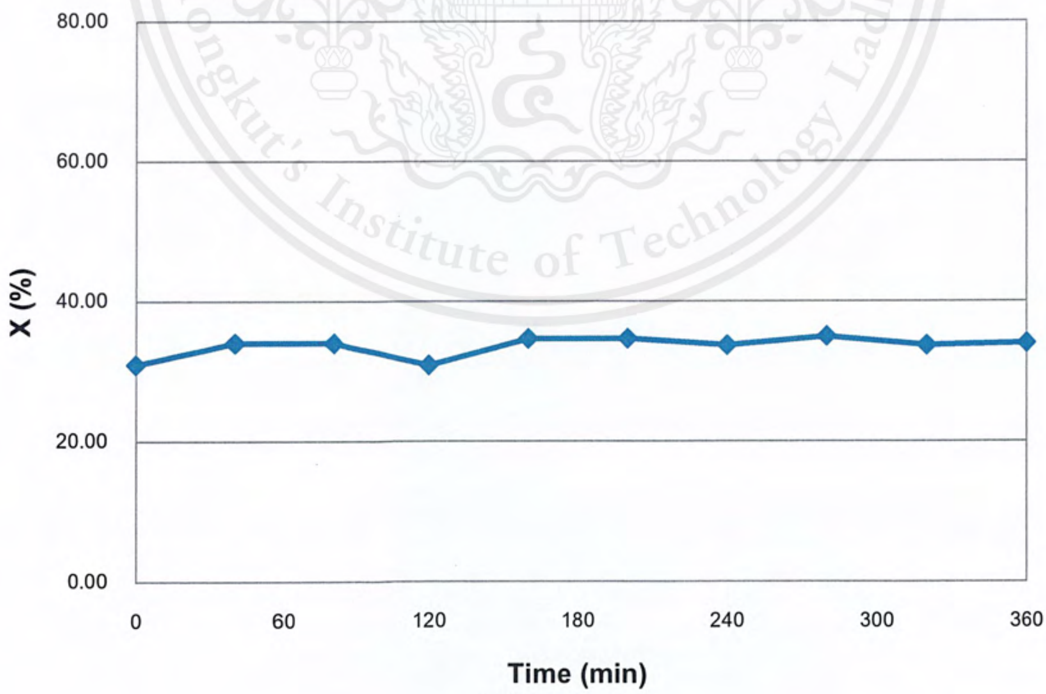

Figure B.1 Oleic acid conversion at T = 60°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.2 Oleic acid conversion at T = 60°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	13.01	0
0	9.09	33.40
40	8.53	38.17
80	8.32	40.01
120	8.40	39.26
160	8.40	39.27
200	8.27	40.37
240	8.53	38.18
280	8.14	41.48
320	8.66	37.07
360	8.53	38.17
Average conversion (%)		38.54

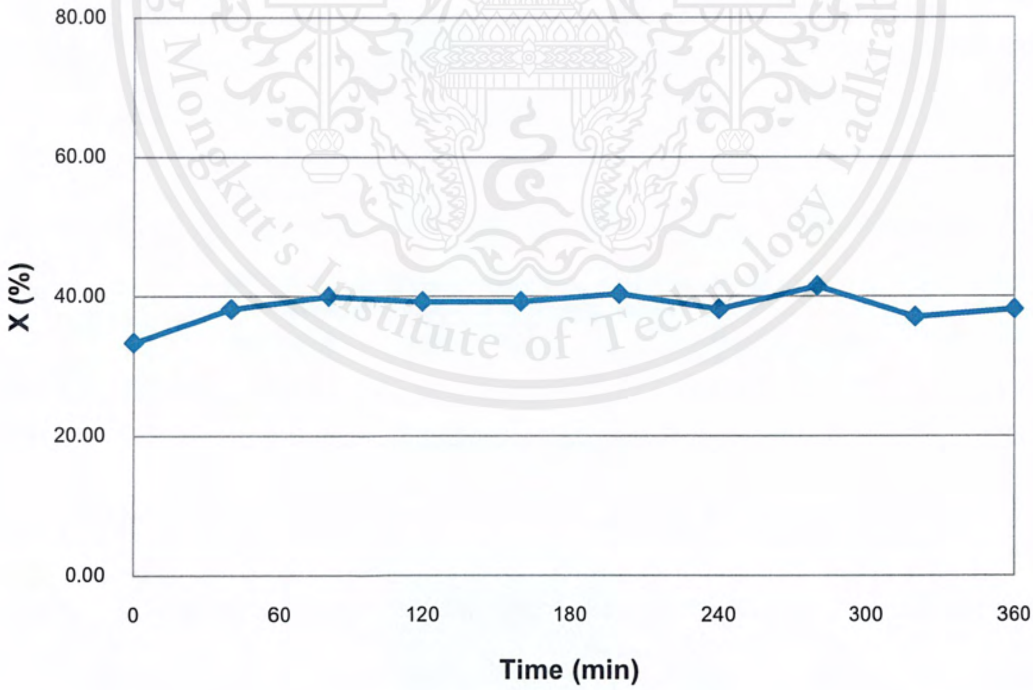

Figure B.2 Oleic acid conversion at T = 60°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.3 Oleic acid conversion at T = 70°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	17.81	0
0	12.32	30.84
40	12.56	29.47
80	12.32	30.84
120	11.72	34.24
160	11.90	33.22
200	12.02	32.55
240	12.50	29.81
280	11.95	31.53
320	11.89	32.89
360	11.89	33.24
Average conversion (%)		31.86

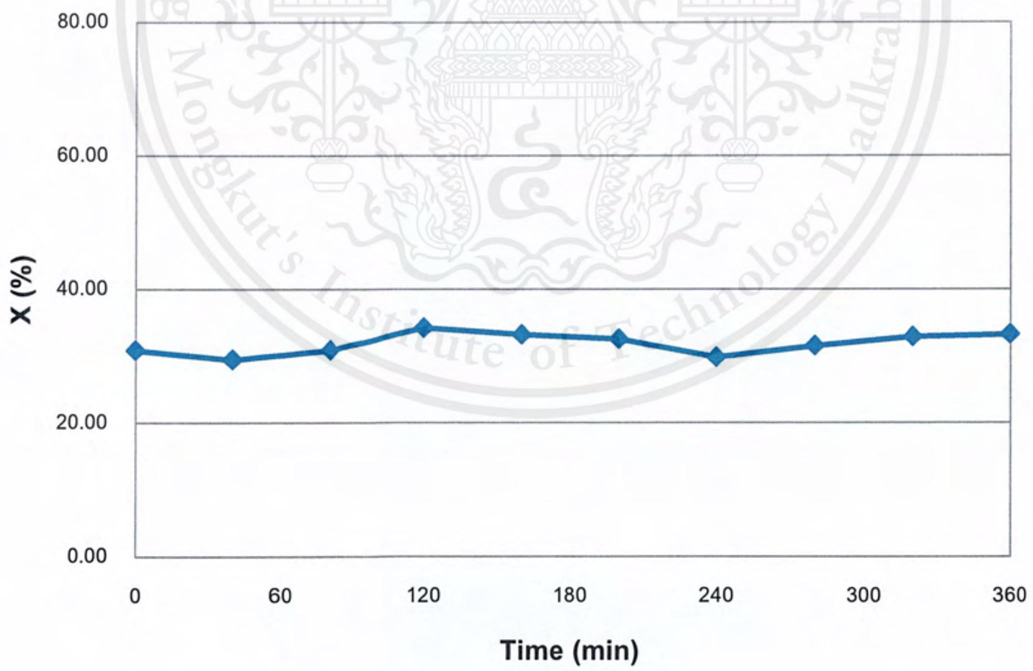

Figure B.3 Oleic acid conversion at T = 70°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.4 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	13.00	0
0	9.72	25.23
40	8.38	35.56
80	8.70	33.13
120	8.05	37.99
160	8.73	32.83
200	8.80	32.29
240	8.65	33.49
280	8.70	33.13
320	8.46	34.95
360	9.67	25.67
Average conversion (%)		32.43

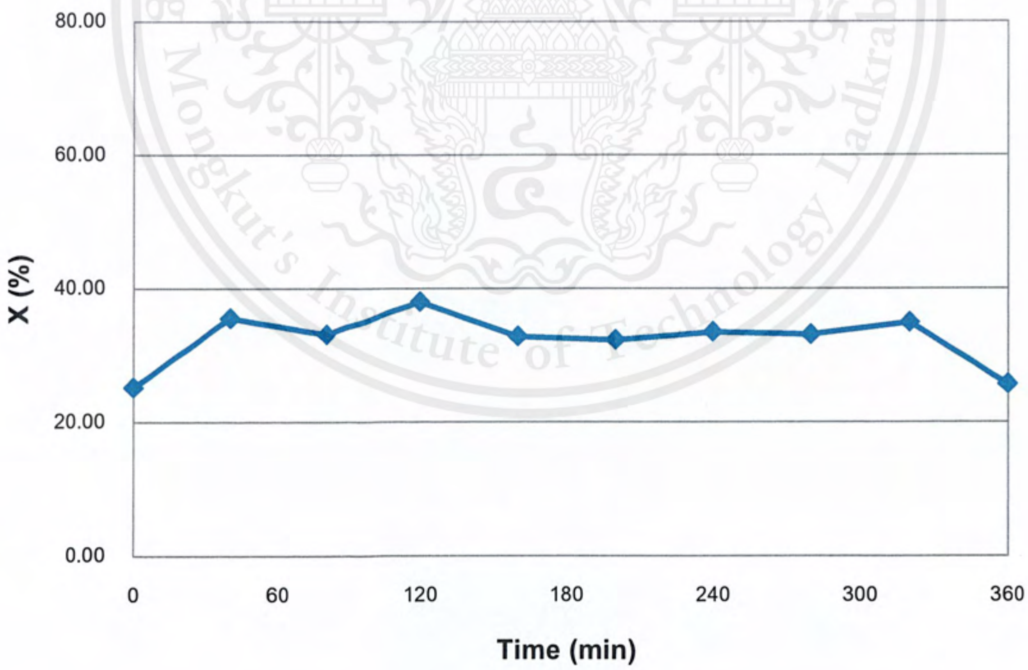

Figure B.4 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.5 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	11.74	0
0	7.15	39.06
40	7.83	33.33
80	7.71	34.33
120	7.71	34.34
160	7.11	39.39
200	7.23	38.38
240	7.31	37.71
280	6.97	40.66
320	6.88	41.41
360	6.60	43.77
Average conversion (%)		38.24

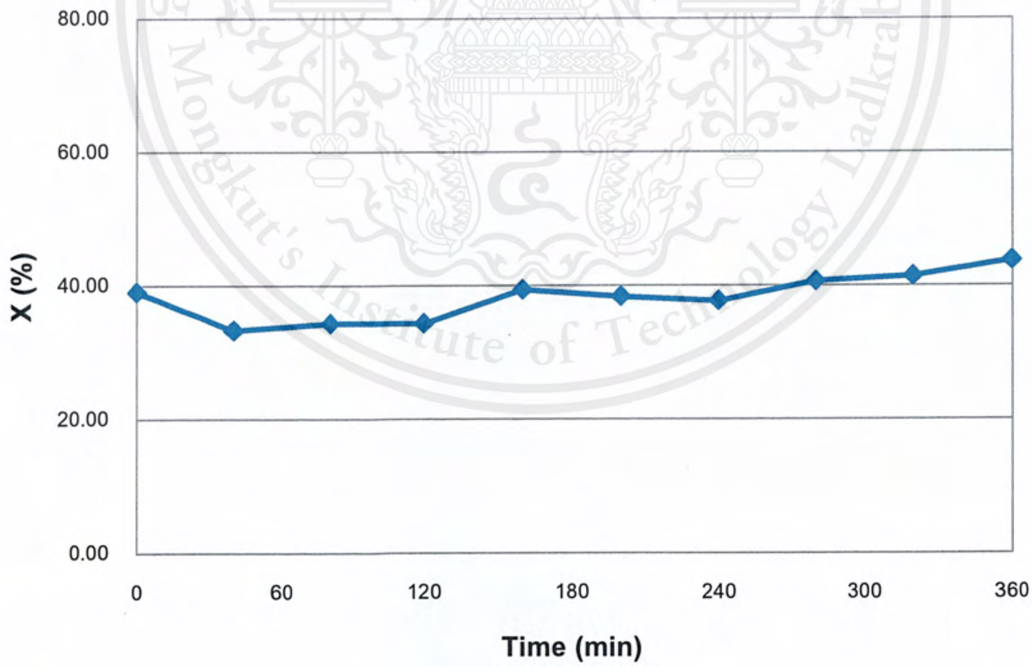

Figure B.5 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.6 Oleic acid conversion at T = 90°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	18.72	0
0	7.50	59.93
40	8.15	56.46
80	8.11	56.68
120	6.89	63.19
160	6.89	63.19
200	6.77	63.84
240	6.16	67.10
280	7.32	60.91
320	5.67	69.71
360	6.89	69.71
Average conversion (%)		62.42

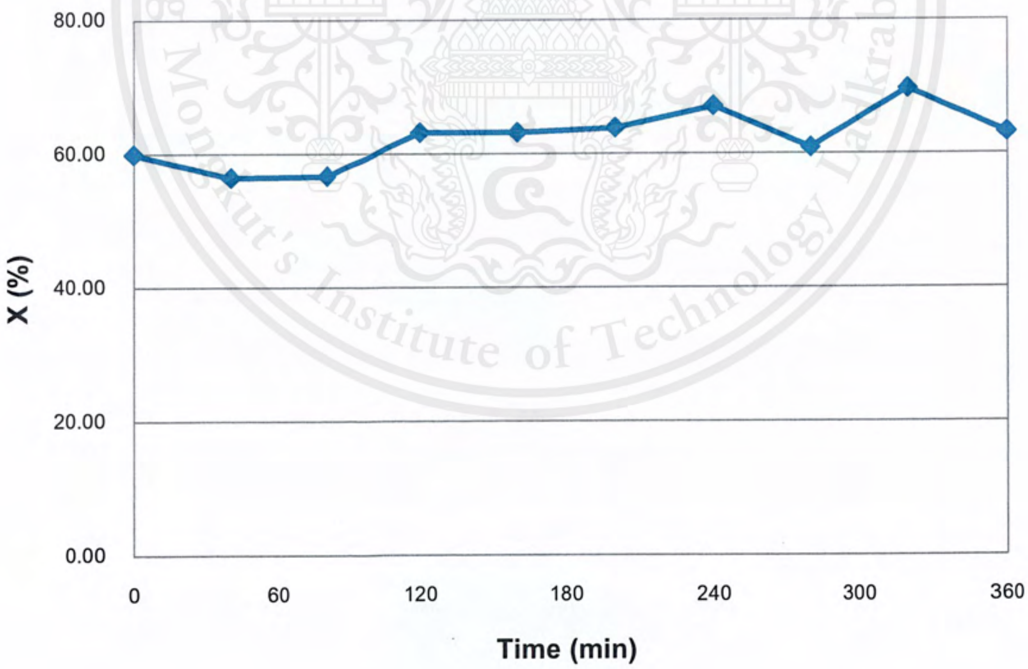

Figure B.6 Oleic acid conversion at T = 90°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.7 Oleic acid conversion at T = 100°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	17.14	0
0	7.61	55.60
40	5.43	68.33
80	5.18	69.75
120	4.64	72.95
160	4.27	75.09
200	4.39	74.38
240	4.35	74.63
280	4.45	74.02
320	4.71	72.52
360	4.03	76.51
Average conversion (%)		71.38

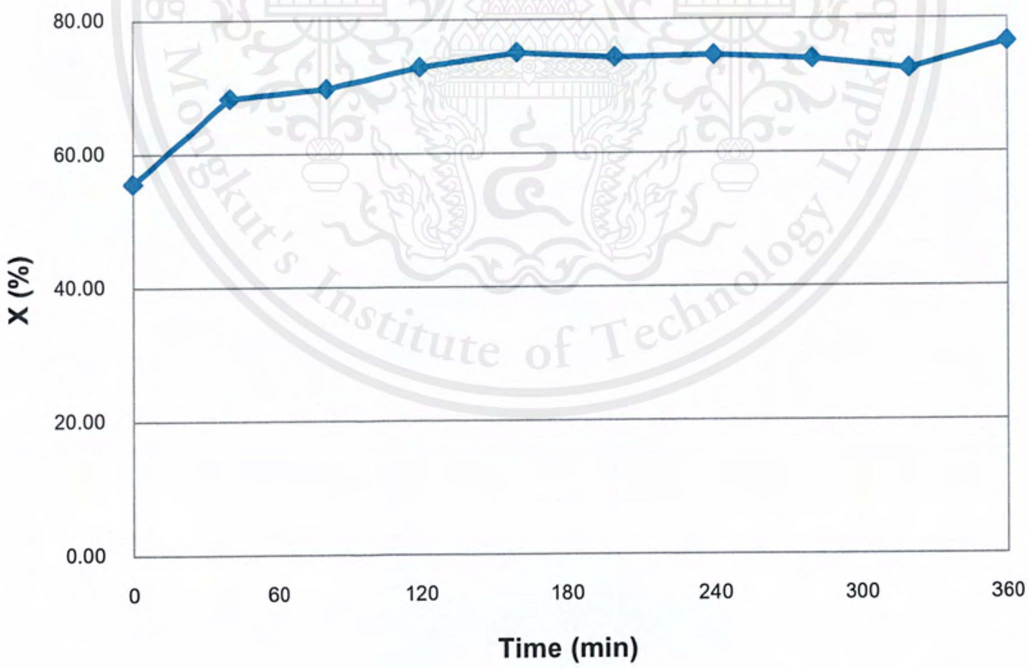

Figure B.7 Oleic acid conversion at T = 100°C, MeOH:Oleic = 30:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.8 Oleic acid conversion at T = 80°C, MeOH:Oleic = 10:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	15.98	0
0	13.51	14.72
40	10.74	31.29
80	10.84	30.67
120	10.58	32.23
160	10.63	31.90
200	10.89	30.37
240	10.83	30.71
280	10.99	29.75
320	10.94	30.06
360	10.99	29.75
Average conversion (%)		29.15

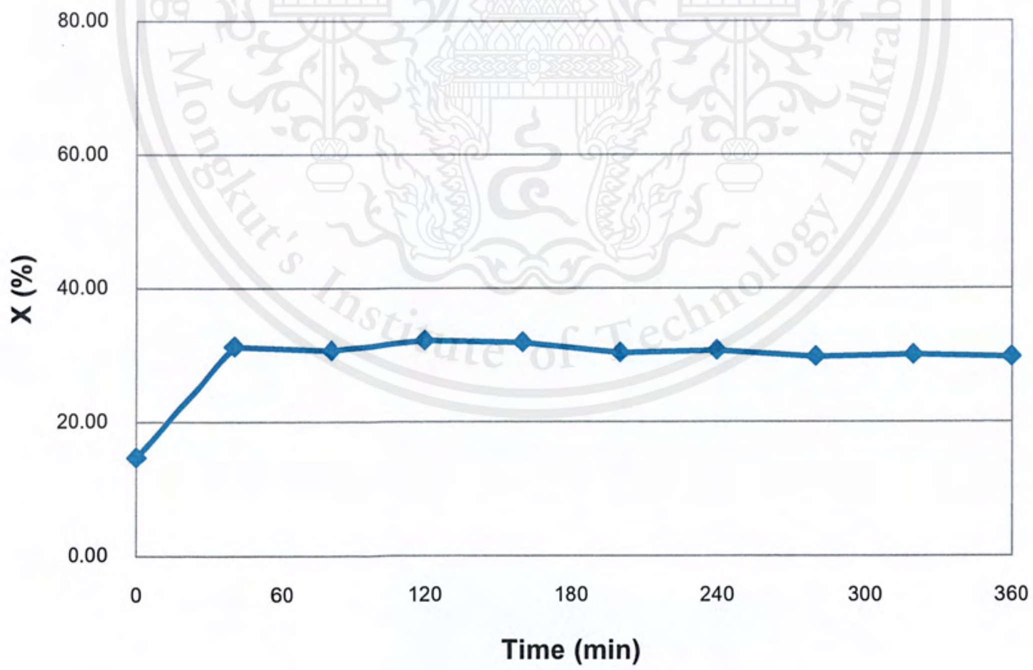

Figure B.8 Oleic acid conversion at T = 80°C, MeOH:Oleic = 10:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.9 Oleic acid conversion at T = 80°C, MeOH:Oleic = 20:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	16.75	0
0	11.20	33.13
40	11.25	32.82
80	11.51	31.29
120	11.34	32.27
160	11.20	33.13
200	11.40	31.90
240	11.50	31.36
280	11.61	30.67
320	11.44	31.66
360	11.51	31.29
Average conversion (%)		31.95

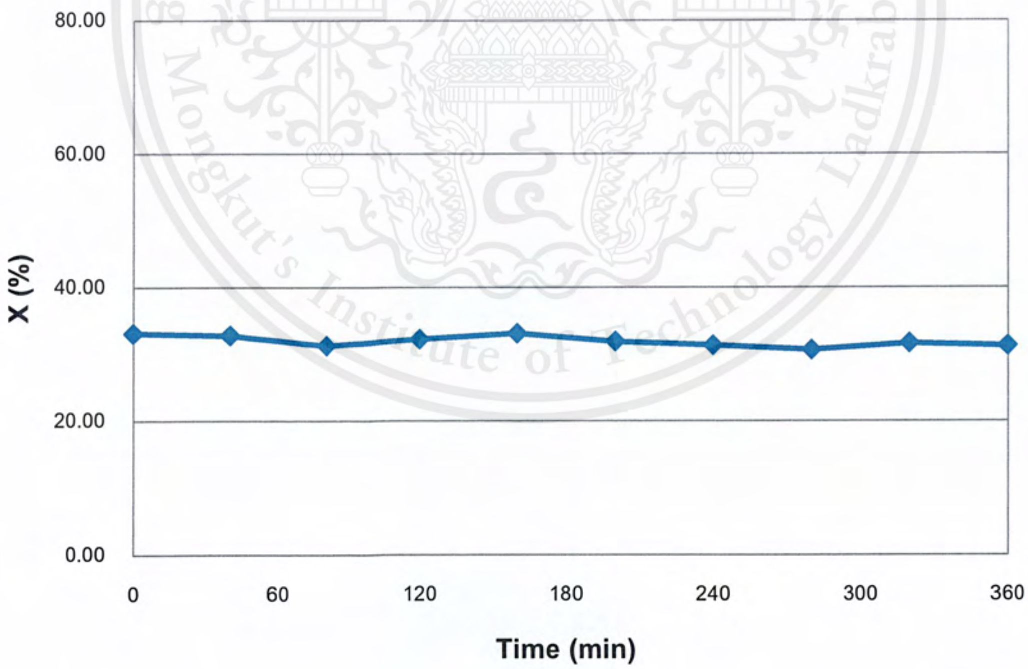

Figure B.9 Oleic acid conversion at T = 80°C, MeOH:Oleic = 20:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.10 Oleic acid conversion at T = 80°C, MeOH:Oleic = 40:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	15.57	0
0	7.70	50.55
40	8.61	44.69
80	8.27	46.89
120	8.84	43.22
160	8.92	42.70
200	8.90	42.86
240	9.64	38.10
280	9.58	38.46
320	9.41	39.56
360	9.47	39.19
Average conversion (%)		42.62

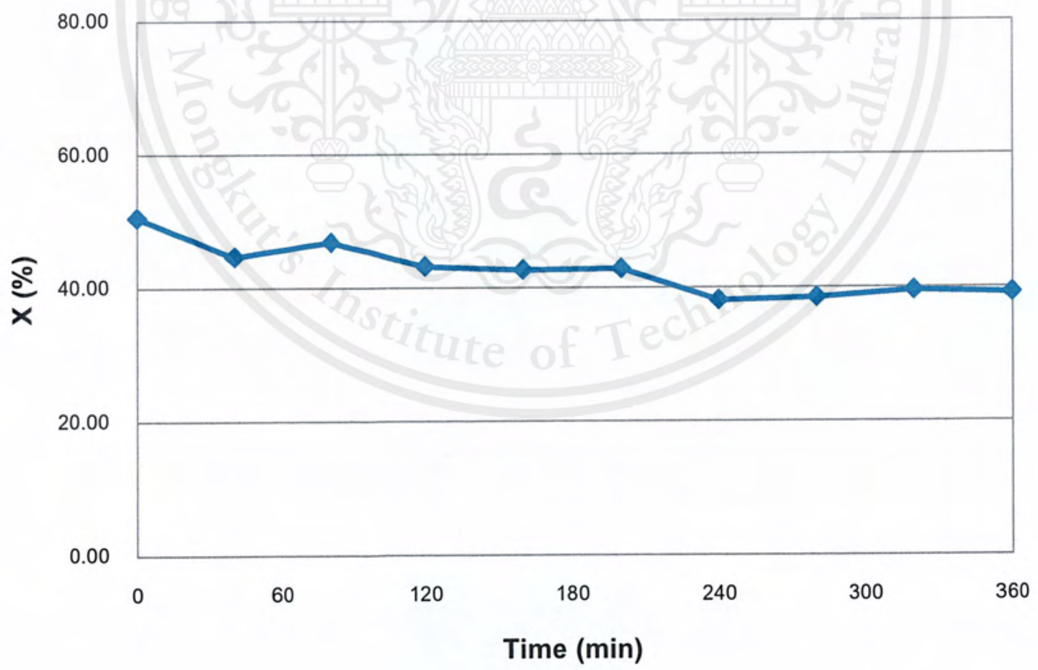

Figure B.10 Oleic acid conversion at T = 80°C, MeOH:Oleic = 40:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.11 Oleic acid conversion at T = 80°C, MeOH:Oleic = 50:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	21.74	0
0	-	-
40	13.60	37.44
80	9.18	57.78
120	9.42	56.67
160	9.36	56.94
200	10.00	53.99
240	10.43	52.03
280	10.43	52.03
320	9.64	55.67
360	9.70	55.39
Average conversion (%)		53.10

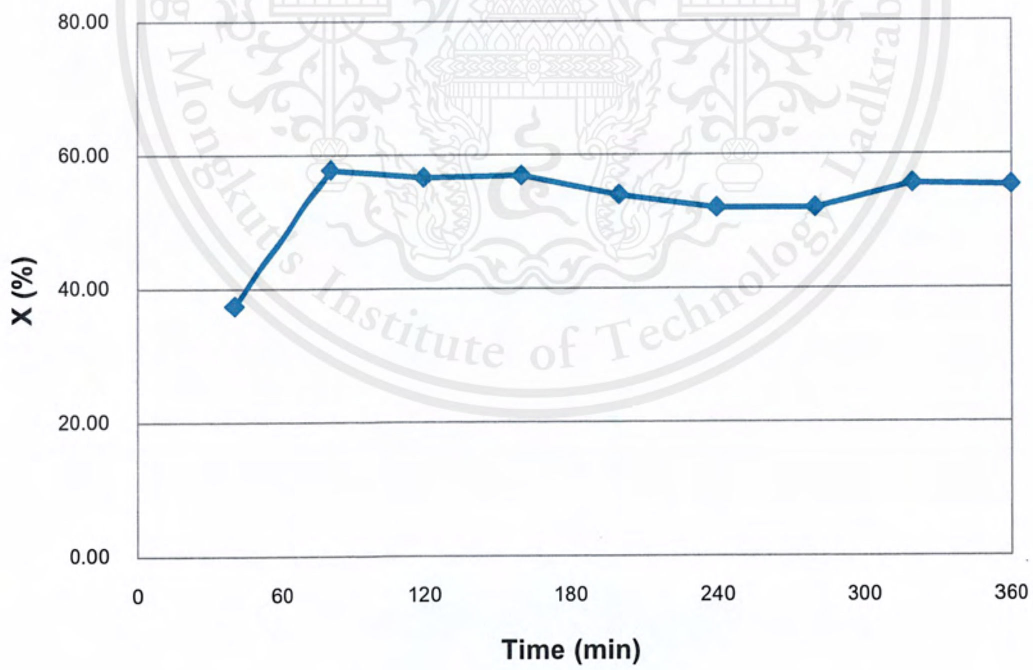

Figure B.11 Oleic acid conversion at T = 80°C, MeOH:Oleic = 50:1, H_2SO_4 = 6 wt% of oleic acid and τ = 10 min

Table B.12 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 2 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	14.69	0
0	9.50	35.31
40	9.09	38.11
80	9.35	36.36
120	9.04	38.46
160	9.56	34.97
200	9.20	37.41
240	9.26	36.99
280	9.50	35.31
320	10.07	31.47
360	9.14	37.76
Average conversion (%)		36.22

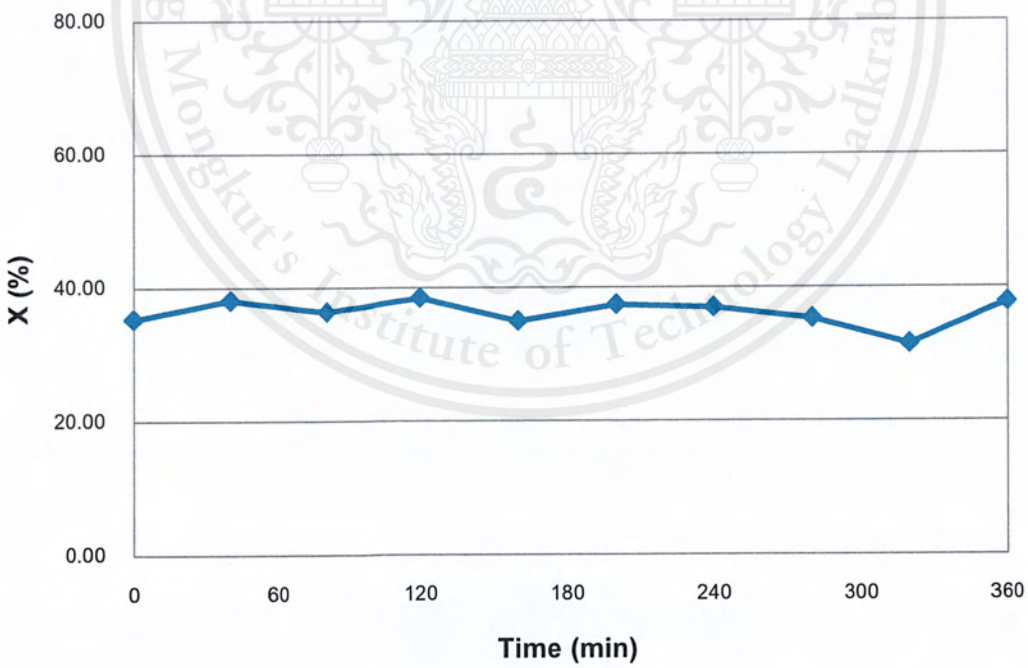

Figure B.12 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 2 wt% of oleic acid and τ = 10 min

Table B.13 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 4 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	14.14	0
0	8.19	42.09
40	8.63	41.26
80	-	-
120	8.58	41.61
160	8.48	42.31
200	8.94	39.16
240	9.09	38.11
280	8.68	40.91
320	8.94	39.16
360	8.80	40.11
Average conversion (%)		40.52

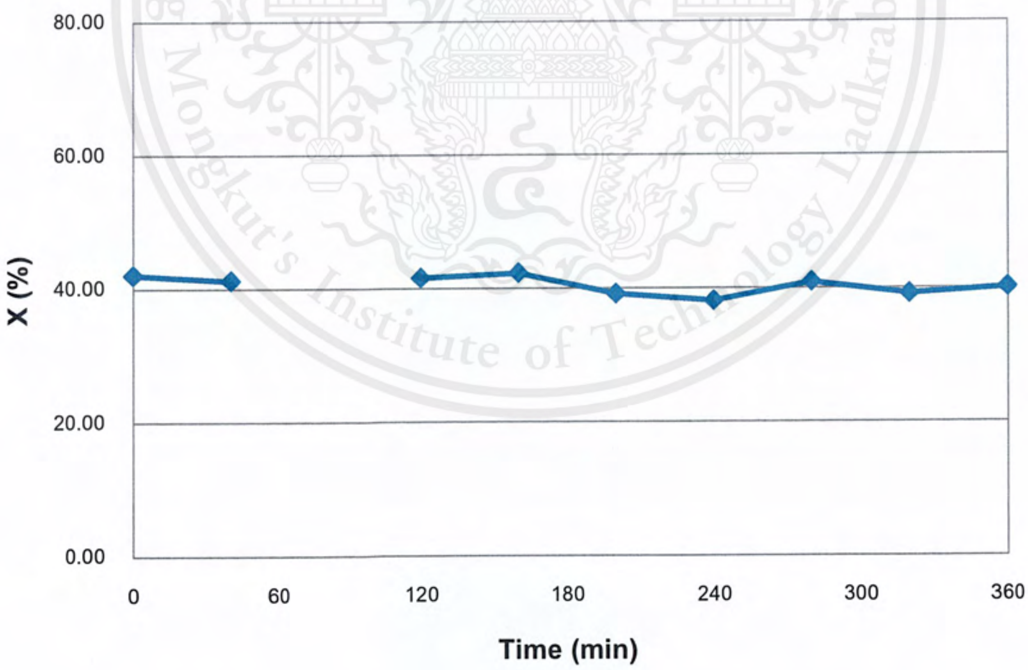

Figure B.13 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 4 wt% of oleic acid and τ = 10 min

Table B.14 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 8 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	15.36	0
0	9.30	39.46
40	9.30	39.46
80	9.25	39.80
120	9.25	39.80
160	8.84	42.47
200	8.94	41.81
240	9.25	39.80
280	9.09	40.80
320	9.14	40.47
360	9.14	40.47
Average conversion (%)		40.43

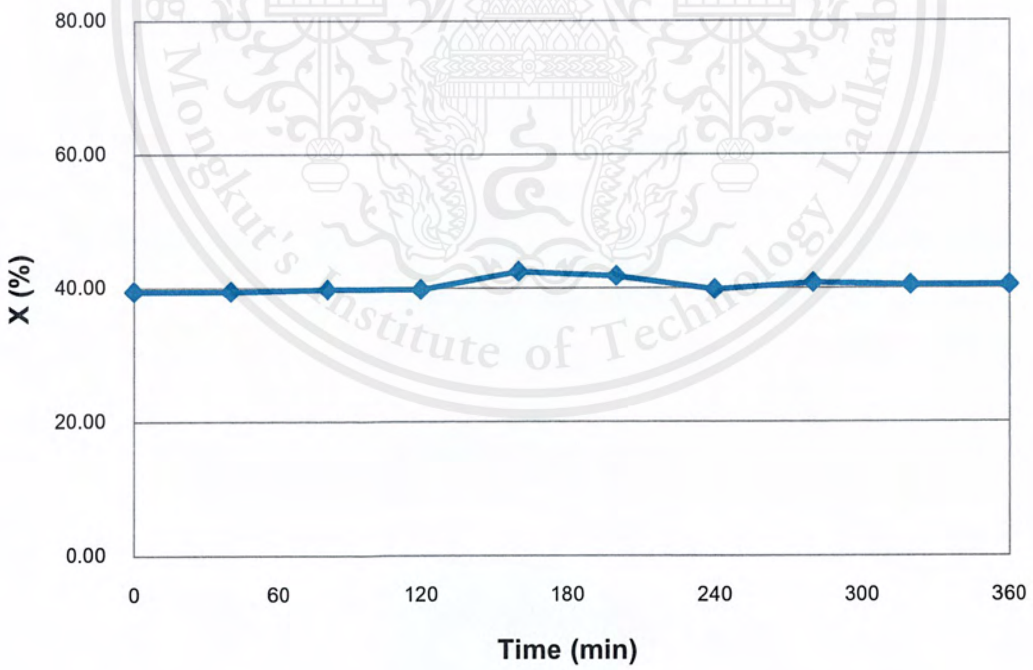

Figure B.14 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 8 wt% of oleic acid and τ = 10 min

Table B.15 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 10 wt% of oleic acid and τ = 10 min

Reaction time (min)	Acid value (mg KOH/ g Oil)	Oleic acid Conversion (%)
Initial	15.26	0
0	9.40	38.38
40	9.76	36.03
80	9.20	39.73
120	9.20	39.73
160	8.60	43.66
200	8.89	41.75
240	8.70	42.99
280	8.73	42.76
320	8.63	43.43
360	8.32	45.45
Average conversion (%)		41.39

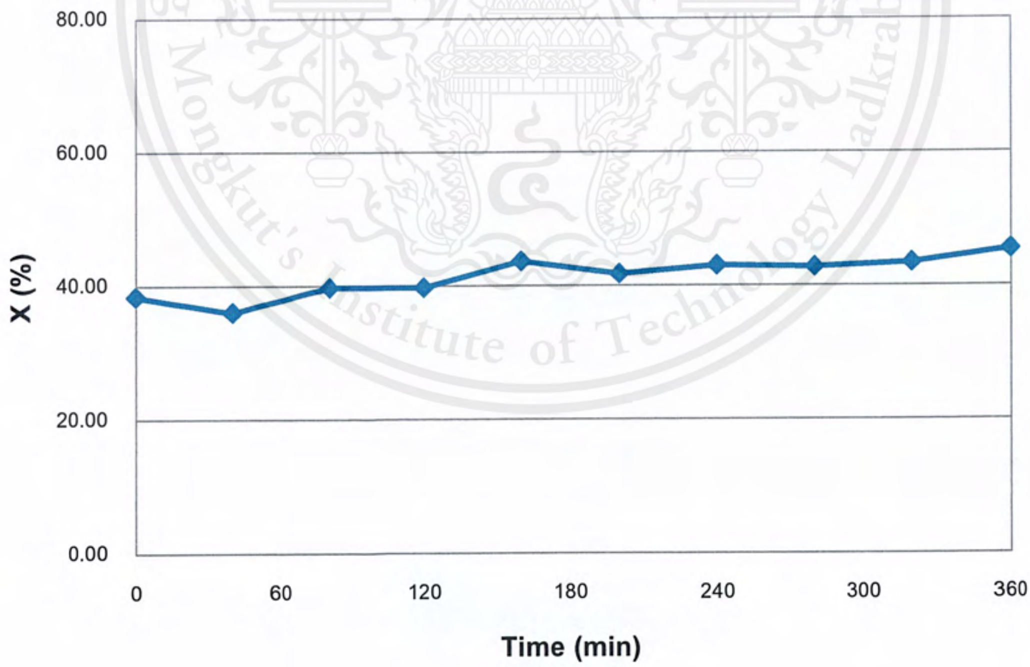

Figure B.15 Oleic acid conversion at T = 80°C, MeOH:Oleic = 30:1, H_2SO_4 = 10 wt% of oleic acid and τ = 10 min

Table B.16 Experimental results show effect of reaction temperature on oleic acid conversion

Molar ratio of oleic acid to methanol	Sulfuric acid concentration (%wt)	Residence time (min)	Reaction temperature (°C)	Average conversion (%)
1:30	6	10	60	36.05
			70	31.86
			80	35.33
			90	62.42
			100	71.38

Table B.17 Experimental results show effect of methanol to oleic acid on oleic acid conversion

Molar ratio of oleic acid to methanol	Sulfuric acid concentration (%wt)	Residence time (min)	Reaction temperature (°C)	Average conversion (%)
1:10	6	10	80	29.15
1:20				31.95
1:30				35.33
1:40				42.62
1:50				53.10

Table B.18 Experimental results show effect of catalyst concentration on oleic acid conversion

Molar ratio of oleic acid to methanol	Sulfuric acid concentration (%wt)	Residence time (min)	Reaction temperature (°C)	Average conversion (%)
1:30	2	10	80	36.22
	4			40.52
	6			35.33
	8			40.43
	10			41.39

BIOGRAHPY

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