

**REACTION KINETICS OF THE CATALYTIC ESTERIFICATION OF  
OLEIC ACID WITH METHANOL**

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## ABSTRACT

Biodiesel is now considered as an alternative to liquid fuel from petroleum. The production of biodiesel from vegetable oils has been widely researched; however, it is not an economical process because of using valuable vegetable oils. Therefore, waste vegetable oil or animal fat are recommended as raw materials to produce biodiesel. However, the presence of moisture and free fatty acids (FFAs) in these materials may influence the performance and efficiency of such a process. Both water and FFAs can react with the catalyst rapidly and form long chain soaps, which may bring on serious separation problems; an esterification pretreatment step is generally required to decrease the FFAs amount to below 1 wt%. Therefore, the reaction kinetics of the reversible esterification reaction of oleic acid with methanol to methyl oleate is studied. The reaction was carried out in a 3-necked round bottom flask heated by a rotamantle which is the isothermal reactions are catalyzed by amberlyst ion exchange resin. Temperature was varied from 45-60°C, molar ratio of methanol to oleic acid was varied from 4:1, 8:1, 12:1, 16:1 and catalyst loading was varied from 3g to 12g. The sample was withdrawn at certain time interval and it was analyzed using titration method. The conversion of oleic acid was increased when the parameters such as temperature, catalyst loading and molar ratio of methanol/acid was increased. The catalyst has exhibited maximum conversion (75.4wt.%) under the conditions of 55 °C, methanol/oleic acid molar ratio of 16:1 and catalyst amount 12g. The experimental data is well fitted to the Pseudo-homogeneous model. This optimum operating condition and the kinetic model is useful for the designing the reactor size and pretreatment process for transesterification of triglycerides into esters.

## ABSTRAK

Biodiesel dianggap sebagai alternative untuk bahan bakar cair dari petroleum. Pengeluaran biodiesel dari minyak sayur telah banyak dikaji, tetapi bukan merupakan proses ekonomi kerana menggunakan minyak sayur yang berharga. Oleh kerana itu, sisa sayuran minyak atau lemak haiwan yang disyorkan sebagai bahan mentah untuk menghasilkan biodiesel. Namun, kewujudan air dan asid lemak bebas (FFA) dalam bahan mentah boleh menjejaskan prestasi dan kecekapan proses. Air dan asid lemak bebas boleh bertindak balas dengan mangkin untuk menghasilkan sabun dalam bentuk rantai panjang yang boleh membawa masalah pemisahan serius. Sebab itu, langkah-langkah pengesteran sebagai rawatan proses diwajibkan untuk mengurangkan jumlah asid lemak bebas dibawah 1% dalam peratusan berat. Oleh kerana itu, reaksi pengesteran asid oleic dengan methanol untuk menghasilkan metal oleic dipelajari. Reaksi dilakukan dalam satu tabung dan dipanaskan oleh rotamantle yang merupakan reaksi isothermal dikatalisis oleh amberlyst. Suhu bervariasi dari 45 ke 60°C, nisbah molar methanol kepada asid oleic divariasikan dari 4:1, 8:1, 12:1, 16:1 dan mangkin divariasikan dari 3g ke 12g. Sampel diambil pada selang masa yang tertentu dan dianalisis dengan kaedah titrasi. Penukaran asid oleic meningkat ketika parameter seperti suhu, kuantiti pemangkin dan nisbah molar methanol kepada asid meningkat. Penukaran maksimum (75.4% dalam peratusan berat) berlaku di bawah keadaan 55°C, methanol/asid oleic dalam nisbah 16:1 dan jumlah mangkin 12g. Data eksperimental juga dapat dimuatkan dalam model Pseudohomogeneous. Keadaan operasi optimum dan model kinetik dapat membantu dalam pembinaan saiz reactor dan proses rawatan untuk pengtransesteran trigliserida kepada ester.

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	<b>ACKNOWLEDGEMENTS</b>	i
	<b>ABSTRACT</b>	ii
	<b>ABSTRAK</b>	iii
	<b>TABLE OF CONTENTS</b>	iv-v
	<b>LIST OF TABLES</b>	vi
	<b>LIST OF FIGURES</b>	vii
	<b>LIST OF ABBREVIATION</b>	viii
	<b>LIST OF SYMBOL</b>	ix
<b>1</b>	<b>INTRODUCTION</b>	1-3
	1.1 Properties of ester	4
	1.2 Esterification	5
	1.2.1 Homogeneous catalyst for esterification	6
	1.2.2 Heterogeneous catalyst for esterification	6
	1.3 Reaction kinetics	7
	1.4 Identification of problems	8
	1.5 Objectives	8
	1.6 Scopes of the research	9
	1.7 Rationale and Significance	9
<b>2</b>	<b>LITERATURE REVIEW</b>	10-12
	2.1 Esterification	13-15
	2.2 Heterogeneous catalysis	16-17
	2.3 Homogeneous catalysis	18-19
	2.4 Biocatalyst	20
	2.5 Kinetic models	21-23

2.6	Effect of different parameters on esterification	
2.6.1	Effect of reaction temperature	24-25
2.6.2	Effect of methanol to acid ratio	26-27
2.6.3	Effect of catalyst loading	28-29
2.6.4	Other important parameters that affecting reaction	30-31
<b>3</b>	<b>METHODOLOGY</b>	<b>32</b>
3.1	Introduction	32
3.2	Materials and Equipments	32-33
3.3	Experimental procedure	34
3.3.1	Preparation of phenolphthalein indicator	34
3.3.2	Preparation of aqueous potassium hydroxide	34
3.3.3	Activity studies	34-35
3.3.3.1	The activity studies with different Manipulated variable	36-37
3.3.4	Titration analysis	
<b>4</b>	<b>RESULTS AND DISCUSSION</b>	<b>38</b>
4.1	Catalytic activity experimental studies	38
4.1.1	Effect of temperature	38-39
4.1.2	Effect of catalyst amount	39-40
4.1.3	Effect of molar ratio of alcohol to oleic acid	40-41
4.2	Kinetics of esterification	41-49
<b>5</b>	<b>CONCLUSIONS AND RECOMMENDATION</b>	<b>50</b>
5.1	Conclusions	50-51
5.2	Recommendation	51
	<b>LITERATURE CITED</b>	<b>52-56</b>
	<b>APPENDIX</b>	<b>57-73</b>

**LIST OF TABLE**

<b>TABLES NO</b>	<b>TITLE</b>	<b>PAGE</b>
TABLE 1.1	Fatty acid composition of vegetable oil samples	2
TABLE 1.2	Properties of ester	4
TABLE 1.3	Method to produce ester	5
TABLE 2.1	A survey on the homogeneously esterification	14
TABLE 2.2	A survey on the heterogeneously esterification	15
TABLE 2.3	A survey on the mechanism and kinetic reaction	23
TABLE 3.1	Function of materials	32
TABLE 3.2	The function of each component in the experiment setup	33
TABLE 3.3	Runs for experiment	36
TABLE 4.1	Regression data	44
TABLE 4.2	Data to plot $\ln k$ VS $1/T$	45

**LIST OF FIGURES**

<b>FIGURES NO</b>	<b>TITLE</b>	<b>PAGE</b>
Figure 2.1	A schematic diagram of a continuous unit for Biodiesel production from PFAD	11
Figure 2.2	Process flow diagram of a two steps biodiesel Production	12
Figure 3.1	The esterification reaction system	35
Figure 4.1	Influence of reaction temperature on the conversion	39
Figure 4.2	Influence of catalyst amount on the conversion	40
Figure 4.3	Influence of methanol/acid molar ratio on the conversion	41
Figure 4.4	Effect of temperature	42
Figure 4.5	Plot of $\ln k$ Vs $1/T$	46
Figure 4.6	Concentration of oil (CA) Vs Reaction time at $T=318.15$ K	48
Figure 4.7	Concentration of oil (CA) Vs Reaction time at $T=323.15$ K	48
Figure 4.8	Concentration of oil (CA) Vs Reaction time at $T=328.15$ K	49

**LIST OF ABBREVIATIONS**

FAME	-	Fatty Acid Methyl Ester
FAEE	-	Fatty Acid Ethyl Ester
FFA	-	Free Fatty Acid
DNA	-	Deoxyribonucleic Acid
PFAD	-	Palm Fatty Acid Distillate
CSTR	-	Continuous Stirred Tank Reactor
RPM	-	Round Per Minute
WZ	-	Tungstated Zirconia



**LIST OF SYMBOL**

$-r_A$	-	The consumption of reactant A per unit time
$k'$	-	Rate constant
$C_A$	-	Concentration of A after time t
$C_B$	-	Concentration of B after time t
$\alpha$	-	Reaction order of reactant A
$\beta$	-	Reaction order of reactant B
$C_{AO}$	-	Initial concentration of A
$C_{BO}$	-	Initial concentration of B
$X$	-	Conversion
$\theta_B$	-	Ratio of $C_{BO}$ to $C_{AO}$
$A$	-	Pre-exponential factor
$E$	-	Activation energy
$R$	-	Gas constant
$T$	-	Absolute temperature

## CHAPTER 1

### INTRODUCTION

One of the main topics in the framework of a “sustainable development” is organic acid esters. It produced by the reaction of organic acids and alcohols. It is an alternative way to handle the fuel disaster because the organic acid esters can replace the petroleum –based solvents and it is biorenewable.

The most attractive biofuel is represented by biodiesel, which is constituted by a mixture of fatty acids methylesters (FAME) or ethylesters (FAEE), produced by a transesterification reaction performed on high-quality vegetable oils with methanol or ethanol. This transesterification process is affected by several factors such as catalyst concentration, reactant molar ratio, and water and free fatty acids content in the raw materials. The catalysts that are more widely used, and which are the most effective in this step of the process, are sodium and potassium hydroxide. The acid catalysts, such as sulfuric or hydrochloric acid, have also been proven as effective in this reaction.[Chongkhong et al. ,2007]

Fats and oils are primarily water-insoluble hydrophobic substances of plant and animal origin and are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides. Fatty acids vary in carbon chain length and in the number of unsaturated bonds. Natural vegetable oils and animal fats

are solvent extracted or mechanically pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Even refined oils and fats contain small amounts of free fatty acids and water. The free fatty acid and water contents have significant effects on the transesterification of glycerides with alcohols using alkaline or acid catalysts. They also interfere with the separation of fatty acid alkyl esters and glycerol because of salt formation in the product. Table 1.1 shows the Fatty acid compositions of vegetable oil.

**Table 1.1: Fatty acid compositions of vegetable oil samples (Gunstone, 2007)**

<b>Vegetable oil</b>	<b>Palmitic acid</b>	<b>Stearic acid</b>	<b>Oleic acid</b>	<b>Linoleic acid</b>	<b>Linolenic acid</b>	<b>Other</b>
Sunflower oil	7.0	3.5	33.5	55	0	1.0
Rapeseed	4	2	56	26	10	2
Soybean oil	11	4	33	53	8	2
Palm oil	44	4	40	10	0	2

Despite the fact that alkaline catalysis is characterized by a higher reaction rate with respect to an acid-catalyzed reaction, some drawbacks must be accounted for in this case where presence of moisture and free acidity that strongly influences the process performance and economics. In fact, both water and free fatty acids (FFAs) rapidly react with the catalyst, consuming it and giving way to longchain soaps for which do not allow an efficient separation of the pure glycerol in the final step of the process. In the case of an oil with a high content of free fatty acids (FFAs), like usually happens in waste materials, a pretreatment esterification step must be considered in order to eliminate the free acidity that must be reduced below 1 wt %. On the other hand, the opportunity to employ low-quality or waste raw materials, as a starting point in the biodiesel production cycle, is an essential aspect for decreasing the production costs and making this alternative fuel competitive with traditional fossils fuels. On the basis of these considerations, the improvement of the esterification step could represent one of the key points through which the whole process can result in being economically convenient.[Tesser et al. ,2005]

## 1.1 Properties of ester

Esters are ubiquitous. Many naturally occurring fats and oils are the fatty acid esters of glycerol. Esters with low molecular weight are commonly used as fragrances and found in essential oils and pheromones. Phosphoesters form the backbone of DNA molecules. Nitrate esters, such as nitroglycerin, are known for their explosive properties, while polyesters are important plastics, with monomers linked by ester moieties. Table 1.2 shows the properties of esters.

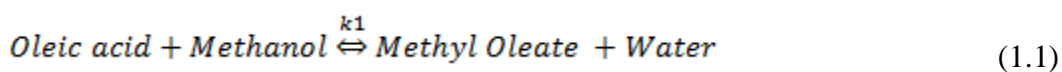
**Table 1.2: Properties of Esters**

Ester	Methyl Oleate	Ethyl Oleate	Methyl Palmitate	Methyl Stearate
Appearance	Colorless to pale yellow clear	Colorless to pale yellow clear	White solid	White solid
Specific Gravity	0.876 to 0.882	0.868 to 0.873	-	0.847 to 0.853
Melting point	-2.0 to -1.0 °C	-32.00 °C	32.00 to 35.00 °C	37.00 to 41.00 °C
Boiling point	351.00 to 353.00 °C	205.00 to 208.00 °C	185.00 °C	181 to 182 °C
Flash point	>110.00 °C	91.67 °C	>110.00 °C	>110.00 °C

## 1.2 Esterification

Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product. Vigorous reaction of an acyl chloride with alcohol, a vigorous at room temperature could produce ester and clouds of steamy acidic fumes of hydrogen chloride. Other than that, reaction between acid anhydride with alcohol can form ester. Esters are common in organic chemistry and biological materials, and often have a characteristic pleasant, fruity odor. This leads to their extensive use in the fragrance and flavor industry. The most common esterification processes involve nucleophilic acyl substitution where the carbonyl compound is used as an electrophile and is attacked by a nucleophilic alcohol. Table 1.3 shows the different methods of producing ester.

Oleic acid ( $C_{18}H_{34}O_2$ ) can be esterified with alcohols like methanol ( $CH_3OH$ ) to produce methyl oleate ( $C_{19}H_{36}O_2$ ).



**Table 1.3: Method to produce ester**

METHOD	EQUATION
Carboxylic Acid	$\text{Carboxylic acid} + \text{alcohol} \xrightleftharpoons{k_1} \text{ester} + \text{Water}$
Acyl Chlorides	$\text{Acyl Chloride} + \text{alcohol} \xrightleftharpoons{k_1} \text{ester} + \text{HCl}$
Acid Anhydrides	$\text{Acid Anhydrides} + \text{alcohol} \xrightleftharpoons{k_1} \text{ester} + \text{Acid}$

$k_1$  = rate of equilibrium

### **1.2.1 Homogeneous catalyst for esterification**

Homogeneous catalyst is the catalyst in the same phase as the reactants. Typically everything will present as a gas or contain in a single liquid phase. The example of the homogeneous catalyst are enzymes, sulfuric acid, dimethylaminopyridine and nitric oxide.[Sepulveda et al. ,2005] If the homogeneous catalyst is used, there are many shortcomings like intermediate product removal, mechanical separation of catalyst from reaction media and corrosion problems.

### **1.2.2 Heterogeneous catalyst for esterification**

Heterogeneous a catalyst in a different phase from the reactants . Typical examples involve a solid catalyst with the reactants as either liquids or gases. The example of the heterogeneous catalyst are ammonia, Amberlyst-15 ion exchange resin and tungstated zirconia(WZ).[Sanz et al. ,2002] The advantages of using heterogeneous catalyst is easy separation, efficient recycling, minimization of metal leaching, improved handling and process control, low production cost even higher selectivity than homogeneous ones in some cases.

### **1.3 Reaction kinetics**

Reaction kinetics is the study of rates of chemical reactions. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products. When performing catalytic cracking of heavy hydrocarbons into gasoline and light gas, for example, kinetic models can be used to find the temperature and pressure at which the highest yield of heavy hydrocarbons into gasoline will occur.



## 1.4 Identification of problems

The advantages of heterogeneous catalyst is easy separation and improved handling and process control. The kinetic models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products meanwhile useful in pretreatment of transesterification process.

At present, there is a lack in the information of describing kinetics of heterogeneously catalysed oleic acid esterification with methanol .Therefore, isothermal experimental batch studies on the esterification of oleic acid with methanol in the presence of amberlyst ion exchange resin as catalyst is carried out to develop the kinetic model.

## 1.5 Objectives

Considering the intricacies associated with the homogeneously catalyzed esterification process, the overall goal of this study is to design and develop a heterogeneously catalyzed chemical process to produce methyl oleate in an efficient manner.

The aims of this study are:

1. To determine the rate law for the esterification of oleic acid and methanol
2. To determine the optimum operation conditions for the esterification of oleic acid and methanol

## 1.6 Scopes of the research

In the present study, several important parameters have been investigated.

These parameters are ratio of alcohol to acid, temperature, and amount of catalyst used. The detail of the scope is as below:

- (i) To study the effect of molar ratio of oleic acid with methanol
- (ii) To study the effect of catalyst loading
- (iii) To study the effect of reaction temperature

## 1.7 Rationale and Significance

**Rationale.** The objective of the present studies is to perform the esterification of oleic acid with methanol using heterogeneous catalysis and assisted by heating.

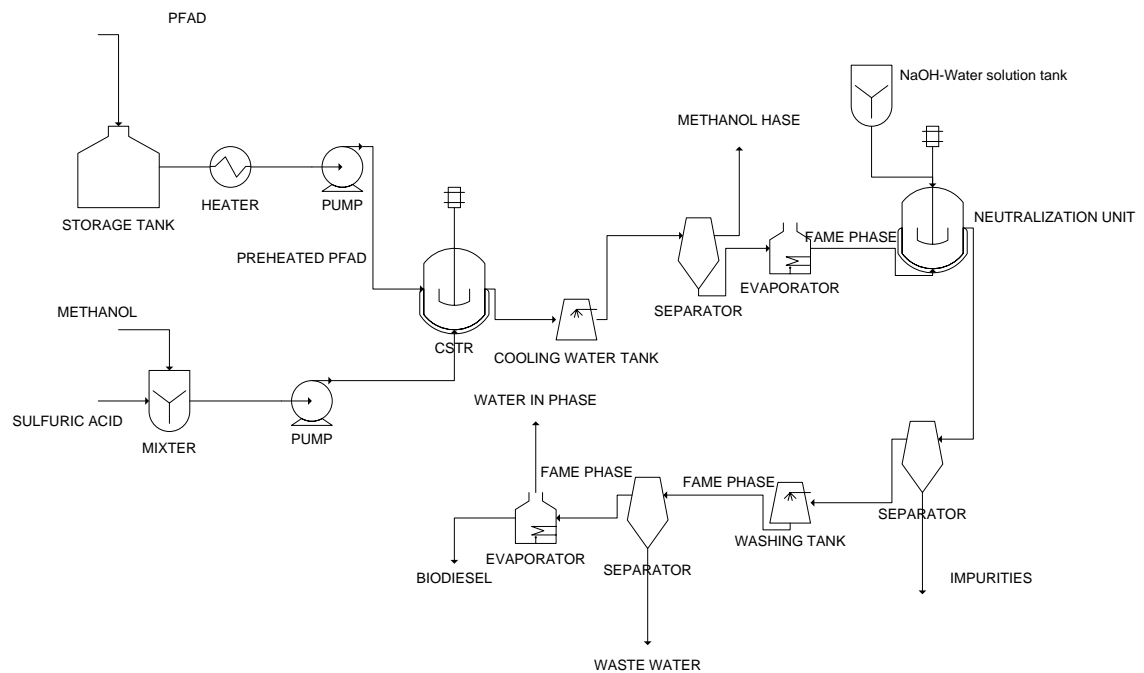
**Significance.** Methyl oleate used as a plasticizer and softener and the present research is trying to develop a rate law which could help us to design an intensified process such as reactive distillation column. The heterogeneously catalysed intensified process could reduce the production cost and environmental problems. Besides that, present research is useful in the pretreatment process for biodiesel production.

## CHAPTER 2

### LITERATURE REVIEW

**Esterification.** The continuous esterification for biodiesel production from palm fatty acid distillate (PFAD) was investigated. The continuous experiments contain two processes: (1) an esterification process, which is carried out in a continuous stirred tank reactor (CSTR) and (2) a purification process, where fatty acid methyl esters (FAME) was purified to meet the standard requirements for biodiesel fuel. A schematic diagram of the continuous experiments is shown in Fig 2.1. The reaction operating parameters were set to a 8.8:1 molar ratio of methanol to PFAD, a 0.05:1 molar ratio of sulfuric acid ( $H_2SO_4$ ) to PFAD, a reaction temperature of 75 °C under its own pressure (about 133 KPa) for residence time of 60 min. Fresh methanol (2.3 kg/h), recycled methanol (6.5 kg/h) and  $H_2SO_4$  (0.16 kg/h) were mixed first and pumped into a 22.4 L (Liters) CSTR. PFAD was fed into the CSTR after being heated to 75 °C. The mixture was mixed at a constant stirring rate of 400 rpm(round per min). After that, the product mixture overflowed to the cooling water tank before entering a 30 L separator. The esterified products were allowed to settle into two phases. The top phase, consisting of un-reacted methanol together with water formed during the reaction, was then overflowed at the top of the 30 L separator. The methanol phase was purified by distillation and then recycled. The FAME phase underflowed at the bottom pipe line of the separator. The FAME phase was passed into the evaporator to recover traces of methanol and further treated in

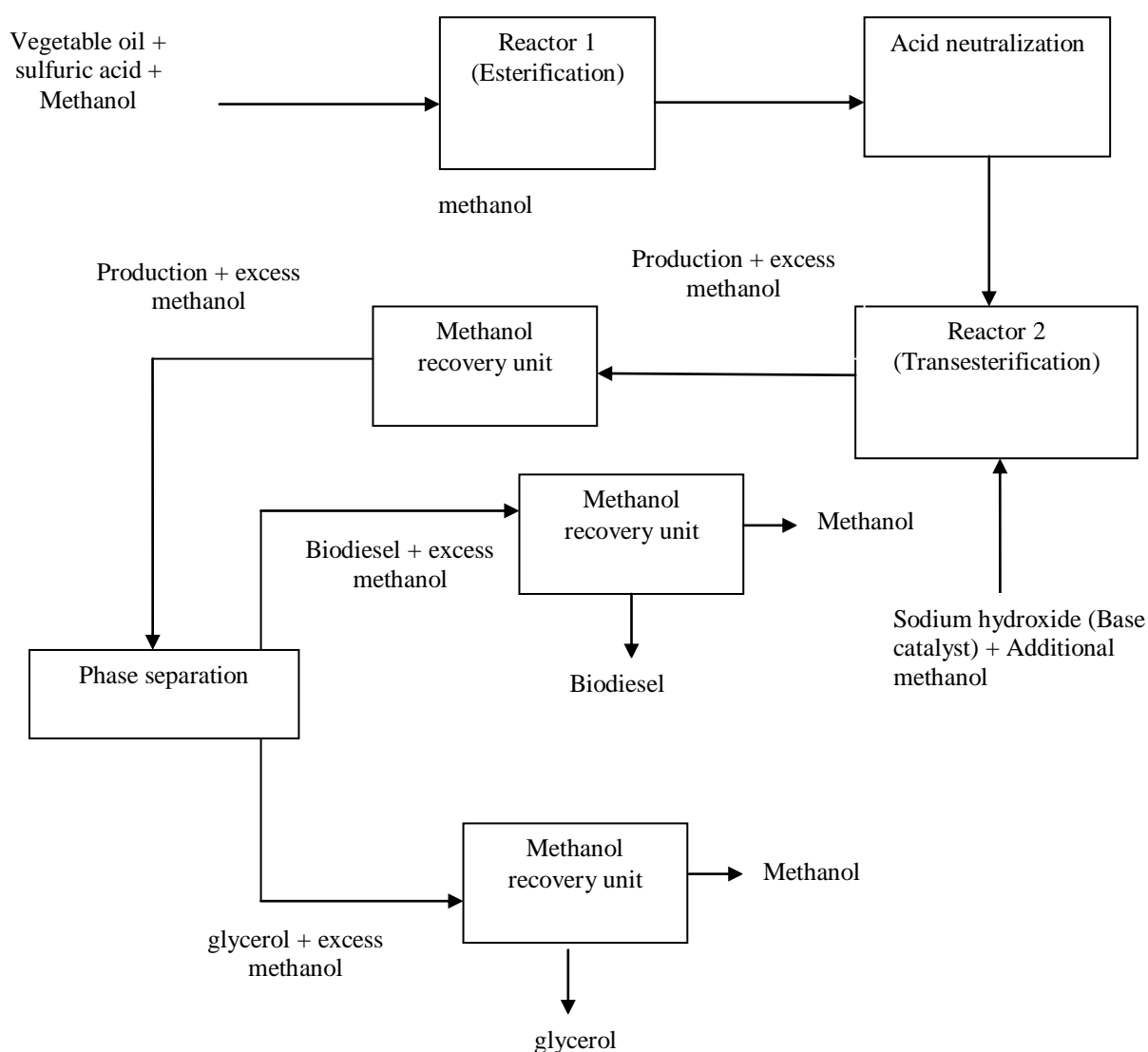
the purification unit. To meet biodiesel specifications, the FAME phase having a residual free fatty acid (FFA) of about 1.4%wt was neutralized with 10.24%wt of 3 M (molarity) NaOH–H<sub>2</sub>O (sodium hydroxide-water) solution. The NaOH– H<sub>2</sub>O solution (0.8 kg/h) and the FAME phase (8.3 kg/h) were preheated to 80 °C before entering a 4.2 L CSTR. The mixture was mixed at a 500 rpm stirring rate with a reaction temperature of 80 °C for 20 min. After that, the neutralized products settled into two phases in a 12.6 L separator. The FAME product overflowed at the top of the separator and the soap phase was removed at the bottom. The FAME product was passed into a 20 L water washing tank with a water feed rate of 10 L/h and then overflowed into a 20 L separator for water separation. Finally, the biodiesel product was heated by an evaporator to remove the residual water in the product.[Chongkhong et al. ,2009]



**Figure 2.1: A schematic diagram of a continuous unit for biodiesel production from PFAD**

**Pretreatment (esterification) process in biodiesel production.** One limitation to the alkali-catalyzed process is its sensitivity to the purity of reactants. The alkali-catalyzed system is very sensitive to both water and free fatty acids. The presence of water may cause ester saponification under alkaline conditions. The free fatty acids can react with an alkali catalyst to produce soaps and water.

Saponification not only consumes the alkali catalyst, but also the resulting soaps can cause the formation of emulsions. Emulsion formation creates difficulties in downstream recovery and purification of the biodiesel. Thus, dehydrated vegetable oil with less than 0.5 wt.% free fatty acids, an anhydrous alkali catalyst and anhydrous alcohol are necessary for commercially viable alkali-catalyzed systems. Therefore, a pretreatment step to reduce the free fatty acid content via an esterification reaction with methanol in the presence of sulfuric acid catalyst. After such a treatment, the oil phase, having a low level of free fatty acids (less than 0.5 wt.%), was subjected to the alkali-catalyzed transesterification. [Zhang et al. ,2003]



**Figure 2.2: Process flow diagram of a two steps biodiesel production**

## 2.1 Esterification

The heterogeneous esterification of oleic acid in subcritical methanol was investigated. The reactions were performed in the autoclave equipped with an electromagnetic beater. The tests were conducted under 160 -220°C and 3-10MPa. The effect of temperature, pressure, molar ratio of methanol with oleic acid from 1 to 10 and reaction time on the esterification was examined.[Song et al. ,2010]

Biodiesel production by homogeneous esterification with methanol using a water adsorption apparatus has been carried out. The study was carried out above the boiling points of methanol and water to evaporate the water produced during the reaction. A condenser placed above the adsorption column was responsible for condensing the water and methanol vapor, returning water-free methanol to the reactor after passing through the adsorption column. The adsorption system was employed to remove the water produced during the reaction to shift the equilibrium toward fatty acid methyl ester production. The effect of catalyst loading, reaction temperature and molar ratio of methanol with oleic acid was evaluated.[ Lucena et al. ,2008]

The heterogeneous esterification kinetics of lactic acid with methanol and catalyzed by ion-exchange resins has been carried out. The effect of catalyst type, stirrer speed, catalyst size, catalyst loading, initial reactant ratio, and temperature on reaction kinetics was evaluated. Reaction kinetics were studied in a four-necked jacketed reactor of 500 mL capacity operating in batch mode. A reflux condenser avoided loss of volatile compounds. The temperature inside the reactor was controlled within  $\pm 0.5$  K. The ion-exchange resin was suspended in the reaction mixture by magnetic stirring.[Sanz et al. ,2002]

Table 2.1 and 2.2 shows the summary of homogeneously and heterogeneously esterification.

**Table 2.1: A survey on the homogeneously esterification**

No.	Acid	Alcohol	Catalyst	Equipment	Reference
1.	Oleic Acid	Isobutyl Alcohol	Sulfuric acid	Flask	[Ling et al. ,1957]
2.	Oleic Acid	Methanol	Sulfuric acid	Round bottom flask	[Lucena et al. ,2008]
3.	Oleic Acid + Sunflower Oil	Methanol	Sulfuric acid	Jacketed reactor	[Marchetti et al. ,2008]
4.	Acetic acid	Butanol	Tungstophosphoric acid	Round bottom flask	[Sepulveda et al. ,2005]
5.	Acetic Acid	Methanol	Hydrogen Iodide	Batch reactor	[Ronback et al. ,1997]

**Table 2.2: A survey on the heterogeneously esterification.**

No.	Acid	Alcohol	Catalyst	Equipment	Reference
1.	Salicylic Acid	Methanol	cation exchange resin, Dowex 50-W (X-8)	Three-necked round- bottomed flask	[Bochner et al. ,1965]
2.	Oleic Acid	Methanol	cation exchange resins, K2411 and K148	Sapphire reactor	[Vieville et al. ,1993]
3.	Oleic Acid	Methanol	Acid ion-exchange polymeric resin (Relite CFS)	Batch stainless steel reactor	[Tesser et al. ,2005]
4.	Lauric Acid	methanol	tungstated zirconia (WZ)	Well-stirred semibatch reactor	[Suwannakarn et al. ,2009]
5.	Oleic Acid	Methanol	zinc acetate	Batch-type autoclave	[Song et al. ,2010]



## 2.2 Heterogeneous catalysis

Suwannakarn et al.(2009) studied the use of a three-phase reaction for the simultaneous esterification of free fatty acid and transesterification of triglycerides using model mixtures of triglycerides and free fatty acid. Transesterification with methanol was carried out using a commercial tungstated zirconia (WZ) solid catalyst. Esterification occurred 4 times faster than transesterification. Under our reaction conditions and in the presence of the catalyst, byproduct water was produced not only from lauric acid esterification but also from methanol dehydration. Because of the presence of this water, triglycerides were converted into the ester product by two routes: direct triglycerides transesterification and triglycerides hydrolysis followed by esterification. The tungstated zirconia catalyst used was able to completely remove lauric acid from reaction mixtures with up to 5 wt % FFA at the reaction conditions employed.

The esterification of oleic acid in subcritical methanol catalyzed by zinc acetate was investigated. The results shown zinc acetate was catalytically active for the esterification of oleic acid. Because all the components were dissolved in the subcritical methanol, the esterification was promoted under subcritical conditions. The oleic acid conversion increased with the molar ratio of methanol to oleic acid; when the molar ratio exceeds 8, oleic acid in the autoclave was almost completely converted to methyl oleate in 30 min. A high molar ratio of methanol to oleic acid is beneficial to the esterification. At 220°C, the conversion of oleic acid was higher than 80.0% after 20 min reaction and approaches 95.0% after 60 min. The condition was near the critical point of methanol and oleic acid was dissolved well in the subcritical methanol. Whereas at 160 °C, only an oleic acid conversion of 60.0% was achieved, because the oleic acid cannot dissolved well in methanol at this condition. The oleic acid conversion reached 95.0% under 220 °C and 6.0 MPa with the molar ratio of methanol to oleic acid being 4 and 1.0 wt% zinc acetate as catalyst.[Song et al. ,2010]

An experimental study was carried out to evaluate the performance of a cation exchange resin(Dowex 50-W) in the acid form as a catalyst for the esterification of salicylic acid with methanol. Rates of conversion were found to be

insensitive to catalyst particle size in the range studied. Inspection of the graph from the study reveals that the effect of preaddition of methyl salicylate is negligible. However, an increase in initial water concentration markedly decreased the rate of formation of methyl salicylate. [Bochner et al. ,1965]