

ผลของฟองแก๊สไนโตรเจนต่อทรานส์เอสเทอร์ิฟิเคชันของน้ำมันพืชในเครื่องปฏิกรณ์แบบเบดนิ่ง

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EFFECT OF N₂ BUBBLES ON TRANSESTERIFICATION OF VEGETABLE OIL
IN A FIXED BED REACTOR

Mr. Itsarapap Saneevong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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อิทธิพลของ ฟองแก๊สไนโตรเจนต่อทรานส์เอสเทอร์ฟิเคชันของน้ำมันพืชในเครื่องปฏิกรณ์แบบเบดนิ่ง. (EFFECT OF N₂ BUBBLES ON TRANSESTERIFICATION OF VEGETABLE OIL IN A FIXED BED REACTOR)

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งานวิจัยนี้ศึกษาผลของฟองแก๊สไนโตรเจนที่มีต่อปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันของน้ำมันปาล์มในเครื่องปฏิกรณ์แบบเบดนิ่ง โดยใช้โดไลไมต์ซึ่งเป็นหินธรรมชาติเป็นตัวเร่งปฏิกิริยา ตัวเร่งปฏิกิริยาเตรียมด้วยวิธีกวนผสม (physical mixing) และขึ้นรูปตัวเร่งปฏิกิริยาให้มีขนาด 2 x 5 มิลลิเมตร ตัวเร่งปฏิกิริยาจะถูกเผาที่อุณหภูมิ 800 องศาเซลเซียสเป็นเวลา 6 ชั่วโมงก่อนนำไปใช้ในปฏิกิริยาทรานส์เอสเทอร์ฟิเคชัน ในระบบที่ไม่มีการป้อนแก๊สไนโตรเจน ทำการศึกษาผลของชนิดของน้ำมันปาล์ม ผลของอัตราส่วนโดยโมลของเมทานอลต่อน้ำมัน ผลของขนาดตัวเร่งปฏิกิริยาและผลของการเติมเมทิลเอสเทอร์ที่มีต่อปฏิกิริยาทรานส์เอสเทอร์ฟิเคชัน ส่วนในระบบที่มีการป้อนแก๊สไนโตรเจนทำการศึกษาภาวะที่เหมาะสมในการทำปฏิกิริยา โดยได้ร้อยละผลได้ของเมทิลเอสเทอร์เท่ากับ 96.7 ภายใต้ภาวะการทำปฏิกิริยาที่เหมาะสมคือ อุณหภูมิในการทำปฏิกิริยาเท่ากับ 60 องศาเซลเซียส อัตราการป้อนแก๊สไนโตรเจน เท่ากับ 30 มิลลิลิตรต่อนาที อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันเท่ากับ 30 ต่อ 1 และอัตราการป้อนสารตั้งต้นรวมเท่ากับ 2.5 มิลลิลิตรต่อนาที และเมื่อทำการเปรียบเทียบเสถียรภาพของการเร่งปฏิกิริยากับระบบที่ไม่มีการป้อนแก๊สไนโตรเจน พบการลดลงของร้อยละผลได้ของเมทิลเอสเทอร์ในระบบที่ไม่มีการป้อนแก๊สไนโตรเจน ซึ่งเกิดจากการที่มีอนุพันธ์ของกลีเซอไรด์เกาะอยู่ที่ผิวของตัวเร่งปฏิกิริยาและทำให้เกิดการเสื่อมสภาพของตัวเร่งปฏิกิริยา ส่วนร้อยละผลได้ของเมทิลเอสเทอร์ในระบบที่มีการป้อนแก๊สไนโตรเจนค่อนข้างคงที่ตลอด 18 ชั่วโมงของการทำปฏิกิริยา ซึ่งการป้อนแก๊สไนโตรเจนน่าจะมีผลทำให้เกิดการชะละลายของสารอนุพันธ์ของกลีเซอไรด์ที่เกาะอยู่บนผิวตัวเร่งปฏิกิริยา จึงไม่เกิดการเสื่อมสภาพของตัวเร่งปฏิกิริยา และพลังงานก่อกัมมันต์ของปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันที่มีการป้อนแก๊สไนโตรเจนเท่ากับ 38.6 กิโลจูลต่อโมล

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**ITSARAPAP SANEEVONG: EFFECT OF N₂ BUBBLES ON
TRANSESTERIFICATION OF VEGETABLE OIL IN A FIXED BED
REACTOR. ADVISOR: ASST.PROF. CHAWALIT**

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The present thesis investigated the effect of nitrogen bubbles on transesterification of palm oil in a fixed bed reactor. Dolomite, a natural calcium rocks was used as the heterogeneous catalyst. The catalysts were prepared by physical mixing technique. The catalyst was formulated with a size of 2x5 mm. After that, the catalyst was calcined at 800 °C for 6 h before used in transesterification. In the non-nitrogen gas feed system, the effect of types of palm oil, effect of molar ratio of methanol to oil, effect of catalyst extrudates size and effect of the addition of methyl ester were investigated. The optimum reaction condition of transesterification with the presence of nitrogen bubbles was studied. The FAME yield of 96.7% was achieved under the optimal conditions. The optimal reaction conditions were, reaction temperature was 60 °C, nitrogen gas feed rate was 30 mL/min, molar ratio of methanol to oil was 30:1 and total flow rate of reactants was 2.5 mL/min. The stability of transesterification of the nitrogen gas feed system was compared with non-nitrogen gas feed system. The decrease of the FAME yield was observed in case of transesterification in non-nitrogen gas feed system. It should be due to the glyceride derivatives covered on the catalyst surface and resulting to the deactivation of catalyst. The FAME yield of transesterification with the presence of nitrogen bubbles was stable throughout the time on stream of 18 h. It should be due to the feed of nitrogen gas can leach glyceride derivative on the catalyst surface which prevents the deactivation of catalyst. The value of activation energy of transesterification in the presence of nitrogen gas was 38.6 kJ mol⁻¹.

Field of Study: Petrochemistry and Polymer Science Student's Signature

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LIST OF ABBREVIATIONS

°C	Degree Celsius
g	Gram (s)
H	Hour (s)
mm	Millimeter
cm	Centimeter
µm	Micrometer (s)
ml	Milliliter (s)
min	Minute (s)
M	Molarity
nm	Nanometer (s)
%	Percentage
SEM	Scanning Electron Microscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy
TGA	Thermogravimetric analysis

CHAPTER I

INTRODUCTION

1.1 Statement of problem

Biodiesel has become more attractive as an alternative fuel because of its environment benefits such as non-toxic and biodegradable. It can be used directly in diesel engines without any modification. Commonly, biodiesel is industrially produced through transesterification of triglycerides, presenting in animal fat and vegetable oil with small alcohols, e.g. methanol and ethanol, by which the bulky glycerides are converted to fatty acid alkyl esters and glycerol. Methanol is preferentially used as the alcohol due to its high reactivity and low cost.

Biodiesel production is generally operated in the presence of a homogeneous acid or base catalyst. The homogeneous bases, such as sodium hydroxide, potassium hydroxide, are more favored than the acid catalysts because they accelerate the reaction at higher rate under mild conditions and provide smaller corrosion problem. However, since the homogeneous catalysts are present in the same phase as the reaction products, many stages of the subsequent processes for catalyst separation and product purification are necessary. These bring about a significant loss of the esters yield and a large amount of alkali wastewater that require a proper treatment before being discharged to the environment. Heterogeneous catalysts can be used to overcome these problems because they possess low solubility in alcohols and high reaction rate, and exist in the different phases of the reaction products.

Generally, most heterogeneous catalyst are in powder form, to increase surface areas and avoid the limitation of mass transfer. However, in industrial scale, pelletization is necessary. It is common to use binder such as silica alumina and clay, in the catalyst preparation. The use of binder may result to decrease surface area and

active site of catalyst. Accordingly, type and quantity of binder are key parameters to archive the suitable catalyst.

In the present research, the biodiesel production in a continuous fixed-bed reactor packed with the heterogeneous catalyst extrudates prepared from the natural calcium rocks in a presence of nitrogen gas bubbles has been investigated. Effects of various factors such as, molar ratio of methanol to oil, total flow rate of reactants and flow rate of nitrogen gas were studied to find suitable conditions. The kinetics of transesterification in a nitrogen gas feed system was also studied.

1.2 Objective

The objectives of this research are

1. To study effects of N₂ bubble on transesterification of vegetable oil with methanol using in a fixed bed reactor with dolomite as a heterogeneous catalyst
2. To study effect of reaction conditions on transesterification of vegetable oil with methanol in a fixed bed reactor with N₂ bubble

1.3 Scopes of work

1. Review previously published research articles related to this thesis
2. Design experimental procedures, and prepare equipment and reagents.
3. Study kinetic of transesterification of vegetable oil with methanol in a nitrogen gas fed system.
4. Characterize the fatty acid methyl esters (FAME) by using a gas chromatography technique.
5. Study effects of reaction conditions on biodiesel production
 - 5.1 Molar ratio of methanol to oil, 30:1 and 50:1.
 - 5.2 Total flow rate of reactant, 2.5, 3.5 and 5 ml/min.
 - 5.3 Nitrogen gas flow rate, 30, 50, 75, 100 cc/min.

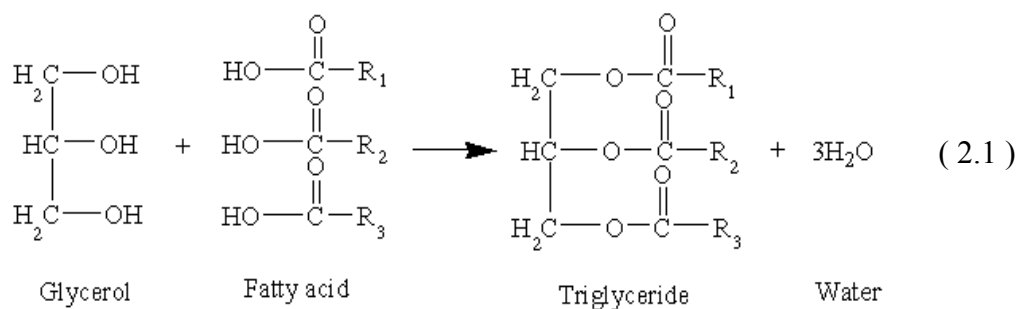
6. Study the stability of catalyst.
7. Study the reusability of catalyst.

Chapter II

Theory and Literature reviews

2.1 Vegetable Oils

The main constituent of vegetable oils is triglycerides. Vegetable oil comprises of 90 to 98% of triglycerides and small amounts of mono- and diglycerides. A triglyceride molecule is made up of one mole of glycerol and three moles of fatty acids [1]. The reaction for the formation of triglyceride is esterification (Eq.(2.1)). When three fatty acids are identical, the product is a simple triglyceride, whereas a so-called mixed triglyceride consists of dissimilar fatty acids



Fatty acids vary in the number of carbon atoms and double bonds in hydrocarbon chain. They are designated by two numbers separated by a colon. The first number represents the number of carbon atoms in the fatty acid chain and the second number shows the number of double bonds. For example, C18:1 (oleic acid) represents the fatty acid with 18 carbon atoms and 1 double bond. Table 2.1 summarized fatty acids frequently found in different vegetable oils.

Table 2.1 Properties of fatty acid that found in vegetable oil [2]

Fatty acid	Molecular Weight	Melting point (°C)	Boiling point (°C)	Heat of combustion (kcal/mol)
Caprylic acid (C8:0)	144.2	16.5	240	-
Capric acid (C10:0)	172.3	31.6	271	1,453
Lauric acid (C12:0)	200.3	44.8	130	1,763
Myristic acid (C14:0)	228.4	54.4	149	2,073
Palmitic acid (C16:0)	256.4	62.9	167	2,384
Stearic acid (C18:0)	284.5	70.1	184	2,696
Oleic acid (C18:1)	282.5	16.3	286	2,657
Linoleic acid (C18:2)	280.4	-5.0	229	-
Linolenic acid (C18:3)	278.4	-11.0	231	-
Erucic acid (C22:1)	338.6	33.7	265	-

2.1.1 Palm oil [3]

Palm oil is a potential raw material for biodiesel production in Thailand due to its high crop yield. Palm tree is mainly growing in the South of Thailand. The major area for palm plantation are in three provinces; Krabi, Chumporn and Surat Thani. Palm oil and palm kernel oil are both derived from the *Elaeis guineensis* palm tree. Its origin is believed to be in the humid forests of East Africa. The palm fruit is oval shaped, about 3-cm long, and looks like a small red plum as shown in Figure 2.1a. The outer fleshy mesocarp gives the viscous orange palm oil while the kernel, which is inside a hard shell, gives the clear white palm kernel oil (Figure 2.1b). Both oils from the same fruit have difference in the fatty acid composition.

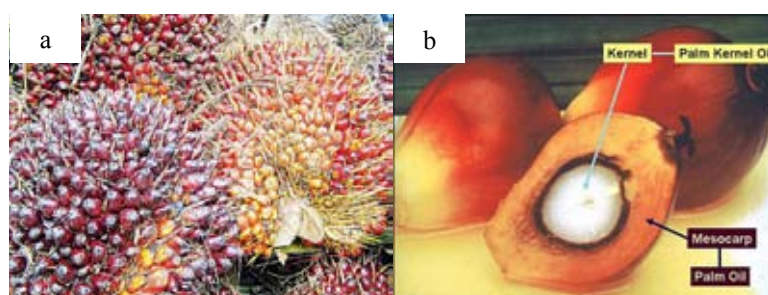


Figure 2.1 Palm bunches (a) and palm fruits (b).

The major acid components of palm oil are palmitic acid (C16:0) and oleic acid (C18:1). Others found with significant amount are linoleic acid (C18:2), stearic acid (C18:0) and myristic acid (C14:0). C₈-C₁₂ fatty acids, which may be derived from the endocarp rather than the mesocarp, are present at trace amounts. On the other hand, the major fatty acids in palm kernel oil are lauric acid (C12:0).

2.2 Biodiesel

Biodiesel is a renewable fuel derived from the renewable sources, such as vegetable oil or animal fats. Biodiesel production is efficiently operated through transesterification reaction in the presence of a catalyst. Biodiesel has a potential to be an alternate fuel to the conventional diesel fuel. It can be used directly as fuel or blended with petroleum diesel in a diesel engine without any modification. Pure biodiesel fuel is called B100. A biodiesel blend is a mixture of pure biodiesel with the conventional diesel. For example, B20 is derived from 80 % petroleum diesel blended with 20 % B100.

Advantages of biodiesel are following;

- It is derived from renewable sources.
- It is biodegradable, non-toxic and environment friendly.
- It reduces emission of carbon monoxide, sulfur dioxide and unburnt hydrocarbon during combustion process.
- It has no aromatic and sulfur compounds.

In Thailand, the biodiesel properties are evaluated according to the standard issued by Department of Energy Business, Ministry of Energy, which is adopted from the ASTM and EN standards. The standard specification for biodiesel in Thailand is listed in Table 2.2.

Table 2.2 Standard specification for biodiesel in Thailand [4]

Property	Lower limit	Upper limit	Test method
Methyl ester (wt.%)	96.5	-	EN 14103
Density at 15°C (kg l ⁻¹)	860	900	ASTM D 1298
Viscosity at 40°C (cSt)	3.5	5	ASTM D 445
Flash point (°C)	120	-	ASTM D 93
Sulphur (wt.%)	-	0.0010	ASTM D 2622
Carbon residue, on 10% distillation residue (wt.%)	-	0.30	ASTM D 4530
Cetane number	51	-	ASTM D 613
Sulfated ash (wt.%)	-	0.02	ASTM D 874
Water (wt.%)	-	0.050	ASTM D 2709
Total contaminate (wt.%)	-	0.0024	ASTM D 5452
Copper strip corrosion	-	No.1	ASTM D 130
Oxidation stability at 110°C (hour)	-	6	EN 14112
Acid value (mg KOH g ⁻¹)	-	0.50	ASTM D 664
Iodine value (g I ₂ 100 g ⁻¹)	-	120	EN 14111
Linolenic acid methyl ester (wt.%)	-	12	EN 14103
Methanol (wt.%)	-	0.20	EN 14110
Monoglyceride (wt.%)	-	0.80	EN 14105
Diglyceride (wt.%)	-	0.20	EN 14105
Triglyceride (wt.%)	-	0.20	EN 14105
Free glycerin (wt.%)	-	0.02	EN 14105

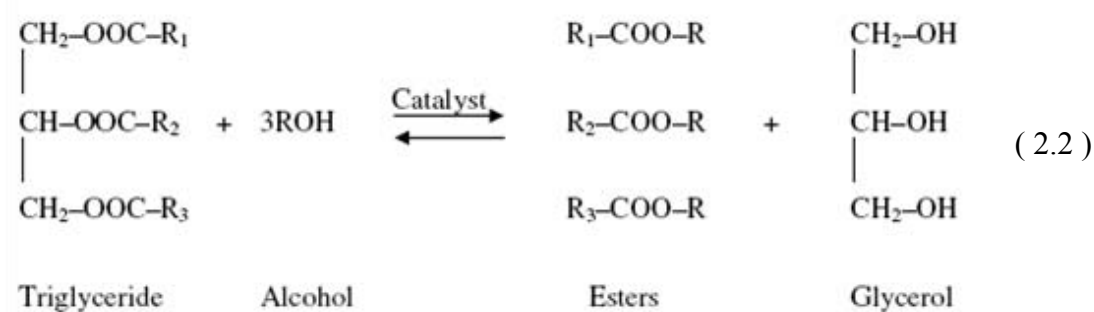
Table 2.2 Standard specification for biodiesel in Thailand (continued) [4]

Property	Lower limit	Upper limit	Test method
Total glycerin (wt.%)	-	0.25	EN 14105
Group I metals (Na+K) (mg kg ⁻¹)	-	5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg) (mg kg ⁻¹)	-	5.0	pr EN 14538
Phosphorus (wt.%)	-	0.0010	pr EN 14538

2.2.1 Biodiesel production technology [5-6]

2.2.1.1 Transesterification reaction

The main reaction for the production of biodiesel is transesterification, also called alcoholysis. The transesterification process reacts an alcohol with the triglyceride, the main component of vegetable oils and animal fats forming fatty acid alkyl esters and glycerol. The general equation for the transesterification of triglyceride with alcohol is expressed in Eq. (2.2).

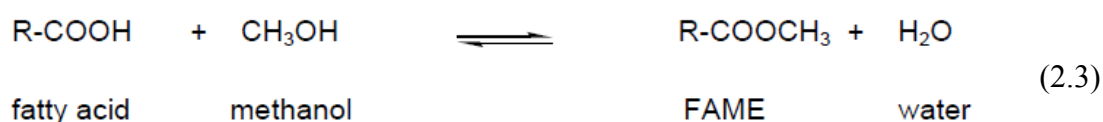


In the transesterification, one mole of triglyceride reacts with three moles of alcohol to form one mole of glycerol and three moles of the respective fatty acid alkyl

esters. In practice, the high molar ratios of alcohol to triglyceride are needed to shift the reaction equilibrium to achieve a maximum alkyl ester yield. Methanol is the most commonly preferred as the alcohol in the biodiesel production because of its lower cost, high reactivity, and physicochemical properties (polar and shortest hydrocarbon chain). It can easily react with the triglyceride molecules.

2.2.1.2 Esterification and transesterification

When fatty acid(FFA) rich feedstock, such as waste cooking oil, was used to produce biodiesel, the pretreatment step, so-called esterification, is necessary. The esterification is the reaction between FFA and methanol, as shown in Eq. (2.3).



Acid catalysts including sulfuric acid, phosphoric acid, are commonly used for the esterification reaction. The high molar ratio of methanol to oil is required, usually ranging from 20:1 to 40:1. The esterification of FFAs with methanol produces water as by-product that must be removed since the acid catalyst is soluble in water, resulting in slower reaction rate. The water can be removed by vaporization, settling, or centrifugation as a methanol-water mixture. The mixture of esters and glycerides can be used directly in a conventional base catalyzed transesterification.

2.2.2 Biodiesel production method [5-7]

2.2.2.1. Batch process

Batch process is the simplest method to produce biodiesel. Commonly, the molar ratio of methanol to oil is in range of 4:1 to 20:1. The reactor may be sealed or equipped with a reflux condenser. The operating temperature is usually about 65 °C. The most commonly used catalyst is sodium hydroxide, with potassium hydroxide also used. The amount of catalyst loading is in range of 0.3 wt.% to about 1.5 wt.%.

Thorough mixing is necessary at the initial period of the reaction to bring the oil, catalyst and alcohol into intimate contact. Towards the end of the reaction, less mixing can help increase the extent of reaction by allowing the inhibitory product, glycerol, to phase separate from the ester – oil phase. Some groups use a two-step reaction, with glycerol removal between steps, to increase the final reaction extent to >95 %. Higher temperatures and higher alcohol/oil ratios also can enhance the percent completion.

Figure 2.2 shows a process flow diagram for a typical batch system. The oil is first charged to the system, followed by the catalyst and methanol. The system is agitated during the reaction time. Then the agitation is stopped. In some processes, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol. In other processes, the reaction mixture is pumped into a settling vessel, or is separated using a centrifuge.

The alcohol is removed from both the glycerol and the ester stream using an evaporator or a flash unit. The esters are neutralized, washed gently using warm, slightly acid water to remove residual methanol and salts, and then dried. The finished biodiesel is then transferred to a storage. The glycerol stream is neutralized and washed with soft water. The glycerol is then sent to the glycerol refining section.

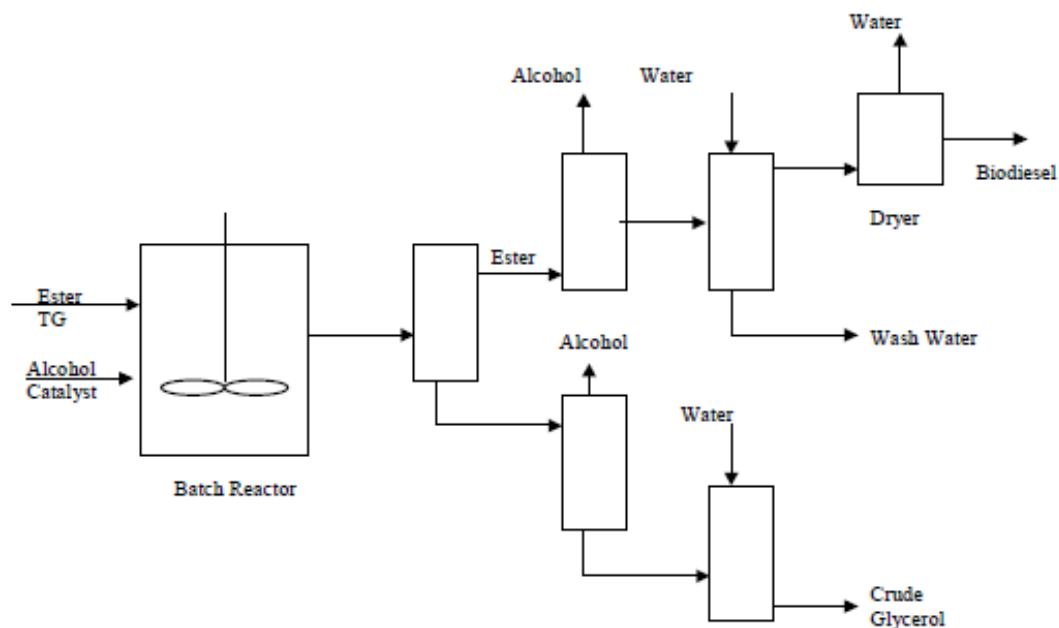


Figure 2.2 Batch reaction process [7].

2.2.2.2. Continuous process

There are several processes that use intense mixing, either from pumps or motionless mixers, to initiate the esterification reaction. Instead of allowing time for the reaction in an agitated tank, the reactor is tubular. The reaction mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. This type of reactor, called a plug-flow reactor (PFR), behaves as if it were a series of small CSTRs chained together. The result is a continuous system that requires rather short residence times, as low as 6 to 10 minutes, for near completion of the reaction. The PFRs can be staged, as shown, to allow decanting of glycerol. Often this type of reactor is operated at an elevated temperature and pressure to increase reaction rate. A PFR system is shown in Figure 2.3.

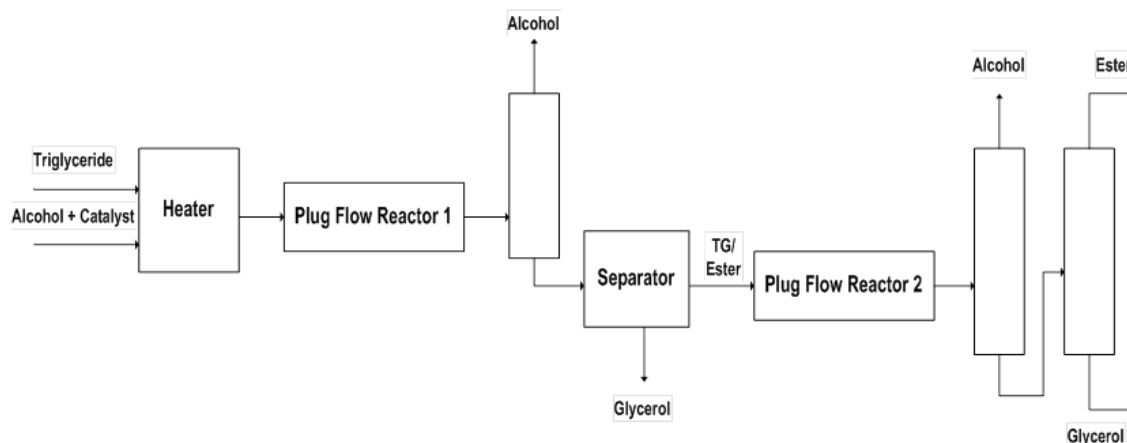
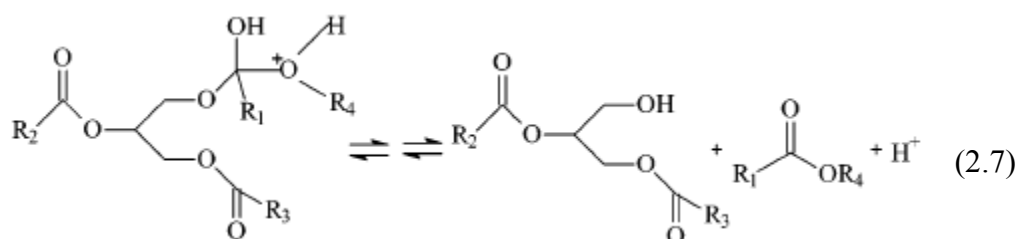
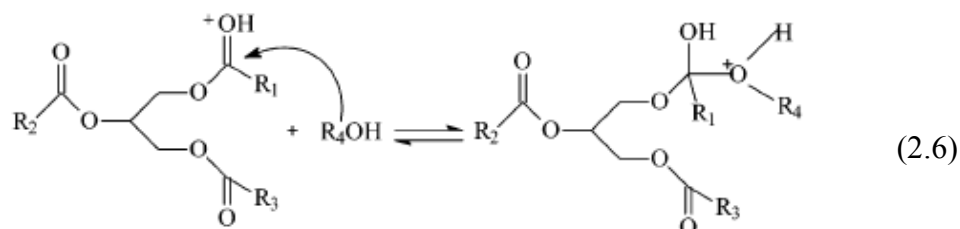
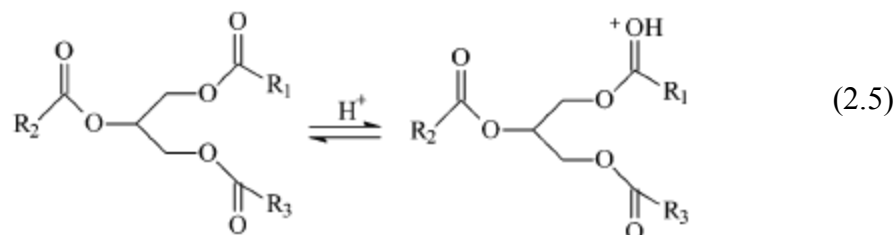


Figure 2.3 Plug flow reaction system [7].

2.3 Transesterification mechanism

2.3.1 Acid catalyzed transesterification

Figure 2.4 shows the mechanism of acid-catalyzed transesterification of representative triglyceride. Firstly, the triglyceride carbonyl group is protonated by the acid catalyst (Eq.(2.5)). The activated carbonyl group then undergoes nucleophilic attack from an alcohol molecule, forming a tetrahedral intermediate (Eq.(2.6)). Solvent assisted proton migration give rise to a leaving group, promoting the cleavage of the tetrahedral intermediate and yielding a protonated alkyl monoester and a diglyceride molecule (Eq.(2.7)). The transfer of proton then regenerates the acid catalyst. This sequence is repeated twice to yield 3 molecules of alkyl monoesters and 1 molecule of glycerol as the final products [8].



$\text{R}_1, \text{R}_2, \text{R}_3$: carbon chains of the fatty acids

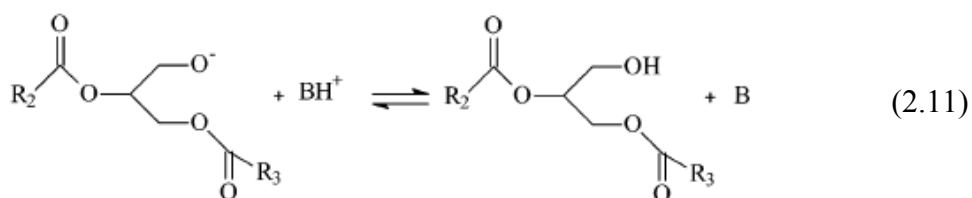
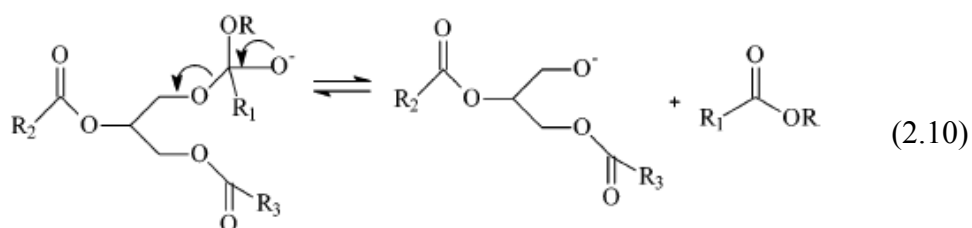
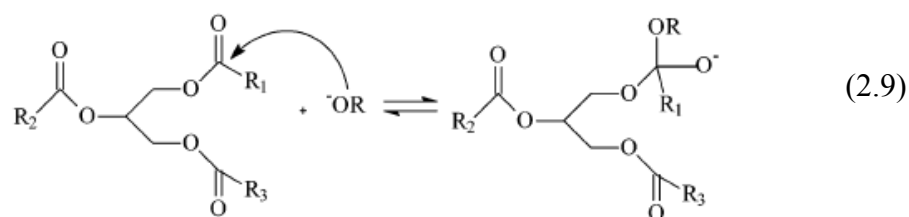
R_4 : alkyl group of the alcohol

Figure 2.4 Mechanism of transesterification of vegetable oils catalyzed by acid.

2.3.2 Base catalyzed transesterification

The mechanism of base-catalyzed transesterification of vegetable oil is shown in Figure 2.4. The first step (Eq.(2.8)) is the reaction of base with alcohol, producing an alkoxide and the protonated catalyst. The alkoxide ion is a strong nucleophile and attacks the carbonyl group of triglyceride, generating a tetrahedral intermediate (Eq.(2.9)), from which the alkyl ester and the corresponding anion of diglyceride are formed (Eq.(2.10)). In the last step, the deprotonation of the catalyst results in the regeneration of active species (Eq.(2.11)). The regenerated catalyst is

able to react with the second molecule of alcohol for another catalytic cycle. Diglyceride and monoglyceride are converted by the same mechanism to a mixture of alkyl esters and glycerol [9].



B: base catalyst

R₁, R₂, R₃: carbon chains of the fatty acids

R₄: alkyl group of the alcohol

Figure 2.5 Mechanism of the transesterification of vegetable oils catalyzed by base.

2.4 Catalyst

2.4.1 Homogeneous catalyst

Homogeneously catalyzed transesterification is the major route for the biodiesel production. The homogeneous base catalyst, such as sodium hydroxide, potassium hydroxide, is more favored than the acid catalysts because they accelerate the reaction at higher rate under mild conditions and provide smaller corrosion problem. However, since the homogeneous catalysts are present in the same phase as the reaction products, many stages of the subsequent processes for catalyst separation and product purification are necessary. These bring about a significant loss of the esters yield and a large amount of alkali wastewater that require a proper treatment before being discharged to the environment.

2.4.2 Heterogeneous catalyst

Although the homogeneous catalysis using alkali hydroxides or alkoxides results in the fast reaction rate under mild conditions, there are some disadvantages that occurred from the homogeneous catalysts.

To minimize the problems associated with the use of homogeneous catalysis, heterogeneous catalysts have been extensively used. The heterogeneous catalysts can be easily separated from the reaction mixture. The cost of biodiesel could be reduced by the use of a heterogeneous catalyst due to simplification of the separation and purification of the products. However, higher temperatures is necessary for the heterogeneous catalyst process to promote the conversion at a reasonable rate.

2.5 Preparation of heterogeneous catalysts

Heterogeneous catalysts are frequently defined as solids or mixtures of solids which accelerate chemical reaction without themselves undergoing changes. Generally, the catalysts may be classified according to the preparation procedure as: (i) bulk catalysts or supports and (ii) impregnated catalysts. On this basis the relative preparation methods are: (i) the catalytic active phase is generated as a new solid phase and (ii) the active phase is introduced or fixed on a pre-existing solid by a process which intrinsically depends on the support surface [10].

The catalytic properties of heterogeneous catalysts are strongly affected by the catalyst preparation. The choice of method for preparing a catalyst depends on the physical and chemical characteristics desired in the final composition.

2.5.1 Bulk catalysts and support preparation [11-12]

2.5.1.1 Precipitation

Precipitation is one of the most widely employed preparation methods and may be used to prepare both single component catalysts and supports. Precipitation is usually understood as obtaining a solid from a liquid solution. In the production of precipitated catalysts, the first step is mixing of two or more solutions or suspensions of materials, causing the precipitation of an amorphous or crystalline precipitate or gel. The formation of the precipitate from a homogeneous liquid phase may occur as a result of physical transformations (change of temperature or of solvent, solvent evaporation) but most often is determined by chemical processes (addition of bases or acids, use of complex forming agents).

It is generally desirable to precipitate the desired material in such a form, that the counterions of the precursor salts and the precipitating agent, which can be occluded in the precipitate during the precipitation, can easily be removed by a calcination step. If precipitation is induced by physical means, i.e. cooling or evaporation of solvent to reach supersaturation of the solution, only the counterion of

the metal salt is relevant. If precipitation is induced by addition of a precipitating agent, ions introduced into the system via this route also have to be considered. Favorable ions are nitrates, carbonates, or ammonium, which decompose to volatile products during calcination. If the ions do not decompose to volatile products, careful washing of the precipitate is advisable.

The equilibrium between concentrations of particular ions in solution and the solid precipitate is expressed in terms of the solubility product. The solubility product constant, K_{sp} , is a particular type of equilibrium constant. The equilibrium is formed when an ionic solid dissolves in water to form a saturated solution. The equilibrium exists between the aqueous ions and the undissolved solid. A saturated solution contains the maximum concentration of ions of the substance that can dissolve at the solution's temperature. Table 2.3 showed the solubility product constant for various compounds.

Table 2.3 Solubility product constant for various compounds [11]

Name	Formula	K_{sp}
<i>Carbonates</i>		
Calcium carbonate	CaCO_3	3.4×10^{-9}
Magnesium carbonate	MgCO_3	6.8×10^{-6}
Zinc carbonate	ZnCO_3	1.6×10^{-10}
<i>Hydroxides</i>		
Calcium hydroxide	Ca(OH)_2	5.0×10^{-6}
Magnesium hydroxide	Mg(OH)_2	5.6×10^{-12}
Zinc hydroxide	Zn(OH)_2	1.2×10^{-17}

The wet solid is converted to the finished catalyst by filtration, washing, drying, forming, calcination and activation. Adjusting production conditions can vary crystallinity, particle size, porosity, and composition of the precipitate or gel.

2.5.1.2 Co-precipitation

In the synthesis of multicomponent systems, the problems are even more complex. Co-precipitation allows one to obtain good macroscopic homogeneity. The term “co-precipitation” is usually reserved for preparation of multicomponent precipitates, which often are the precursors of binary or multimetallic compound. The composition of the precipitate depends on the differences in solubility between the components and the chemistry occurring during precipitation.

The choice of salts and/or alkali (precursor) depends on availability at a moderate cost, the solubility in the solvent (water), and avoiding an introduction of compounds that can cause negative effects in the final catalyst. Chlorine ions are known as common poisons and their presence has to be avoided as well as sulfate, which can be reduced to sulfide during the last step of activation. Therefore, nitrate salts or organic compounds, such as formate and oxalate, are preferred although some problems can arise with them. However, the formate and oxalate compounds are expensive and may not completely decompose during calcination. Nitrate is inexpensive and particularly soluble in water, but calcination has to be controlled because of the exothermic evolution of nitrogen oxides. An alkali, Na^+ , K^+ , NH_4^+ hydroxides, carbonates and bicarbonates can be used as precipitating agents.

2.5.2 Supported catalysts preparation [11]

2.5.2.1 Impregnation

Impregnation is the procedure whereby a certain volume of solution containing the metal precursor is contacted with the solid support, then it is aged, usually for a short time, dried and calcined. According to the volume of solution used, two types of impregnation can be distinguished: wet impregnation and incipient wetness impregnation.

In the wet impregnation technique (also called soaking or dipping), an excess of solution is used. After a certain time, the solid is separated from solution, and the excess solvent is removed by drying. The composition of the batch solution will change and the release of debris can form a mud which makes it difficult to completely use the solution.

In the incipient wetness impregnation, the volume of the solution of appropriate concentration is equal or slightly less than the pore volume of the support. Control of the operation must be rather precise and repeated applications of the solution may be necessary. The maximum loading is limited by the solubility of precursor in the solution.

2.5.2.2 Ion exchange

Ion exchange consists of replacing an ion in an electrostatic interaction with the surface of a support by another ion species. The support containing ions A is plunged into an excess volume (compared to the pore volume) of a solution containing ions B. Ions B gradually penetrate into the pore space of the support, while ions A pass into the solution, until equilibrium is established corresponding to a given distribution of the two ions between the solid and the solution. For example, using a proper salt solution at ca. 100°C (to increase the exchange rate), it is possible to

prepare the acid form of zeolite by exchanging NH_4^+ for Na^+ and successive calcination.

2.5.2.3 Adsorption

Adsorption allows the controlled anchorage of a precursor (in an aqueous solution) on the support. The term adsorption is used to describe all processes where ionic species from aqueous solutions are attracted electrostatically by charged sites on a solid surface. Often consideration is not given to the difference between true ion exchange processes and electrostatic adsorption at the charged surface of oxides. Catalyst systems, which need charge compensating ions are ideal materials for ion exchange (zeolites, cationic clays or layered double hydroxides). Instead most oxide supports, when placed in an aqueous solution, develop a pH-dependent surface charge. These oxides may show a tendency for adsorption of cations ($\text{SiO}_2\text{-Al}_2\text{O}_3$, SiO_2), or anions (ZnO , MgO) or both, cations in basic solutions and anions in acid solutions (TiO_2 , Al_2O_3). The surface charge of an oxide depends on its isoelectric point as well as on the pH and ionic strength of the solution.

2.5.2.4 Deposition-precipitation

In deposition-precipitation two processes are involved: (1) precipitation from bulk solutions or from pore fluids; (2) interaction with the support surface. Slurries are formed using powders or particles of the required salt in amounts sufficient to give the desired loading, then enough alkali solution is added to cause precipitation. However, precipitation in the bulk solution must be avoided, since it gives rise to deposition outside the pores of the support. A well-dispersed and homogeneous active phase is reached when the hydroxyl groups (-OH) of the support (for example, the silanols of silica) interact directly with the ions present in the solution, thereby also determining the nature of the phase formed. The nucleation rate must be higher at the surface than in the bulk solution and the homogeneity of the solution must be preserved. A method to obtain uniform precipitation is to use the

hydrolysis of urea as a source of OH^- instead of conventional alkali. Urea dissolves in water and decomposes slowly at ca. 90 °C, giving a uniform concentration of OH^- in both the bulk and pore solutions. Thus the precipitation occurs evenly over the support surface, making the use of urea the preferred method for amounts higher than 10–20%.

2.6 Formulation of power catalyst [13]

Before using the catalyst in the reactor, the formulation of catalyst is required. The suitable shape and size are necessary to improve the efficiency of catalyst. Generally, binder such as, silica and clay, were used together to improve the mechanical strength of the formulated catalyst. However, the formulation of catalyst may affect the physicochemical properties of the initial catalyst. The change of specific surface area, active phase and the stability of catalyst may occur.

2.6.1 Paste extrusion process

Dry mixing

Dry mixing is the method to uniform distribution of all of solid components. However, this is a difficult unit operation and it is often not possible to achieve homogeneously. The dry mixing stage is a necessary precursor to paste formation.

Wet mixing

Wet mixing is important process since it is necessary to ensure that the liquid is distributed uniformly. The rheology of the liquid paste must be compatible with the mixing process, for if the viscosity is too high the mixer may be ineffective.

High shear mixing

High shear mixing is required to break down the agglomerates inherent in the starting powder and those formed during mixing. It is

desirable to ensure the creation of single particles with a liquid layer or film covering the whole surface of each particle. In this process, It necessary that the liquid viscosity to be high so that liquid seepage does not occur giving regions of wetter and less wet solid, an effect also promoted by the imposition of high stresses.

Degassing

This process is necessary to prevent the creation of void in the structure of catalyst.

Extrusion

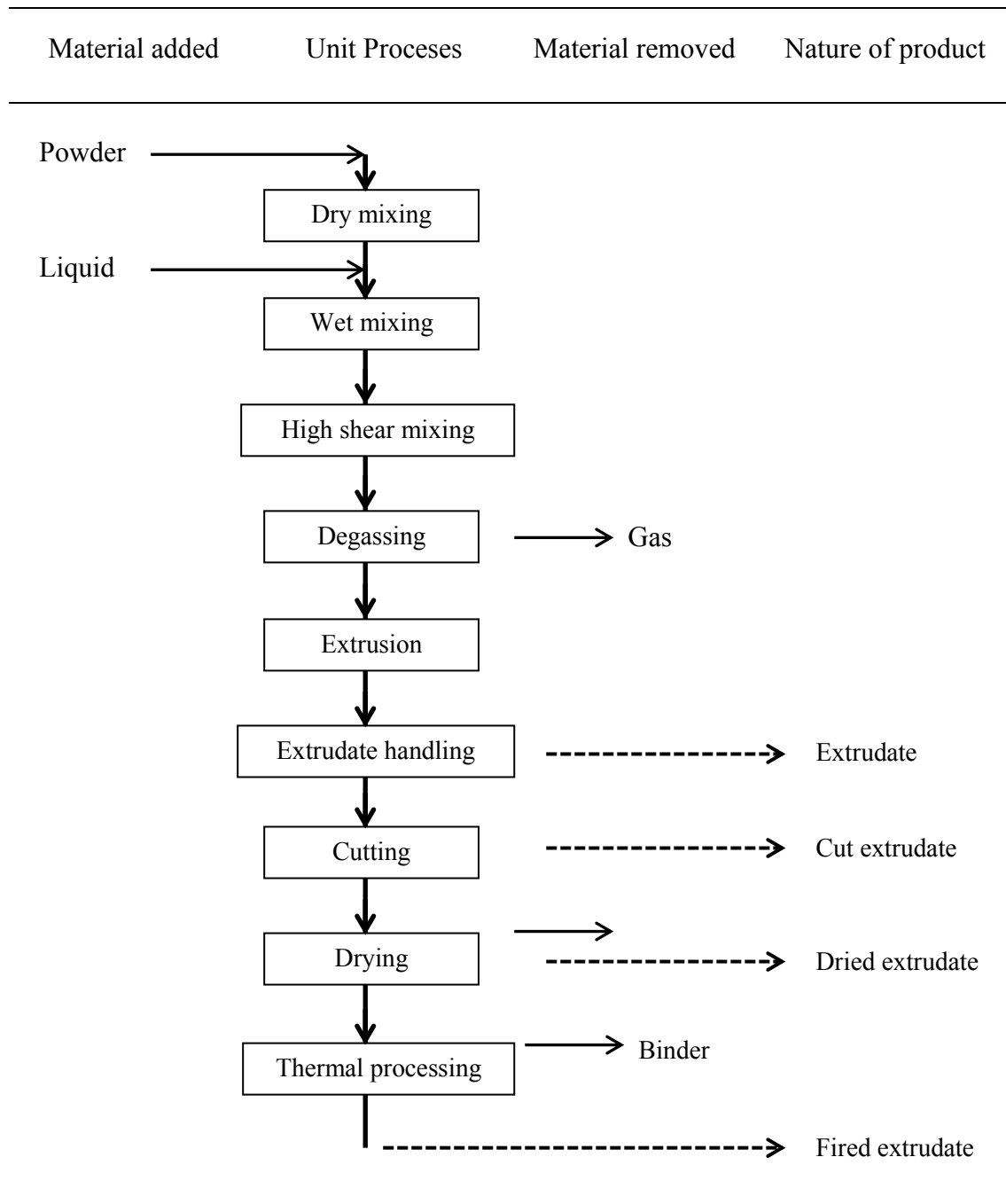
Extrusion is operated by pressing the paste through a die of size and cross-sectional shape appropriate to that of product.

Extrudate handling and cutting

The extrudate is taken from the die face by a removal system and this required carefully consideration as the extrudate is not normally not at all strong. To form short uniform, extrudate is cut by cutter at the die face. It is necessary that cutting does not distort the extrudate.

Thermal processing

This stage has a purpose to burn out any organic material out from the extrudate and enables the solid to develop mechanical strength. The strength can be controlled by the relationship between temperature and time imposed during firing process.

Table 2.4 Paste extrusion stages [13]

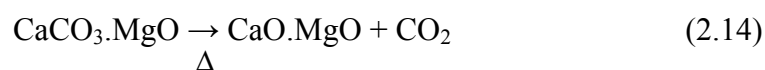
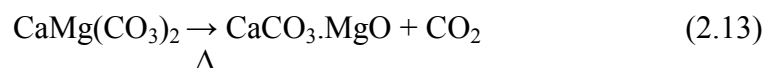
2.7 Calcium oxide as heterogeneous base catalyst

CaO is one of the solid catalysts possessing a great potential for the transesterification of vegetable oils with methanol, due to its availability, low cost, high basicity and low solubility in methanol. CaO caused by the thermal decomposition of calcium carbonate at a temperature higher than 850 °C. There are many natural sources of calcium carbonate, such as, limestone, dolomite and shell.

2.8 Dolomite [14]

Dolomite is the natural calcium rock found in several areas of Thailand. It mainly consists of calcium and magnesium with a small amount of ferrite and silica. The chemical formula of dolomite is $\text{CaMg}(\text{CO}_3)_2$ or $\text{CaO} \cdot \text{MgO}(\text{CO}_2)$. The crystalline structure of dolomite is trigonal-rhombohedral type. Dolomite has been found in several colors such as, white, pink and grey. The hardness of dolomite based on Mohs' scale is about 3.5 -4 and its specific gravity is 2.82.

Due to the presence of two main components, MgCO_3 and CaCO_3 , two-step thermal decomposition of dolomite was observed. MgCO_3 is decomposed at the lower temperature than CaCO_3 , in range of 402 – 480 °C, depending on the dolomite source. In addition, MgCO_3 in dolomite is decomposed at higher temperatures when compared with pure MgCO_3 . CaCO_3 starts to decompose in range of 500 – 700° C and completely decomposition occurs at 725 °C. The thermal decomposition of dolomite is shown in Eq.(2.13) and Eq.(2.14).



The source of natural dolomite in Thailand includes,

- North of Thailand: Amphoe Umphang in Tak Province
- South of Thailand: Amphoe Don Sak in Surat Thani province
- Central of Thailand: Amphoe Tha Muang in Kanchanaburi Province
- East of Thailand: Amphoe Ko Sichang in Chonburi Province

2.9 Characterization of catalyst

2.9.1 X-ray diffractometer (XRD) [15]

The structure and cluster size of the catalysts were determined by techniques of powder XRD using a Bruker D8 Discover equipped with Cu K α radiation.

X-ray powder diffractometry is recognized as a powerful technique for the identification of crystalline phases. The technique can also be used for the quantitative analyses of solids.

When an X-ray beam strikes a surface of crystalline sample at an angle θ , a portion of the radiation is scattered by the layer of atoms at the surface. The effect of scattering from the regularly spaced centers of the crystal is a diffraction of the beam. The data of X-ray diffraction indicates that the spacing between layers of atoms and the scattering centers must be spatially distributed in a higher regular way. The diffraction of X-rays by crystal is shown in Figure 3.3.

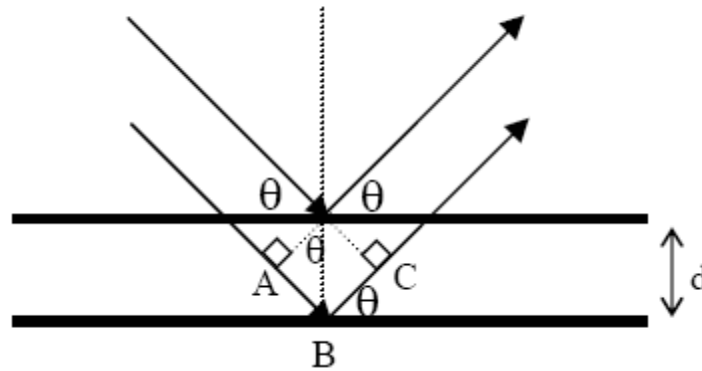


Figure 2.6 Diffraction of X-rays by a crystal.

A narrow beam strikes the crystal surface at angle θ ; scattering occurs as a consequence of interaction of the radiation with atoms located at B. The distance was calculated from Equation (3.1).

$$AB + BC = n\lambda \quad (3.1)$$

The scattered radiation will be in phase, and the crystal will appear to reflect the X-ray radiation. It is investigated with Equation (3.2).

$$AB = BC = d \sin \theta \quad (3.2)$$

Thus, the condition for constructive interference of the beam at angle θ is expressed by the Equation (3.3), called Bragg's law.

$$2d \sin \theta = n\lambda \quad (3.3)$$

Where n = an integer
 d = interplanar distance of the crystal (\AA ; $1 \text{\AA} = 10^{-10} \text{ m}$)
 θ = angle between X-ray and crystal planes (degree)
 λ = wavelength (\AA)

2.9.2 Thermogravimetric/differential thermal analyzer [16]

Thermogravimetric analysis (TGA) was carried out by using a Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer. Typically, 10 mg of a sample was placed in a platinum pan and heated from 40 to 1,000°C at a ramping rate of 8°C /min with air flow rate of 50 mL/min.



Figure 2.7 Thermogravimetric/Differential Thermal Analyzer.

2.9.3 X-ray fluorescence spectrometer [17]

Elemental analysis was performed on a Philips PW-2400 ED-2000 Energy Dispersive X-ray Fluorescence Spectrometer (XRF).

An electron can be ejected from its atomic orbital by the absorption of a light wave (photon) of sufficient energy. The energy of the photon must be greater than the energy with which the electron is bound to the nucleus of the atom. When an inner orbital electron is ejected from an atom, an electron from a higher energy level orbital will be transferred to the lower energy level orbital. During this transition a photon may be emitted from the atom. This fluorescent light is called the characteristic X-ray of the element. The energy of the emitted photon will be equal to the difference in energies between the two orbitals occupied by the electron making the transition. Because the energy difference between two specific orbital shells, in a given element, is always the same (i.e. characteristic of a particular element), the photon emitted when an electron moves between these two levels, will always have the same energy. Therefore, by determining the energy (wavelength) of the X-ray light (photon) emitted by a particular element, it is possible to determine the identity of that element.

For a particular energy (wavelength) of fluorescent light emitted by an element, the number of photons per unit time (generally referred to as peak intensity or count rate) is related to the amount of that analyte in the sample. The counting rates for all detectable elements within a sample are usually calculated by counting, for a set amount of time, the number of photons that are detected for the various analytes' characteristic X-ray energy lines. It is important to note that these fluorescent lines are actually observed as peaks with a semi-Gaussian distribution because of the imperfect resolution of modern detector technology. Therefore, by determining the energy of the X-ray peaks in a sample's spectrum, and by calculating the count rate of the various elemental peaks, it is possible to qualitatively establish

the elemental composition of the samples and to quantitatively measure the concentration of these elements.

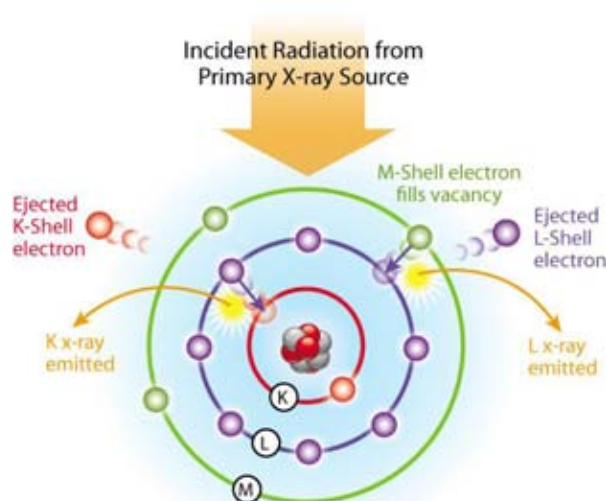


Figure 2.8 Schematic of the XRF process. Incident x-ray knocks out an inner shell electron, higher shell electron fills the empty vacancy and excess energy given up as an x-ray (photon).

2.10 Literature review

Bournay *et al.* [18] reported about new heterogeneous process for biodiesel production that had been developed by French Institute of Petroleum (IFP). In this process, the transesterification of vegetable oils was continuously carried out in two-fixed bed reactor packed with heterogeneous catalyst. The catalyst was a spinel structure mixed oxide of zinc and aluminum, which promoted the reaction without an activity loss. However, the reaction must be performed at temperature and pressure higher than the conventional homogeneous catalysis processes. The excess methanol was evaporized and recovered into the reaction. The major advantage of this process is that glycerin produced has high purity (at least 98%).

Ngamcharussrivichai *et al.* [19] studied the transesterification of palm kernel oil (PKO) with methanol over various natural calciums, including calcite, cuttlebone, dolomite, hydroxyapatite, and dicalcium phosphate. The reaction was performed at 60 °C. The experimental showed that dolomite calcined at 800 °C, resulting in a formation of highly active mixed oxide, was the most active catalyst. Under the suitable reaction conditions, the amount of dolomite calcined at 800 °C is 6 wt.% based on the weight of oil, the methanol/oil molar ratio is 30, and the reaction time is 3 h, the methyl ester content of 98.0 wt.% can be achieved. The calcined dolomite can be reused many times.

Kouzu *et al.* [20] studied the activity of CaO compared with other calcium compound such as, calcium hydroxide (Ca(OH)₂) and calcium carbonate (CaCO₃) on transesterification of soy bean oil. At 1 h of the reaction time, the yield of FAME was 93% for CaO, 12% for Ca(OH)₂, and 0% for CaCO₃. However, CaO was also rapidly poisoned by the moisture and carbon dioxide in the ambient atmosphere.

Kouzu *et al.* [21] studied the use of limestone as heterogeneous catalyst in transesterification of rapeseed oil. The limestone precursor was calcined at 800 °C for 2 h. Methanol and oil were mixed in the batch unit consist of a circulating system passing through the column reactor. The FAME yield was about 60% at 2 h of reaction time. Moreover, the column was blocked up due to the agglomeration of the particle catalyst. In order to hurdle the feeding trouble, the catalyst particle was dispersed in the active carbon that filled the top and bottom space in the column. As a result, the FAME yield reached to 96.5% at 2 h of reaction time and the good reaction efficiency went on for the successive 10 operations without changing the catalyst.

Cho *et al.* [22] carried out the transesterification of tributyrin with methanol over CaO catalysts prepared from various calcium precursors such as CaCO₃, Ca(OAc)₂, Ca(NO₃)₂, Ca(OH)₂ and CaC₂O₄. The precursors were transformed into

CaO by calcination at different temperatures depending on the types of precursor. Ca(OH)₂ calcined at 600-800 °C showed the highest activity in the transesterification. The calcination at excessively high temperature caused a significant loss of basic sites due to a sintering. The CaO catalyst maintained its advantages as a heterogeneous catalyst in terms of its separation and repeated use.

Ngamcharussrivichai *et al.* [23] studied the effects of binder addition on the preparation of catalyst extrudates from limestone. The hydroxide and the oxide of Mg acted as solid lubricants that helped the extrusion of the catalyst pastes smoothly. Combining these Mg precursors with the Al precursors generated the spinel MgAl₂O₄ as the new active phase, which promoted the transesterification and improved the strength of the catalyst extrudates. The suitable Mg/Al ratio in the mixed catalyst precursors was 3. The transesterification activity and the extrudate strength were optimized through the thermal treatment of the limestone at 600 °C, followed by the calcination of the mixed precursors at 800 °C. The addition of NaAlO₂ was a key to attain the dense and hard extrudates by inducing the formation of the mixed Ca and Al phases. The catalyst can be regenerated and used repeatedly. The catalytic test in the transesterification of various oils with methanol and ethanol in the continuous-flow fixed bed reactor suggested the good activity and stability of the catalyst extrudates.

Behzadi *et al.* [24] studied the biodiesel production from fats and oil using a continuous gas-liquid reactor. the process operates by injecting oil or fats through a high pressure nozzle into a reactor filled with methanol vapor carrying the catalyst and moving in counter current flow direction. This allowed direct contact between the two phases with large contact area thereby promoting more heat and mass transfer. The high pressure nozzle in this system atomizes the oil into small droplets in the range of 100-200 µm diameter. Sodium hydroxide and sodium methoxide was used as catalyst. Conversions of 94-96 were achieved while operating with 5-7 g of sodium methoxide/L of methanol at methanol flow rate of 17.2 L/h and oil flow rate of 10L/h.

Sung *et al.* [22] carried out transesterification of sunflower oil with methanol in a countercurrent trickle-bed reactor, using calcium oxide particles 1–2 mm in diameter as a packed, solid base catalyst. The reaction temperature was varied from 80 to 140 °C to confirm the progress of transesterification in a gas–liquid–solid phase reaction system. Oil droplets released from a thin tube flowed downward, while vaporized methanol flowed upward in the bed. The effects of the reaction temperature, methanol and oil flow rates, and the bed height on the FAME yield were investigated. The oil residence time in the reactor, which was controlled by changing both the oil flow rate and the bed height, had a significant effect on the FAME yield. In addition, the FAME yield increased with reaction temperature and was maximal at 373 K due to the change in residence time associated with reduced oil viscosity at higher temperatures. The FAME yield was 98% at a reaction temperature of 373 K when the methanol and oil flow rates were 3.8 and 4.1 mL/h, respectively. One of the most important advantages of biodiesel production in a countercurrent trickle-bed reactor is the simplicity of product separation from methanol. Vaporized methanol and the reaction products, i.e., FAMES and glycerol, were continuously separated without the use of an additional evaporation unit.

Ren *et al.* [23] studied transesterification of soybean oil with methanol in a fixed bed reactor packed with D261 anion-exchange resin as the heterogeneous catalyst. The effect of co-solvent such as MTBE, n-hexane, TBA and THF on the FAME yield was investigated. As a result, n-Hexane as an appropriate co-solvent can highly increase the FAME conversion. Under the optimal conditions, reaction temperature was 323.15 K, n-hexane/soy bean oil weight was 0.5, molar ratio of methanol to oil was 9:1 and feed flow rate was 1.2 mL/min, the conversion to biodiesel achieved to 95.2 % with 56 min of resident time. The resin can be regenerated in-situ and restored to the original activity. GC–MS analysis reveals that the product is simplex and mainly composed of C16:0 (palmitic), C18:2 (linoleic), C18:1 (oleic) and C18:0 (stearic) acids of methyl esters. No glycerol in the product was detected due to the resin adsorbing glycerol in the fixed bed, which solved the issue of glycerol separation from biodiesel.

CHAPTER III

EXPERIMENTALS

3.1 Chemicals

3.1.1 Commercial catalysts

1. Dolomite ($\text{CaMg}(\text{CO}_3)_2$)
2. Calcium hydroxide ($\text{Ca}(\text{OH})_2$) (AR grade, Ajax Finechem)
3. Magnesium hydroxide (MgO) (AR grade, Ajax Finechem)
4. Aluminium hydroxide ($\text{Al}(\text{OH})_3$) (AR grade, s.d. Finechem)
5. Sodium aluminate anhydrous (NaAlO_2) (AR grade, Riedel-de Haën)

3.1.2 Chemicals for esterification

1. Refined bleach deionized palm oil was donated from Patum vegetable Oil Co., Ltd.
2. Methanol (CH_3OH , 99.5%)
3. Tetrahydrofuran (THF) (AR grade, QRëC)
4. Nitrogen gas (99.99 %, TIG)

3.1.3 Chemicals for reaction product analysis

1. Methyl heptadecanoate ($\text{C}_{18}\text{H}_{36}\text{O}_2$) (GC grade, Fluka)
2. Heptane (C_7H_{16}) (AR grade, MERCK)

3.2 Instruments and equipments

1. Glass column with 50 cm. of length and 3 cm. of diameter
2. Heater band
3. Temperature controller
4. Thermocouple
5. Peristaltic pump
6. Manual extruder

7. Rotary evaporator
8. Oven
9. Crucible
10. Muffle furnace
11. Desiccator
12. Bruker D8 Discover
13. Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer
14. Philips PW-2400 ED-2000 Energy Dispersive X-ray Fluorescence Spectrometer

3.3 Catalyst preparation

The catalyst was prepared by physical mixing technique. Dolomite was calcined at 800 °C for 5 h in a muffle furnace and followed by mixing with binder. The composition of catalyst was 62.5% calcined dolomite, 15% Ca(OH)₂, 12.5% MgO, 5% Al(OH)₃ and 5% NaAlO₂. Deionized water was slowly added to the powder mixture and stirred until forming the paste. The paste was shaped into an extrudate form by the manual extruder (Fig.3.1). The extrudate was dried at 100 °C in an oven overnight. After drying, the extrudate was sized to 2 mm of diameter and 5 mm of length (Fig.3.2) and followed by calcination in a muffle furnace at 800 °C for 6 h before used.



Figure 3.1 The manual extruder.



Figure 3.2 The catalyst extrudates.

3.3 Transesterification of palm oil with methanol

3.3.1 Transesterification in a non-nitrogen gas feed system

The transesterification of palm oil was carried out in a glass column packed with catalyst extrudates. A heater band covered by a jacket and equipped with a temperature controller and a thermocouple was used to control the reaction temperature. 10 %wt. of palm oil of tetrahydrofuran (THF) was mixed in palm oil to reduce the viscosity and prevent the solidification of palm oil during feed into the reactor. Palm oil and methanol were separately fed into the column by peristaltic pumps with the total flow rate of reactant was 2.5 mL/min. Effect of types of oil, effect of molar ratio of methanol to oil, effect of extrudates size and effect of the addition of methyl esters were studied. The product was collected at 3 h and every hour until 8 h and followed by evaporation with a rotary evaporator to remove excess methanol. The fatty acid methyl esters (FAME) content was determined by a Shimadzu GC-14 B gas chromatograph equipped with a 30-m DB-Wax capillary column and a flame ionization detector (FID).

3.3.2 Transesterification in a nitrogen gas feed system

The transesterification of palm oil was carried out in a glass column packed with catalyst extrudates. A heater band covered by a jacket and equipped with a temperature controller and a thermocouple was used to control the reaction temperature. 10 %wt. of palm oil of tetrahydrofuran (THF) was mixed in palm oil to reduce the viscosity and prevent the solidification of palm oil during feed into the reactor. Palm oil and methanol were separately fed into the column by peristaltic pumps with the molar ratio of methanol to oil was 30 and 50 and with the total flow rate of reactant was 2.5, 3.5 and 5 mL/min. Nitrogen gas was fed into the column at the bottom of column with 30, 50, 75, 100 cc/min of flow rate. The product was collected at 3 h and every hour until 8 h and followed by evaporation with a rotary evaporator to remove excess methanol. The fatty acid methyl esters (FAME) content was determined by a Shimadzu GC-14 B gas chromatograph equipped with a 30-m DB-Wax capillary column and a flame ionization detector (FID).

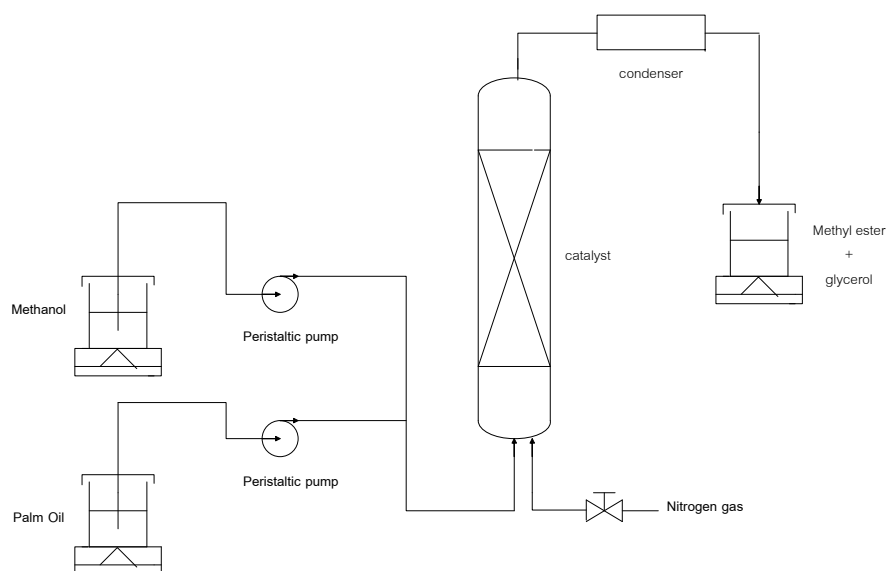


Figure 3.3 The experiment set up of transesterification of vegetable oil in a fixed bed reactor in the presence of nitrogen gas bubbles.

Table 3.1 GC conditions for determination of methyl ester content

Condition	Value
Carrier gas (He) flow rate	1.5 mL/min
Make up gas (He) pressure	25 kPa
Air pressure (for FID)	300 kPa
Detector temperature	250°C
Split ratio	1 : 20
Injection port temperature	250°C
Inject volume	1 μ L
Initial column temperature	180 °C
Ramp rate	10°C /min
Final column temperature	200°C

**Figure 3.4** Gas chromatograph.

3.5 Kinetic study

The transesterification of palm oil was carried out in a glass column packed with 15 cm of the catalyst bed height. Reaction conditions were, molar ratio of methanol to oil was 30:1, total flow rate of reactant was 2.5 ml min^{-1} and nitrogen gas feed rate was 30 cc/min. Reaction temperature was controlled in the range of 40-60 °C.

3.6 Catalyst characterization

The Elemental analysis of dolomite was analyzed by using X-ray Fluorescence Spectrometer (XRF) technique. The crystalline structure of catalyst was analyzed by using X-ray diffractometer (XRD) technique. The thermaldecomposition of catalyst was analyzed by using Thermogravimetric analysis (TGA) technique.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst characterization

The elemental analysis of natural dolomite determined by XRF technique is shown in Table 4.1. The natural dolomite consisted of Ca and Mg as the main metals with a small amount of Al and Si. It was expected that Ca and Mg were present in the form of mixed carbonate compounds as $\text{CaMg}(\text{CO}_3)_2$ since other elements found were C and O.

Table 4.1 Elemental composition of natural dolomite analyzed by XRF spectroscopy

Catalyst	Composition (wt.%)					Total
	CaO	MgO	Al ₂ O ₃	SiO ₂	Other ^a	
Dolomite	32.42	19.88	0.12	0.27	47.31	99.97

^aCarbon dioxide as the major component.

Figure 4.1 shows the XRD patterns of non-calcined dolomite, dolomite calcined at 600 °C and dolomite calcined at 800 °C. It was found that non-calcined dolomite consisted of CaCO_3 in form of dolomite and calcite. The diffraction peak related of MgCO_3 was observed. The peak of MgO was observed when dolomite was calcined at 600 °C and the peak of CaO was observed when dolomite was calcined at 800 °C. It should be due to the decomposition of MgCO_3 and CaCO_3 , respectively. The presence of $\text{Ca}(\text{OH})_2$ peaks should be related to a rapid reaction of CaO with moisture in the atmosphere during the sample preparation for the XRD analysis

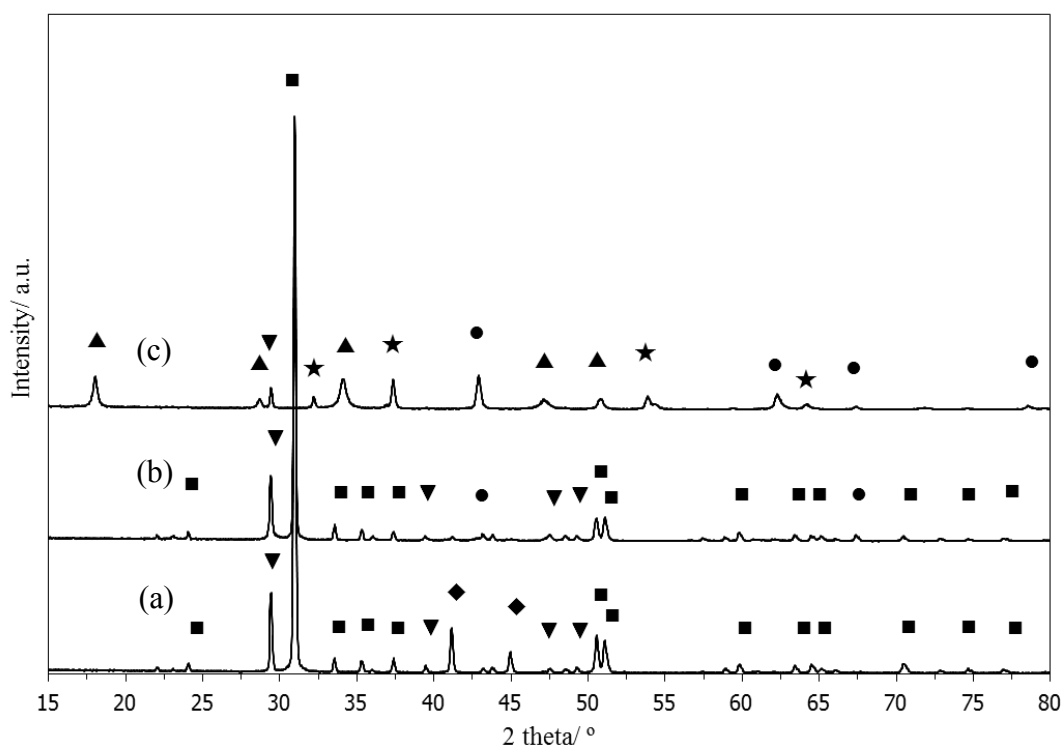


Figure 4.1 XRD patterns of non-calcined dolomite (a), dolomite calcined at 600 °C (b) and dolomite calcined at 800 °C (c). (Symbols: (■) CaCO_3 (dolomite), (◆) MgCO_3 , (▼) CaCO_3 (calcite), (●) MgO , (★) CaO and (▲) Ca(OH)_2)

The catalyst was prepared by physical mixing technique. Dolomite precursor was calcined and followed mixing with binder, Ca(OH)_2 , MgO , Al(OH)_3 and NaAlO_2 . The deionized water was added and stirred until forming the paste. The paste was formulated into an extrudate form by the manual extruder. The extrudate was dried at 100 °C in an oven overnight. The extrudate was calcined at 800 °C for 6 h before used. The effect of the calcination temperature of dolomite on catalyst preparation was studied. Non-calcined dolomite, dolomite calcined at 600 °C and dolomite calcine at 800 °C were used for the catalyst preparation. Catalyst extrudates derived from the non-calcined dolomite as precursor broke after calcined at 800 °C. It was due to the large quantity of decomposition of MgCO_3 and CaCO_3 . $\text{Ca}_{11}\text{Al}_{14}\text{O}_{33}$ and $(\text{CaO})_3\text{Al}_2\text{O}_3(\text{H}_2\text{O})_6$ were observed when dolomite calcined at 800 °C was used. The presence of $\text{Ca}_{11}\text{Al}_{14}\text{O}_{33}$ and $(\text{CaO})_3\text{Al}_2\text{O}_3(\text{H}_2\text{O})_6$ was derived from the reaction of

CaO and Al(OH)₃. They were not active in transesterification. In case of dolomite calcined at 600 °C, it was not an active phase, Ca₁₁Al₁₄O₃₃ and (CaO)₃Al₂O₃(H₂O)₆ were not observed. It was due to CaCO₃ was not decomposed at the calcination at 600 °C. Therefore, the optimal calcination temperature of dolomite is 600 °C [27].

Figure 4.2 shows the XRD pattern of catalyst calcined at 800 °C. It can be seen that the major phases presenting in the catalyst calcined at 800 °C was CaO. The diffraction peak related to MgAl₂O₄ was observed which can promote transesterification. Ca₁₁Al₁₄O₃₃ was also presented in the catalyst. It can improve the dense and hardness of catalyst [27]. Moreover, the diffraction peaks of Ca(OH)₂ were observed, suggesting hydration of CaO by moisture in the atmosphere.

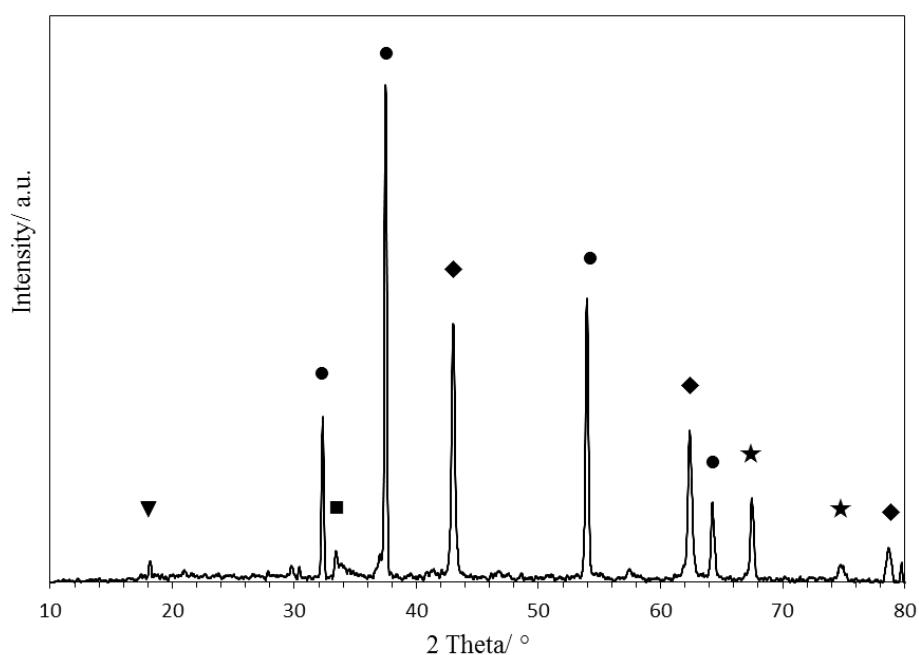


Figure 4.2 XRD patterns of catalyst calcined at 800 °C. (Symbols: (★) MgAl₂O₄, (▼) Ca(OH)₂, (●) CaO, (◆) MgO and (■) Ca₁₁Al₁₄O₃₃).

4.2 Transesterification of vegetable oil in a fixed bed reactor

Transesterification of vegetable oil was carried out in a fixed bed reactor packed with catalyst extrudate. The temperature was controlled at 60 °C. The product was collected when the reaction reached to the steady state at 3 h of time on stream. The effect of various parameters such as, effect of molar ratio of methanol to oil, effect of types of oil, effect of extrudate size and effect of the addition of methyl ester were studied.

4.2.1 Effect of types of palm oil

The effect of types of palm oil, refined bleach deodorized palm oil (RPO) and olein palm oil (POO) (an edible grade) was shown in Figure 4.3. It was found that the methanolysis of POO occurred at lesser extent when compared to that of RPO. It should be due to the presence of some additive in the POO, such as, anti-oxidant, which can affect the performance of catalyst.

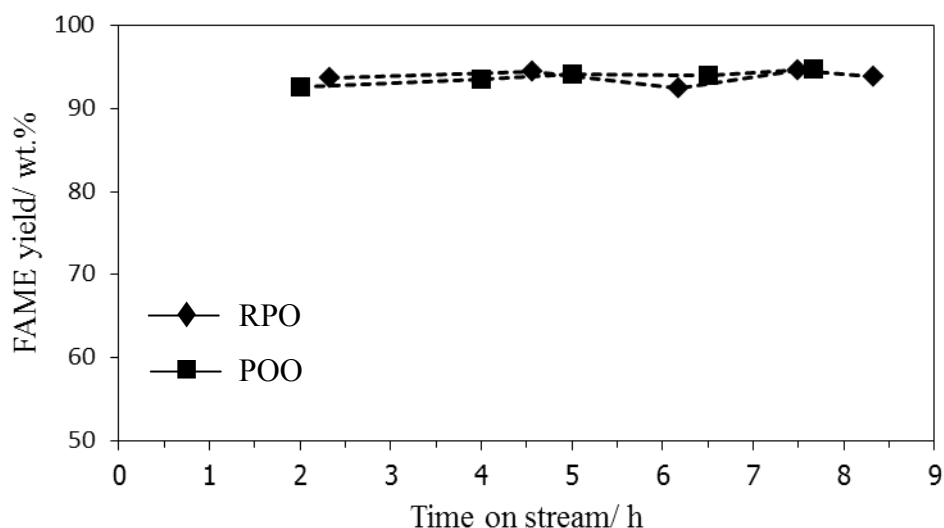


Figure 4.3 Effect of types of oil on transesterification in a fixed bed reactor. Reaction conditions: Methanol/oil molar ratio, 30:1; total flow rate of reactant, 2.5 mL/min; height of catalyst bed, 25 cm; temperature, 60 °C.

4.2.2 Effect of molar ratio of methanol to oil

It is believed that an excess methanol is necessary for driving the equilibrium of the transesterification of triglycerides to attain a high conversion. The effect of molar ratio on transesterification was shown in figure 4.4. 30:1 and 50:1 of molar ratio of methanol to oil was studied. At the methanol/oil molar ratio of 30, the FAME yield of ca. 93% was attained. Although the methanol/oil ratio of 50 yielded a comparable FAME yield, the transesterification under the higher ratio conditions exhibited more stable generation of FAME.

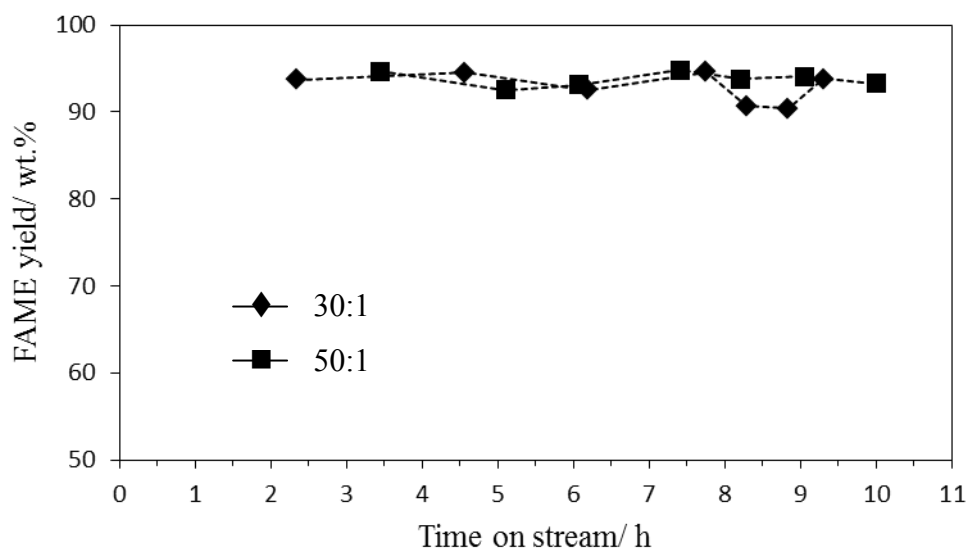


Figure 4.4 Effect of methanol to oil on transesterification of palm oil in a fixed bed reactor. Reaction condition: Total flow rate of reactant, 2.5 mL/min; height of catalyst bed, 25 cm; temperature, 60 °C.

4.2.3 Effect of extrudate size

The effect of extrudate size was shown in figure 4.5. To compare the effects of extrudate sizes, the weight of catalyst was fixed. A certain amount of glass bead with an average diameter of 2 mm was placed at the bottom of the reactor column to maintain the catalyst bed height when the 1 mm catalyst extrudates were used. It can be seen that the higher FAME yield was achieved over the catalyst with the smaller size. The smaller void fraction within the bed of the 1 mm extrudates should promote a good contact between the reactants and the catalyst surface. In other words, the enhancement of the FAME formation should be attributed to a higher surface area-to-volume ratio inside the bed of the smaller catalyst extrudates.

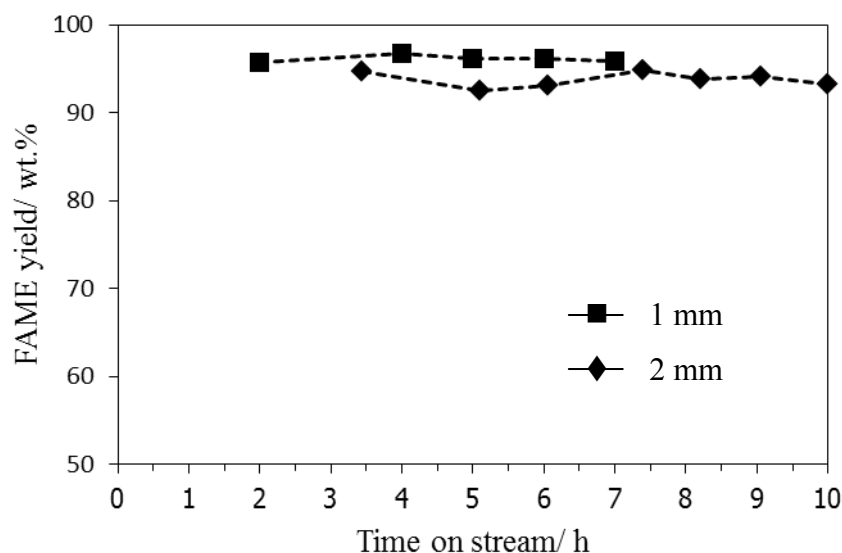


Figure 4.5 Effect of size of extrudate on transesterification of vegetable oil in a fixed bed reactor. Reaction conditions: Methanol/oil molar ratio, 30:1; total flow rate of reactant, 2.5 mL/min; height of catalyst bed, 25 cm; temperature, 60 °C.

4.2.4 Effect of addition of methyl esters

Suppes et al. used a methyl ester as the solvent in the ethanolysis of soybean oil over CaCO_3 packed in a fixed-bed reactor to enhance miscibility of the reactants, resulting in the improvement of the conversion. Glyceride derivatives, i.e. monoglycerides and diglycerides, remaining in an incomplete transesterified oil are suggested to act as emulsifiers that modify the oil-methanol solubility [28].

The effects of addition of methyl esters with different glyceride compositions, denoted as a methyl ester additive or MEA, in the transesterification of olein oil with methanol was investigated (Figure 4.6). MEA was mixed in oil with 15%vol. of oil. The concentration of FAME used as additive were 75% and 96%. The composition of MEA shows in Table 4.2. The FAME yield was slightly increased in the presence of MEA-96. The increased amount of methyl esters was likely to correspond with the amount of methyl esters added in the starting oil. With the addition of MEA-75, the enhanced methyl ester formation in the initial stage should be attributed to the conversion of monoglycerides and diglycerides remaining in the MEA added to the additional methyl esters. However, the use of MEA with a high yield of glyceride derivatives should increase the glycerol concentration in the reaction mixture stream. The decrease of the FAME yield should be due to the high concentration of glycerol may react with Ca-catalyst and formed calcium diglyceroxide that not active in transesterification reaction. The result suggested that the use of high purity methyl esters as the solvent could promote the transesterification of palm oil.

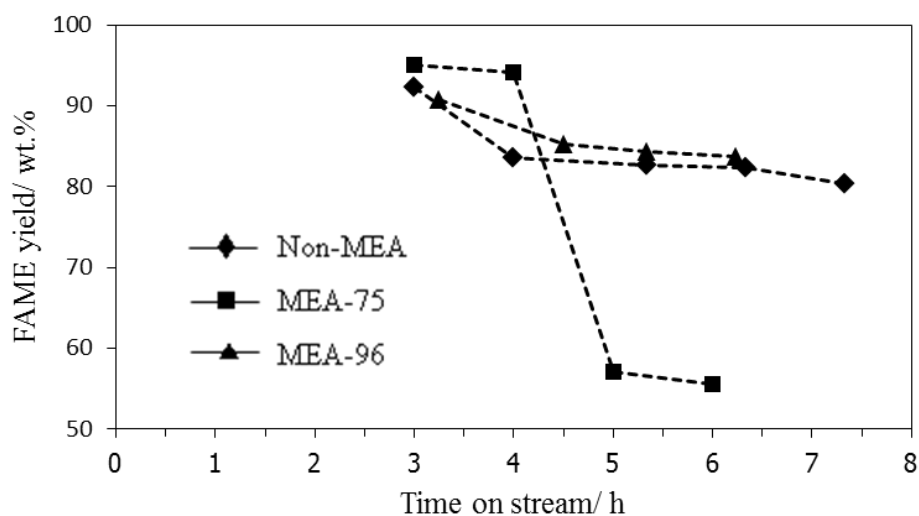


Figure 4.6 Effect of the addition of methyl esters on transesterification of vegetable oil in a fixed bed reactor. Reaction conditions: Methanol/oil molar ratio, 30:1; total flow rate of reactant, 2.5 mL/min; height of catalyst bed, 25 cm; temperature, 60 °C.

Table 4.2 Glyceride composition of methyl esters used as additives

Additive	Composition (wt.%)				
	Monoglycerides	Diglycerides	Triglycerides	FAME	Glycerol ^a
MEA-75	14.54	5.45	1.18	75.12	3.71
MEA-96	1.02	0.13	0.02	96.55	2.28

^a Free glycerol remaining in the fatty acid methyl ester phase after the separation without any washing

4.3 Transesterification of palm oil in a fixed bed reactor with a present of nitrogen gas bubbles

4.3.1 Effect of nitrogen gas feed rate.

Figure 4.7 show the effect of nitrogen gas feed rate on transesterification of palm oil. The nitrogen gas feed rate was used in range of 30 to 100 cc/min. It was found that the FAME decreased when the nitrogen feed rate increased. In case of the nitrogen feed rate of 30 cc/ min, resident time was 1.28 h and the FAME yield was 95.7 at 8 h. While the nitrogen feed rate increased, 50, 75 and 100 cc/min, resident time was 1.20, 1.12, 1.05 h, respectively. The decreased of resident time when the nitrogen gas feed rate increased may result to the FAME yield decrease.

The feed of nitrogen gas into the reactor may affected on the volume of reactor. The volume of reactor was decreased due to the volume of nitrogen gas was placed along the reactor. It resulting that reactants passed through the reactor faster.

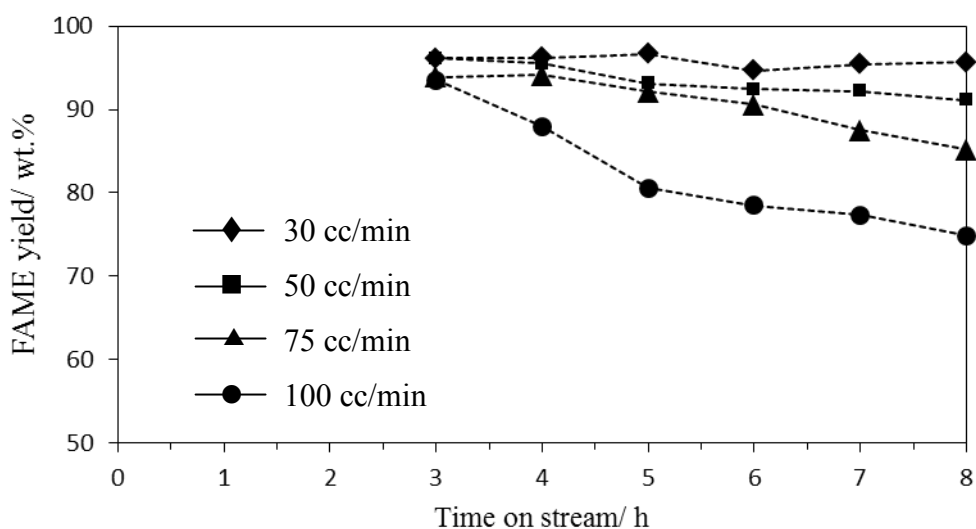


Figure 4.7 Effect of nitrogen gas feed rate on transesterification of palm oil in a fixed bed reactor. Reaction conditions: Methanol/oil molar ratio, 30:1; total flow rate of reactant, 2.5 mL/min; height of catalyst bed, 25 cm; temperature, 60 °C. Resident time, 1.28 h for nitrogen gas feed rate of 30 mL/min; 1.20 h for nitrogen feed rate of 50 mL/min; 1.12 h for nitrogen gas feed rate of 75 mL/min and 1.05 h for nitrogen gas feed rate of 100 mL/min.

4.3.2 Effect of molar ratio of methanol/oil

An excess methanol is necessary for driving transesterification of triglyceride, especially over heterogeneous catalyst. The effect of molar ratio on transesterification was shown in figure 4.8. 30:1 and 50:1 of molar ratio of methanol to oil was studied. From the result, it was no significant different of The FAME yield of the different molar ratio. It should be indicated that 30:1 of molar ratio of methanol to oil was high enough to achieve the high FAME yield. However, in case of the non-nitrogen gas feed system, 50:1 of molar ratio of methanol to oil was better than 30:1. It can be conclude the presence of nitrogen gas can reduced amount of methanol in transesterification.

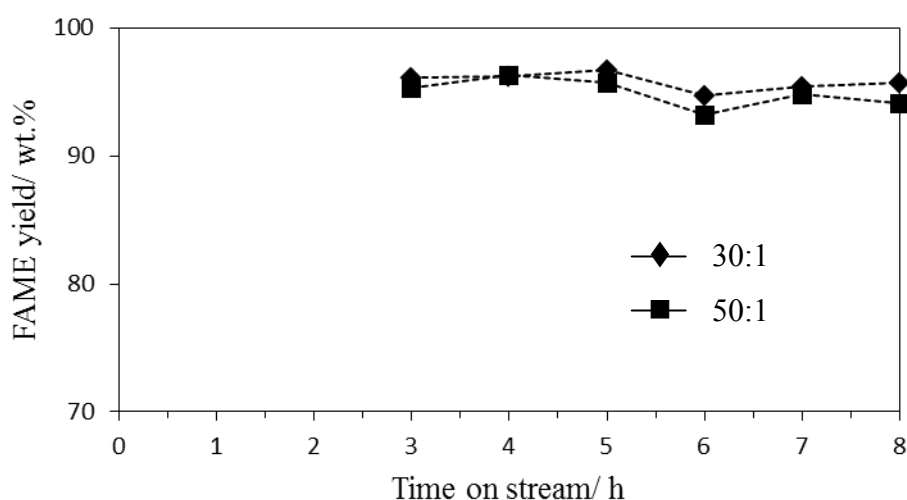


Figure 4.8 The effect of methanol to oil on transesterification of palm oil in a fixed bed reactor. Reaction condition: Total flow rate of reactant, 2.5 mL/min; height of catalyst bed, 25 cm; temperature, 60 °C; nitrogen gas feed rate, 30 mL/min.

4.3.3 Effect of total flow rate of reactant

The effect of total flow rate of reactants on transesterification of palm oil in a fixed bed reactor was shown in figure 4.9. The highest FAME yield was achieved when using 2.5 mL/min of the total flow rate of reactant. It was found that the FAME yield decreased when the total flow rate of reactants increased. The result may be related to the decreased of resident time. Resident time was 1.28 h for using 2.5 of total flow rate of reactants while resident time of 3.5 and 5 mL/min was 55 min and 37 min, respectively. The decreased of resident time may resulting to the less contact time between reactants and catalyst in the column of reactor.

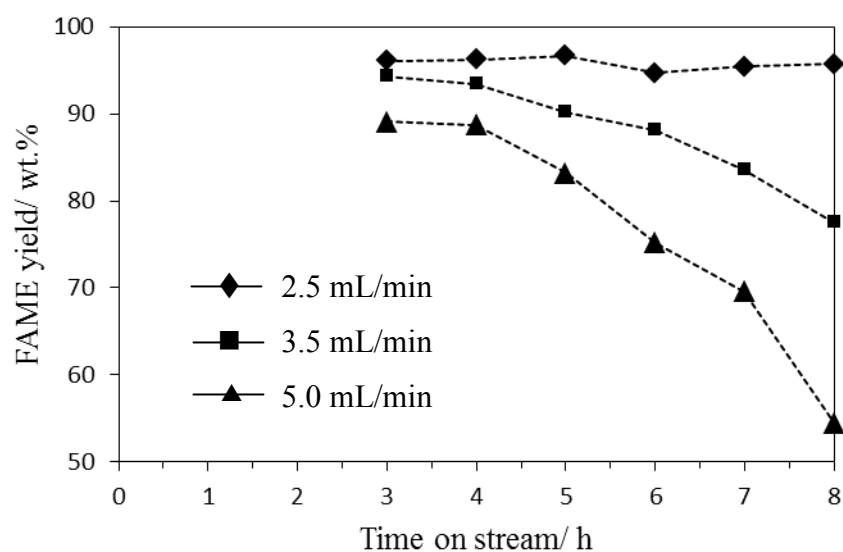


Figure 4.9 The effect of total flow rate of reactants on transesterification of palm oil in a fixed bed reactor. Reaction condition: Methanol/oil molar ratio, 30:1; height of catalyst bed, 25 cm; temperature, 60 °C; nitrogen gas feed rate, 30 mL/min. Resident time, 1.28 h for 2.5 mL/min; 55 min for 3.5 mL/min and 37 min for 5 mL/min.

4.3.4 Effect of nitrogen bubbles

From the results, optimum conditions, nitrogen gas feed rate, 30 cc/min; molar ratio of methanol to oil, 30:1; total flow rate of reactants. 2.5 mL/min, temperature, 60 °C were used to compared the FAME yield in the nitrogen gas feed system and non-nitrogen gas feed system. Figure 4.10 show the effect of nitrogen bubbles on transesterification of palm oil. It was found that the FAME was not difference between two systems. It may indicated that the nitrogen gas feed does not help to improve the FAME yield.

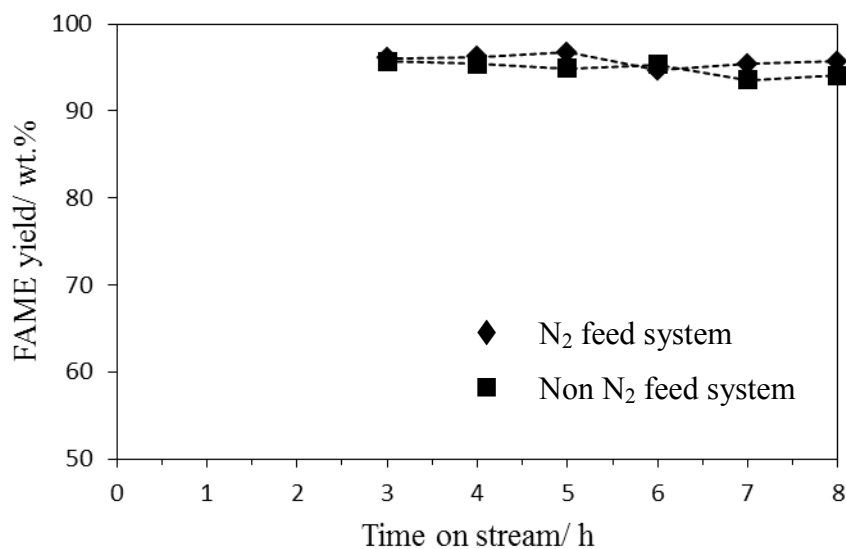


Figure 4.10 The effect of nitrogen bubbles on transesterification of palm oil in a fixed bed reactor. Reaction condition: Methanol/oil molar ratio, 30:1; total flow rate of reactants; 2.5 mL/min; height of catalyst bed, 25 cm; temperature, 60 °C; nitrogen gas feed rate, 30 mL/min.

4.3.5 The stability test of transesterification of vegetable oil in a fixed bed reactor in a presence of nitrogen gas bubbles.

The stability test of transesterification of the nitrogen gas feed system compared with the non-nitrogen gas feed system was shown in Figure 4.11. Transesterification was carried out under the optimum condition. Along time on stream of 18 h, the decrease of the FAME yield of the nitrogen gas feed system was not found. The FAME yield achieved from this system rather stable until the reaction was stopped. While the decrease of the FAME yield was observed in case of the non-nitrogen gas feed system. At the initial period, the FAME yield reached to 97.8 and seems stable until 6 h of time on stream. After 6 h, the FAME yield slightly decreased until 18 h, 91.6 of the FAME yield was obtained. The decrease of The FAME yield should be due to the deactivation of catalyst.

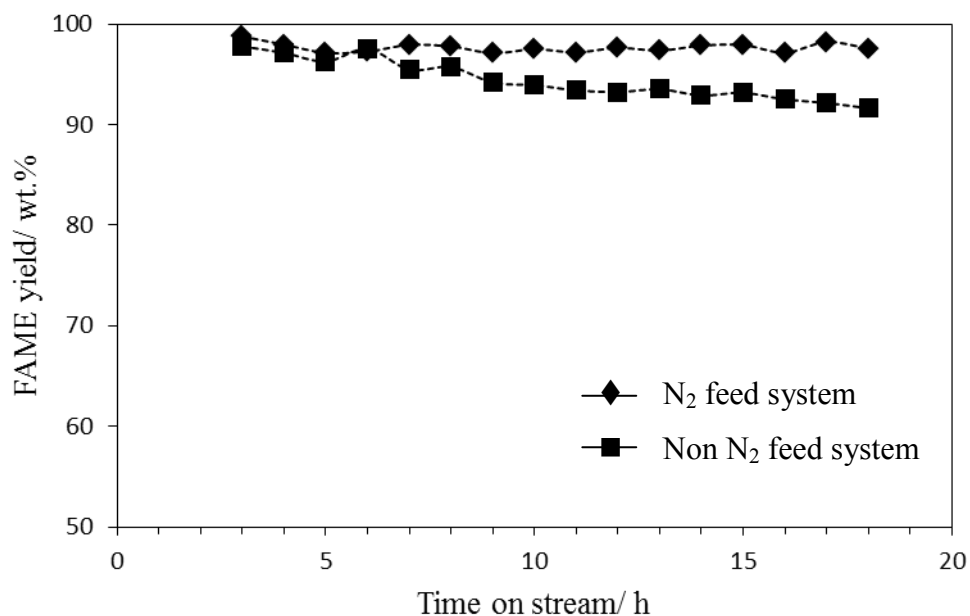


Figure 4.11 The stability test of transesterification compared between the nitrogen gas feed system and the non-nitrogen gas system. Reaction condition: Methanol/oil molar ratio, 30:1; total flow rate of reactants; 2.5 mL/min; height of catalyst bed, 25 cm; temperature, 60 °C; nitrogen gas feed rate, 30 mL/min.

Figure 4.12 reveals the weight loss and DTG curves of the spent catalyst obtained from top and bottom of the reactor. The weight loss at temperature in range of 100-415 °C corresponding the decomposition of glyceride derivative, mono-glyceride and di-glyceride. The weight loss at 450-480 C should be attributed to the dehydration of $\text{Ca}(\text{OH})_2$. The weight loss at 670-690 °C corresponded to the decarbonation of CaCO_3 .

The weight loss in range of 100 - 400 C of spent catalyst in the nitrogen gas feed system was 9% at the top and 6% of the bottom of reactor, less than the weight loss from the non-nitrogen gas feed system, 9.5% at the top and 11% of the bottom of reactor. The deactivation of catalyst in the non-nitrogen gas feed system should be due to the high amount of glyceride derivatives covered on the surface of catalyst resulting loss of active site of catalyst. In the nitrogen gas feed system, The feed of nitrogen gas can leach glyceride derivatives on the surface of catalyst and prevent the loss of active sites.

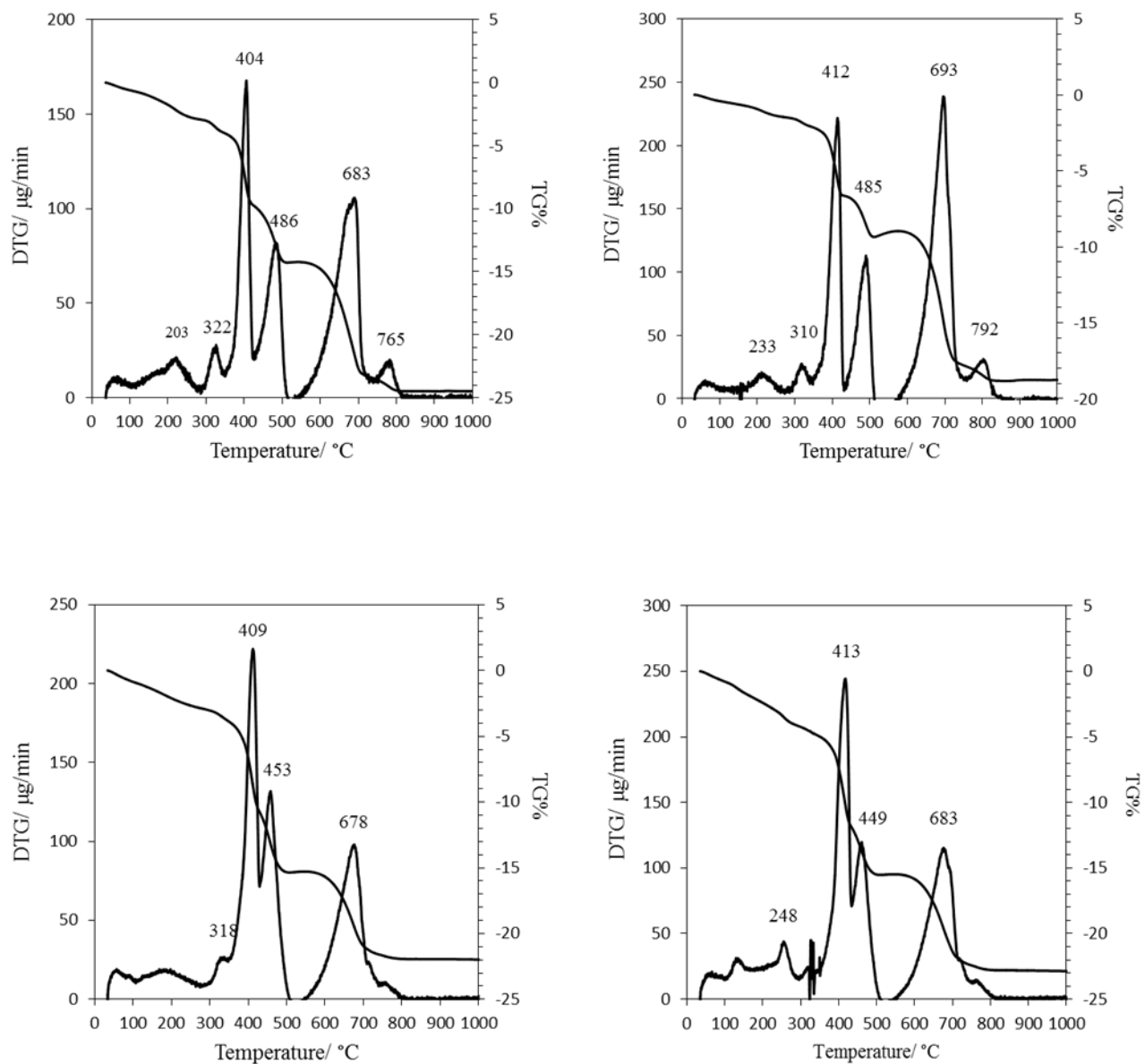


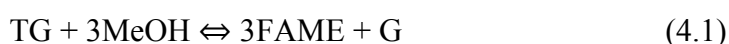
Figure 4.12 TG/DTA profile of spent catalyst at top and bottom of reactor. a) Top N₂, b) Bottom N₂, c) Top non-N₂, d) Bottom non-N₂

Table 4.3 The weight loss at various temperature ranges of spent catalyst

Sample	Weight loss (%) at any temperature (°C)		
	<100	100-415	450-480
Top N ₂	0.5	9	5
Bottom N ₂	0.25	6	3.5
Top non-N ₂	0.8	9.5	5
Bottom non-N ₂	0.8	11	4

4.4 Kinetic study [29,30]

The transesterification reaction is a reversible reaction and therefore, excess methanol is used to drive the reaction forward. (Eq.(4.1)) shows the transesterification reaction, where *TG* is the triglyceride, *MeOH* is methanol, *FAME* is fatty acid methyl esters and *G* is glycerol. The equation also shows the stoichiometric relationship between the reactants and the products.



Rate law of the transesterification reaction can formally be expressed as

$$-r = -\frac{d[TG]}{dt} = k' [TG] \cdot [MeOH]^3 \quad (4.2)$$

where [TG] is the concentration of triglycerides and [MeOH] that of methanol and k' is the equilibrium rate constant.

Three mole-equivalents of the methanol react initially with a triglyceride (TG), and through three consecutive reverse (equilibrium) reactions convert it in a stepwise manner to a diglyceride, monoglyceride, and finally to free glycerol. One moleequivalent of the corresponding ester is produced in every step of these reversible reactions. Strictly speaking this overall conversion should follow a fourth order reaction rate law, however due to a huge surplus of the transesterifying alcohol in the reaction mixture the reaction could be safely considered as obeying the pseudo-first order kinetics [30]. The rate expression can be written as

$$-r = -\frac{d[TG]}{dt} = k \cdot [TG] \quad (4.3)$$

where k is modified rate constant and $k = k'[\text{MeOH}]^3$. It can be assumed that the initial triglyceride concentration was $[TG_0]$ at time $t = 0$, and at time t it falls down to $[TG_t]$. The integration of above (Eq.(4.3)) for $t = 0$, $[TG] = [TG_0]$ and at $t = t$, $[TG] = [TG_t]$ gives the following equation

$$\ln[TG_0] - \ln[TG_t] = k \cdot t \quad (4.4)$$

From mass balance,

$$X_{FAME} = 1 - \frac{[TG]}{[TG_0]} \quad (4.5)$$

or,

$$[TG] = [TG_0](1 - X_{FAME}) \quad (4.6)$$

where X_{FAME} is conversion of methyl ester. In addition, in terms of conversion the rate expression is also given as

$$\frac{dX_{FAME}}{dt} = k(1 - X_{FAME}) \quad (4.7)$$

which on integration and rearrangement gives,

$$-\ln(1 - X_{FAME}) = k \cdot t \quad (4.8)$$

The kinetic data for the formation of fatty acid methyl ester was obtained from transesterification of triglyceride with methanol. Table 4.3 show the rate constant (k) of transesterification of palm oil in a fixed bed reactor at various temperatures. The activation energy (E_a) was calculated from the plot of $\ln k$ versus $1/T$.

Table 4.4 The rate constant (k) of transesterification of palm oil in a fixed bed reactor at various temperatures.

Temperature/ °C	k
40	0.1782
50	0.4018
60	0.4313

The plot of $\ln k$ versus $1/T$, constructed from the data obtained at different temperature of the reaction followed by the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (4.9)$$

or

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4.10)$$

where k is the rate constant, E_a is the activation energy, R is gas constant and T is the reaction temperature in Kelvin. The value of activation energy has been found to be 38.6 kJ mol^{-1}

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Natural dolomite was used as the heterogeneous catalyst in transesterification of palm oil and methanol. The heterogeneous catalyst was prepared by physical mixing technique. The calcination temperature of dolomite was 600 °C. Calcined dolomite were mixed with binders and shaped to extrudates form. Catalyst extrudates was calcined at 800 °C before using in transesterification. From XRD pattern of catalyst calcined at 800 °C, the peaks of CaO, MgO, MgAlO₂ and CaAlO were observed. CaO is the major phase that active in transesterification.

Transesterification of palm oil in a fixed bed reactor packed with catalyst extrudates with the presence of nitrogen gas bubbles was carried out at 60 °C. The optimal conditions, the nitrogen gas feed rate was 30 cc/min, total flow rate of reactant was 2.5 mL/min and molar ratio of methanol/oil was 30:1. The achieved FAME yield was 96.7% when nitrogen gas bubbles were fed into the reactor. To compare with the non-nitrogen gas feed system, the FAME yield was not significant different. However, the amount of methanol used in the nitrogen gas feed system is lesser than the non-nitrogen gas feed system. The optimal molar ratio of methanol to oil was 30:1 in the presence of nitrogen gas, which reduce from 50:1 in the non-nitrogen gas feed system.

Nevertheless, the stability test of two systems was compared. It can be seen that transesterification with the presence of nitrogen gas bubbles was more stable than non-nitrogen gas system. It was due to nitrogen gas can help to wash the glyceride derivatives covering on the surface of catalyst.

5.2 Recommendations

To optimize reaction conditions of transesterification in a presence of nitrogen gas feed by reducing molar ratio of methanol to oil or increasing reaction temperature.

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APPENDICES

Appendix A

Calculation of Methanol to Oil Molar Ratio

Example Calculation of methanol to oil molar ratio of 30

Molecular weight of palm oil = 847 g mol⁻¹

Density of palm oil = 1 g ml⁻¹

Molecular weight of methanol = 32.04 g mol⁻¹

Density of methanol = 0.792 g ml⁻¹

For 30:1 of molar ratio of methanol/oil

Oil 1 mole = 847 g and density of oil is 1 g ml⁻¹

So, oil 1 mole = 847 ml

Methanol 30 mole = 961.2 g and density of methanol is 0.792 g ml⁻¹

So, methanol 30 mole = 1213.63 ml

Total volume of methanol and oil was 2060.63 ml

Total flow rate 2.5 ml was used, the ratio of total volume and total flow rate is

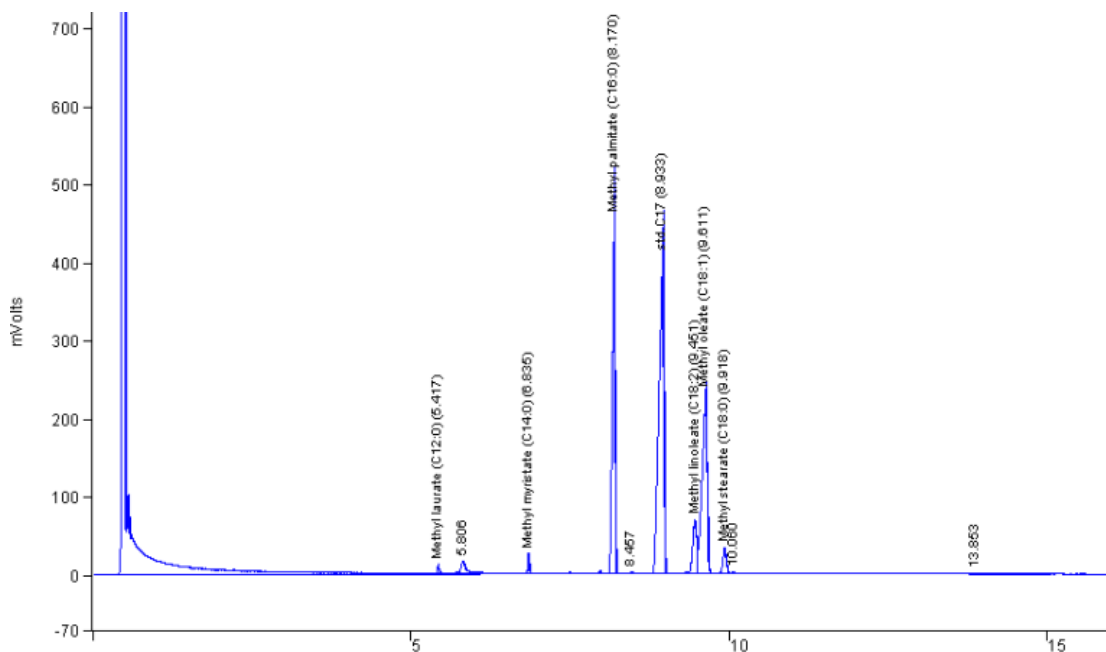
$$2060.63/2.5 = 824.252$$

So, volume of oil is 847/824.252 = 1.0276

So, volume of methanol is 1213.63/824.252 = 1.4724

Appendix B

Calculation of Methyl Ester Content



The methyl ester content (wt.%) was calculate from the formula

$$\text{Wt.}\% = (\sum A_i \times W_{\text{std}}) / A_{\text{std}} \times W_s \times 100$$

Where $\sum A_i$ = The total area from methyl ester, from methyl caprylate (C8:0) to methyl stearate (C18:0)

W_{std} = The weight of methyl undecanoate

A_{std} = The area of methyl undecanoate

W_s = The weight of the sample

Example**Table B1** GC analysis of fatty acid methyl esters

Time/ min	Area
5.028	23223
6.803	56586
9.037	1489
9.415	21176
10.238	6669

The retention time at 5.028 is the retention time of C16

The retention time at 6.803 is the retention time of internal standard (C17)

The retention time at 9.037 is the retention time of C18:0

The retention time at 9.425 is the retention time of C18:1

The retention time at 10.238 is the retention time of C18:2

The weight of sample 0.0253 g

The weight of internal standard 0.0257 g

From, $\text{Wt.\%} = (\sum A_i \times W_{\text{std}}) / A_{\text{std}} \times W_s \times 100$

$$\text{Wt.\%} = ((23223+1489+21176+6669) \times 0.0257 / 56586 \times 0.0253) \times 100$$

$$\text{Wt.\%} = 94.35\%$$

Appendix C

The FAME yield data

Table C1 FAME yield obtained from effect of types of palm oil: RPO oil

Time (min)	FAME yield (wt.%)
	RPO
140	93.7
274	94.5
371	92.5
450	94.6
500	93.8

Table C2 FAME yield obtained from effect of types of palm oil: POO oil

Time (min)	FAME yield (wt.%)
	POO
120	92.6
240	93.5
300	94.2
390	94
460	94.7

Table C3 FAME yield obtained from effect of molar ratio of methanol to oil: 30:1

Time (min)	FAME yield (wt.%)
	30:1
140	93.7
274	94.5
371	92.5
465	94.6
497	90.7
530	90.4
558	93.8
578	93.7

Table C4 FAME yield obtained from effect of molar ratio of methanol to oil: 50:1

Time (min)	FAME yield (wt.%)
	50:1
206	94.7
306	92.5
364	93.1
444	94.8
492	93.8
543	94.1
600	93.3

Table C5 FAME yield obtained from effect of extrudate size: 2mm

Time (min)	FAME yield (wt.%)
	2 mm
206	94.7
306	92.5
364	93.1
444	94.8
492	93.8
543	94.1
600	93.3

Table C6 FAME yield obtained from effect of extrudate size: 1mm

Time (min)	FAME yield (wt.%)
	1 mm
120	95.7
240	96.7
300	96.1
360	96.2
420	95.9

Table C7 FAME yield obtained from effect of the addition of methyl ester: non MEA addition

Time (min)	FAME yield (wt.%)
	1 mm
180	92.3
240	83.5
320	82.7
380	82.4
440	80.4

Table C8 FAME yield obtained from effect of the addition of methyl ester: MEA-75

Time (min)	FAME yield (wt.%)
	1 mm
180	95
240	94.7
320	57.1
360	55.5

Table C9 FAME yield obtained from effect of the addition of methyl ester: MEA-96

Time (min)	FAME yield (wt.%)
	1 mm
195	90.8
270	85.3
320	84.4
374	83.7

Table C10 FAME yield obtained from effect of nitrogen gas feed rate on transesterification of palm oil

Time (min)	FAME yield (wt.%)			
	30 cc/min	50 cc/min	75 cc/min	100 cc/min
180	96.1	96.1	93.9	93.5
240	96.2	95.5	94.1	88
300	96.7	93.1	92.1	80.6
360	94.7	92.4	90.6	78.5
420	95.4	92.2	87.5	77.3
480	95.7	91.1	85.2	74.9

Table C11 FAME yield obtained from effect of molar ratio of methanol/oil

Time (min)	FAME yield (wt.%)	
	30	50
180	96.1	95.3
240	96.2	96.3
300	96.7	95.7
360	94.7	93.2
420	95.4	94.8
480	95.7	94.1

Table C12 FAME yield obtained from effect of total flow rate of reactant

Time (min)	FAME yield (wt.%)		
	2.5 mL/min	3.5 mL/min	5 mL/min
180	96.1	94.3	89.1
240	96.2	93.4	88.7
300	96.7	90.2	83.2
360	94.7	88.1	75.2
420	95.4	83.6	69.6
480	95.7	77.5	54.5

Table C13 FAME yield obtained from effect of nitrogen bubbles

Time (min)	FAME yield (wt.%)	
	nitrogen gas	non nitrogen gas
180	96.1	95.7
240	96.2	95.4
300	96.7	94.9
360	94.7	95.3
420	95.4	93.6
480	95.7	94.1

Table C14 FAME yield obtained from the stability test of transesterification of vegetable oil in a fixed bed reactor in a presence of nitrogen gas bubbles

Time (min)	FAME yield (wt.%)	
	nitrogen gas	non nitrogen gas
180	97.79	98.77
240	97.14	97.96
300	96.29	97.14
360	97.53	97.28
420	95.48	97.93
480	95.73	97.78
540	94.19	97.11
600	93.93	97.51
660	93.41	97.19
720	93.25	97.64
780	93.52	97.37
840	92.91	97.87
900	93.17	97.92
960	92.51	97.16
1020	92.16	98.23
1080	91.63	97.57

Table C15 FAME yield obtained from the kinetic study

Time (min)	FAME yield (wt.%)		
	40 °C	50 °C	60 °C
60	26.2	46.2	61.6
90	32.1	53.4	68.5
120	37.6	60.7	75.6
150	44.3	67.6	82.3
180	50.7	74.2	85.4
210	53.3	78.9	87.2
240	55.4	83.9	88.9

VITAE

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Presentation

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