BIODIESEL PRODUCTION FROM PALM OIL BY TRANSESTERIFICATION PROCESS USING KOH AS CATALYST IN THE PRESENCE OF CO-SOLVENTS

MISS PHAWINEE KRUANGPRADAB

MISS CHALITA SORATHAWORN

MISS ONCHUDA AMORNSAK

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Students	Miss Phawinee Kruangpradab
	Miss Chalita Sorathaworn
	Miss Onchuda Amornsak
Degree	Bachelor of Science
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Advisor	Dr.Amnat Permsubscul

Abstract

The production of biodiesel from transesterification reaction of palm oil and methanol by using KOH as a catalyst in the presence of various types of co-solvent. Three types of co-solvents which are diethyl ether (DEE), diisopropyl ether (DIPE), and methyl ethyl ketone (MEK) were investigated for complete dissolution of methanol and oil. The variables that affect that affect to the biodiesel production such as mole ratio of methanol to oil, amount of catalyst, and reaction time. The temperature of transesterification process was controlled at 60 °c, from the results of experiment can be summarized that MEK was used at the least volume in order to dissolve oil and methanol homogeneously and the best condition that promote high yield of biodiesel was mole ratio of methanol to oil at 1:6, KOH 1%wt to oil. Furthermore the reaction time 1, 2, and 3 hrs gave similar results. The fuel field properties of biodiesel products such as heating value, flash point, acid value, and viscosity were in the range of fuel standard.

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Miss Chalita Sorathaworn

Miss Onchuda Amornsak

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Global emissions of CO_2 and other harmful gases such as CO, SO_x, NO_x and particulates generated by fossil fuel combustion have led to a serious greenhouse effect, acid rain, and the deterioration of human health and the environment. The price of crude petroleum has risen to its highest level. Therefore, the identification of environmentally friendly and renewable sources of alternative energy is becoming an urgent mission for researchers internationally. Biodiesel fuel (BDF) is defined as the mono-alkyl esters of long-chain fatty acids synthesized by transesterification of triglyceride in vegetable oils or animal fats with alcohol, and is therefore a renewable energy resource.

Biodiesel fuel and petroleum diesel have similar properties and performance parameters. Compared with petroleum-based diesel, biodiesel fuel has a relatively high flash point (150 °C) and good lubricating properties. Biodiesel fuel has physical properties and energy content close to those of petroleum diesel, so it can be used directly in conventional diesel engines with no modification. Furthermore, biodiesel fuel is biodegradable and non-toxic, with low emissions of CO, particulates and unburned hydrocarbons. In addition, the promotion of plantation without the destruction of nature in order to get enough feedstock for biodiesel would recycle more CO_2 by photosynthesis and, as a result, minimize the effects of greenhouse gases on the earth's environment. The possible methods for biodiesel fuel production by transesterification of vegetable oils or animal fats with alcohol can be mainly

classified into the following four processes: base-catalysis process; acid-catalysis process; noncatalysis process ; and lipase catalysis process.

Generally, the transesterification reaction is catalysed by a basic or an acid catalyst. Basic catalysis is by far the most commonly used reaction type for biodiesel production because high conversion under mild conditions is reached in comparatively short reaction times. However, basic catalysis produces soaps by neutralizing the free fatty acids in the oils or triglycerides and methyl esters saponification. Heterogeneous catalysts avoid this situation although these catalysts present higher reaction times and deactivation of the catalyst by leaching.

Since the oil and alcohol phases in a transesterification system are immiscible, the mass transfer between the two phases becomes a significant factor that affects the reaction rate. Although the miscibility of the two phases can be enhanced by increasing the temperature, this is an energy-consumptive process. Boocock et al. [1] suggested that addition of a co-solvent such as THF could enhance the miscibility of the phases and speed up the reaction rate, because of the disappearance of interphase mass transfer resistance in the heterogeneous two-phase reaction system [2, 3].

In this research, the co-solvents performance of diethyl ether, diisopropyl ether, and methyl ethyl ketone in transesterification of palm oil to biodiesel is studied. The effects of the reaction conditions such as mole ratio of methanol to oil, mass ratio of catalyst to oil, and reaction time are also investigated.

1.2 Objectives

Transesterification of palm to biodiesel using KOH as a base catalyst and using methyl ethyl ketone (MEK), diethyl ether(DEE), and diisopropyl ether(DIPE) as co-solvents. The main objectives of this study are as follows:

1. To study the co-solvents performance of MEK, DEE, and DIPE in transesterification of palm oil to biodiesel.
2. To investigate the effect of mole ratio of methanol to oil, mass ratio of catalyst to oil, reaction time on biodiesel yield.
3. To evaluate the physical properties and chemical characterization of biodiesel produced from tranesterification of palm oil with co-solvents.

1.3 Scope of study

1. Determination the minimum amount of co-solvent required for the complete dissolution of methanol and oil by turbidimetric analysis.
2. Determination of significant parameters that effected on biodiesel yield are as follows:
   - Types of co-solvents are methyl ethyl ketone (MEK), diethyl ether(DEE), and diisopropyl ether (DIPE).
   - Mole ratios of methanol to palm oil are 4, 6, and 10.
   - Mass ratios of catalyst to palm oil are 0.5%, 1%, and 2%.
   - Reaction times are 1, 2, and 3 hrs.
3. Study about physical properties of biodiesel product such as heating value, flash point and viscosity.

4. Study about chemical properties of biodiesel product determined by acid number and iodine number and chemical characterization determined by Fourier-Transform Infrared Spectrophotometer (FT-IR) and Nuclear Magnetic Resonance Spectrophotometer (NMR).

1.4 Expected Results

1. To know which type of co-solvent that give the highest miscible between oil phase and methanol phase.
2. To know the parameters which effect on transesterification of palm oil to biodiesel by using KOH catalyst and co-solvent.
3. To get the optimum condition for transesterification of palm oil to biodiesel by using KOH catalyst and co-solvent.

CHAPTER 2

FUNDAMENTALS AND RELATED WORKS

2.1 Vegetable oils [4]

Fats and oils constitute a well-defined class of neutral and water insoluble substance that are produced in some quantity by animals and vegetable source Most vegetable oils have the triglyceride structure, which is represented in Figure 2.1. These tri-esters are derived from glycerol and carboxylic acids know as fatty acids. Therefore, vegetable oils are commonly called triglycerides, although a more accurate is triacylglycerols.

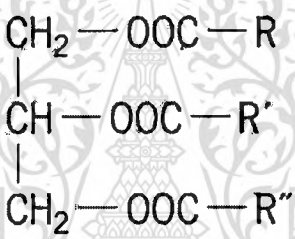

Figure 2.1 Structure of a triglyceride

The fatty acid are almost always straight chain containing between 8 and 22 carbon atoms, and maybe saturate monounsaturated or polyunsaturated. Vegetable oil compositions are normally described in term of their fatty acid contents, referring to the acid ester moieties; actual fatty acids present in the oil are knows as free fatty acids.

The difference chemical and physical properties of vegetable oils depend on the degree of unsaturation of the constituent fatty acids and chain length. Vegetable oils with a proportion of saturate fatty acid are solid or semi-solid at room temperature. The melting point of the fatty acid and their glycerides decrease from saturated to polyunsaturated types, whereas the volatility and boiling points change only slightly.

Table 2.1 Chemical properties of vegetable oil [5]

Vegetable oil	Fatty acid composition, % by weight									Acid[a] value	Phos[b] ppm	Peroxide[c] value
	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3			
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48	0.11	7.00	18.4
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00	0.07	8.00	64.8
Crambe	2.07	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85	0.36	12.00	26.5
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93	0.20	9.00	82.7
Repeseed	3.49	0.85	0.00	0.00	0.00	64.40	0.00	22.30	8.23	1.14	18.00	30.2
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31	0.20	32.00	44.5
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00	0.15	15.00	10.7

[a] Acid values are milligrams of KOH necessary to neutralize the FFA in 1 g of oil sample.

[b] Phosphatide (gum) content varies in direct proportion to phosphorus value.

[c] Peroxide values are milliquivalents of peroxide per 1000 g of oil sample, which oxidize potassium iodide under conditions of the test.

Table 2.2 Fatty acid composition and molecular weight of palm oil [6]

Fatty acid composition (%)	
Dodecanoic acid	0.48
Tetradecanoic acid	0.91
Palmitic acid	37.05
Steric acid	4.82
Oleic acid	46.20
Linoleic acid	10.54
Iodine value	55.91
Saponification	209.53
Molecular weight	850.25

2.2 The production of biodiesel [5]

2.2.1 Direct use and blending

This method is blending vegetable oil and diesel fuel directly. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. The advantages of vegetable oils as diesel fuel are liquid nature-portability, heat content (80% of diesel fuel), ready availability and renewability. The disadvantages are higher viscosity, lower volatility and the reactivity of unsaturated hydrocarbon chains. Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines. The problems include coking and trumpet formation on the injectors to such an extent that fuel atomization does not

occur properly, carbon deposits, oil ring sticking and thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils.

2.2.2 Microemulsions

A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. To solve the problem of the high viscosity of vegetable oils.

2.2.3 Thermal cracking or pyrolysis

Pyrolysis, strictly defined, is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids.

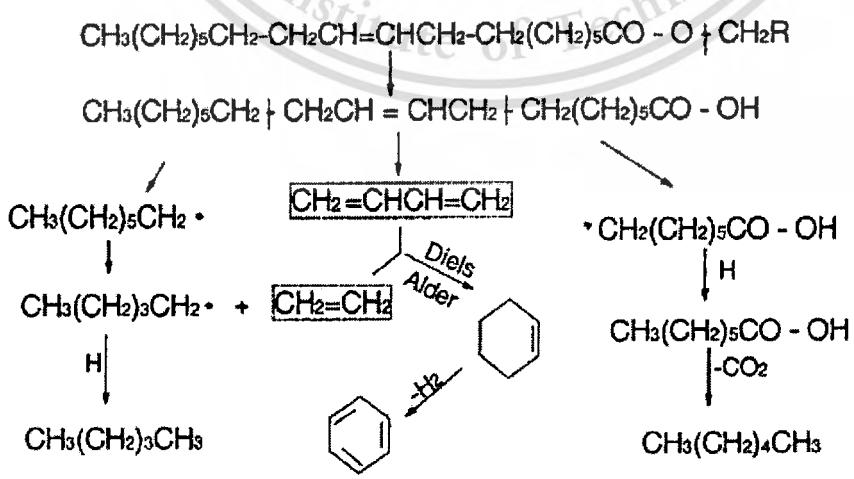

Figure2.2 The mechanism of thermal decomposition of triglycerides

2.2.4Transesterfication

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The overall process is a sequence of three consecutive and reversible reactions, in which diand monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification[7].

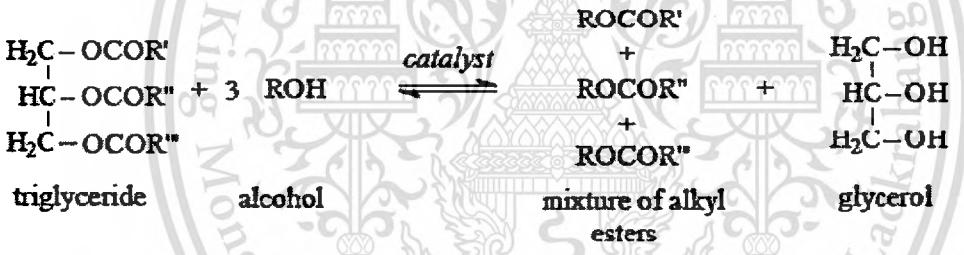

Figure 2.3 Transesterification of vegetable oils

Transesterification reaction can be classified as

2.2.4.1 Acid-Catalyzed Processes

The transesterification process is catalyzed by BrØnsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100°C and more than 3 h to reach complete conversion.

The mechanism of the acid-catalyzed transesterification of vegetable oils, the protonation of the carbonyl group of the ester leads to the carbocation which, after a

nucleophilic attack of the alcohol, produces the tetrahedral intermediate, which eliminates glycerol to form the new ester, and to regenerate the catalyst H^+. According to this mechanism, carboxylic acids can be formed by reaction of the carbocation with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

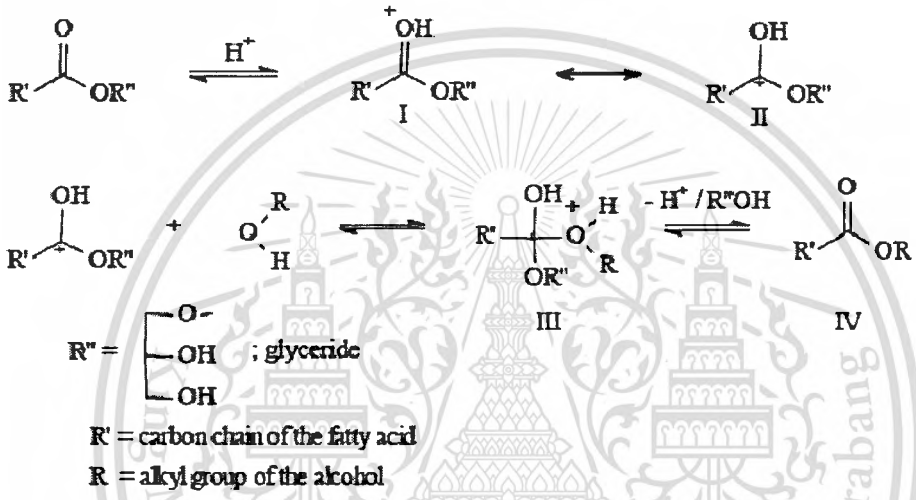

Figure 2.4 Mechanism of the acid-catalyzed transesterification of vegetable oils

2.2.4.2 Base-Catalyzed Processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oils, the first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride

generates a tetrahedral intermediate, from which the alkyl ester and the corresponding anion of the diglyceride are formed. The latter deprotonates the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. This undesirable saponification reaction reduces the ester yields and considerably difficults the recovery of the glycerol due to the formation of emulsions[8].

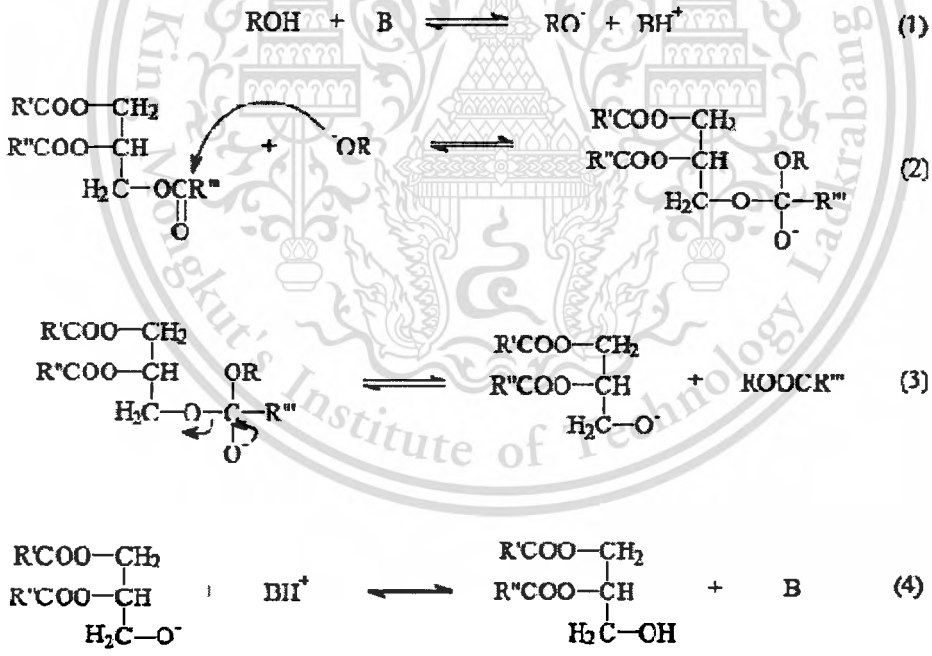

Figure 2.5 Mechanism of the base-catalyzed transesterification of vegetable oils

2.2.4.3 Supercritical Alcohol

Supercritical methanol is believed to solve the problems associated with the two-phase nature of normal methanol/oil mixtures by forming a single phase as a result of the

lower value of the dielectric constant of methanol in the supercritical state. As a result, the reaction was found to be complete in a very short time. Compared with the catalytic processes under barometric pressure, the supercritical methanol process is non-catalytic, involves a much simpler purification of products, has a lower reaction time, and is more environmentally friendly. However, this method requires extreme temperature and pressure conditions, and induces breakdown of unsaturated fatty acids and trans isomerization, leading to adverse effects on the fluidity of the fuel at low temperatures. So that oils and fats can be converted into FAME successfully at lower temperature by supercritical methanol with co-solvent such as propane. Furthermore, CO_2 addition to supercritical methanol can make the reaction temperature lower [9, 10].

2.3 Byproduct from transesterification

In the production of biodiesel, a catalyst is used to promote transesterification, producing methyl esters (biodiesel) and a glycerol byproduct[15].

Properties of glycerol

1) Physical properties

Glycerol is completely soluble in water and alcohol. It is slightly soluble in ether, ethyl acetate, and dioxane and insoluble in hydrocarbons. Glycerol has useful solvent properties similar to those of water and simple aliphatic alcohol's because of its three-hydroxyl groups. Glycerol is a useful solvent for many solids, both organic and inorganic which is particularly important for the preparation of pharmaceuticals. The solubility of gases in glycerol, like other liquids is temperature and pressure dependent.

2) Chemical properties

Glycerol is a reactive molecule that undergoes all the usual reactions of alcohols. The two terminal primary hydroxyl groups are more reactive than the internal secondary hydroxyl group. Under neutral or alkaline conditions, glycerol can be heated to 250°C without formation of acrolein. Reactions with glycerol are therefore best carried out under alkaline or neutral conditions at 180°C, alkaline glycerol begins to dehydrate forming ether-linked polyglycerols. At room temperature glycerol rapidly absorbs water. When dilute it is attacked by microorganism. On oxidation, glycerol yields variety of product depending upon the reaction conditions. By the use of mild oxidizing agent it is possible to oxidize only one hydroxyl group to yield Glyceraldehyde.

2.4 Biodiesel fuel properties [16]

2.4.1Cetane number

As indicator of ignition quality, the CN is a prime indicator of fuel quality in the realm of diesel engines. It is conceptually similar to the octane number used for gasoline. Generally, a compound that has a high octane number tends to have a low CN and vice versa. The CN of a diesel fuel is related to the ignition delay time, i.e., the time that passes between injection of the fuel into the cylinder and onset of ignition. The shorter the ignition delay time, the higher the CN and vice versa.

2.4.2 Heat of combustion

Gross heat of combustion is another fuel property indicating the suitability of fatty compounds as diesel fuel. HG increases with chain length.

2.4.3 Cold flow properties

The cloud point, which usually occurs at a higher temperature than the pour points, is the temperature at which a liquid fatty material becomes cloudy due to formation of crystals and solidification of saturates. Solids and crystals rapidly grow and agglomerate, clogging fuel lines and filters and causing major operability problems. With decreasing temperature, more solids form and the material approaches the pour point, the lowest temperature at which it will still flow. Saturated fatty compounds have significantly higher melting points than unsaturated fatty compounds and in a mixture they crystallize at higher temperature than the unsaturates. Thus biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds will display higher cloud points and pour points.

2.4.4 Oxidative stability

Oxidative stability of biodiesel has been the subject of considerable research. This issue affects biodiesel primarily during extended storage. The influence of parameters such as presence of air, heat, light, traces of metal, antioxidants, peroxides as well as nature of the storage container. The reason for autoxidation is the presence of double bonds in the chains of many fatty compounds. The autoxidation of unsaturated fatty compounds proceeds with different rates depending on the number and position of double bonds. Numerous other methods, including wet-chemical ones such as acid value and peroxide value, pressurized differential scanning calorimetry, etc., have been applied in oxidation studies of biodiesel.

2.4.5 Viscosity

Viscosity affects the atomization of a fuel upon injection into the combustion chamber and thereby ultimately the formation of engine deposits. The higher the viscosity, the greater the tendency of the fuel to cause such problems.

2.4.6 Lubricity

Desulfurization of conventional, petroleum derived diesel fuel reduces or eliminates the inherent lubricity of this fuel, which is essential for proper functioning of vital engine components such as fuel pumps and injectors. However, non-sulfur polar compounds are also eliminated from petrodiesel during the desulfurization process and it is likely the loss of these compounds and not the sulfur-containing materials that causes the loss of lubricity Another study states that phenols and polyaromatic compounds are the species imparting lubricity to petrodiesel fuels.

Table 2.3 Fuel properties of the biodiesel [17]

Biodiesel physical characteristics	
specific gravity	0.87–0.89
kinematic viscosity @ 40°C	3.7–5.8
cetane number	46–70
higher heating value (btu/lb)	16,928–17,996
sulfur by weightt (%)	0.0–0.0024
cloud point (°C)	-11 to 16
pour point (°C)	-15 to 13
iodine number	60–135
lower heating value (btu/lb)	15,700–16,735
flash point(°C)	>120
acid value (mg KOH/g oil)	<0.5

2.5 Advantages of biodiesel [18]

Advantages to environments

1. Biodiesel is not harmful to the environment. Unlike its counterpart, a car using biodiesel produces fewer emissions. If a vehicle uses a traditional diesel, the vehicle emits black, stinky smoke. With biodiesel, the smoke becomes very clean indeed.
2. Biodiesel is reduces the Greenhouse effect.
3. Biodiesel that produce from waste oil can reduce the vegetable oil to provide food again. Because it will make cancer to human health.
4. Biodiesel reduces the environment effect of a waste product. Because biodiesel is made out of waste product itself, it does not contribute to nature's garbage at all. Biodiesel can be made out of used cooking oil. So instead of throwing these substances away, the ability to turn them into biodiesel becomes more than welcome.

Advantages to the diesel engine

1. Biodiesel may not require an engine modification. Some cars can take advantage of biodiesel without the need to undergo engine alterations. Some mix 20% biodiesel with regular diesel. Doing so enables the car to benefit from the good points of biodiesel without the hassle.
2. Biodiesel can make the vehicle perform better. It is noted that biodiesel has a cetane number of over 100. Cetane number is used to measure the quality of the fuel's ignition. If your fuel has a high cetane number, you can be sure that what you get is a very easy cold starting coupled with a low idle noise.

3. Biodiesel can make your car last longer. Because of the clarity and the purity of biodiesel, you can be sure it will not have too many impurities to harm your car. It is actually more lubrication. A car's power output is unaffected by this type of diesel.

Advantages to the economics

1. Biodiesel is energy efficient. If the production of biodiesel is compared with the production of the regular type, producing the latter consumers more energy. Biodiesel does not need to be drilled, transported, or refined like petroleum diesel. Producing biodiesel is easier and it less time consuming.
2. Biodiesel can provide new opportunities to the agriculturist because we keep the waste from agriculture.
3. Reduces importation on foreign oil and fossil fuel.

2.6 Co-solvent for biodiesel production

The main problem for the lower rate of transesterification is that the reaction mixture is not homogeneous because the oils and alcohols are not miscible each other because of their chemical structures. Oil disperses in the methanol medium, so the probability and the rate of collision of the glyceride and the methoxide (the mixture of methanol and the alkaline catalyst – KOH or NaOH) molecules becomes lower. This lowers the rate of collisions of molecules and so the rate of reaction causes longer reaction times, higher operating expenses and labor. To overcome this difficulty of the heterogeneous mixing of the reactants, a single phase reaction has been proposed by Boocock et al. The proposed model includes a cyclic solvent could enhance the miscibility of the phases and speed up the reaction rate, because of

the disappearance of interphase mass transfer resistance in the heterogeneous two-phase reaction system [13, 14].

2.6.1 Diethyl ether

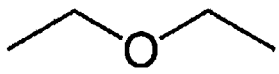

Figure 2.6 Diethyl ether structure

Diethyl ether, also known as ether, is the organic compound with the formula $(CH_3\text{-}CH_2)_2O$. It is a colorless and highly flammable liquid with a low boiling point and a characteristic odor. It is the most common member of a class of chemical compounds known generically as ethers.[11]

2.6.2 Diisopropyl Ether

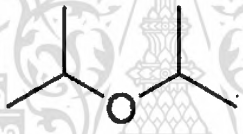

Figure 2.7 Diisopropyl ether structure

Diisopropyl ether is secondary ether that is used as a solvent. It is a colorless liquid that is slightly soluble in water, but miscible with most organic solvents. It is also used as an oxygenate gasoline additive. Diisopropyl ether is sometimes represented by the abbreviation DIPE. [12]

2.6.3 Methyl Ethyl ketone

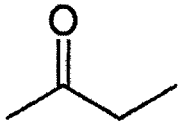

Figure 2.8 Methyl ethyl ketone structure

Butanone, better known as methyl ethyl ketone or MEK, is an organic compound with the formula $CH_3C(O)CH_2CH_3$. This colorless liquid ketone has a sharp, sweet odor reminiscent of butterscotch and acetone. It is produced industrially on a large scale, and also occurs in trace amounts in nature. [19]

Table 2.4 Physical properties of co-solvent

co-solvent	Molecular formula	Molecular weight (g/mol)	Density (g/cm_3)	Boiling point (°C)	Viscosity (cP)	Polarity Index
DEE	$C_2H_5OC_2H_5$	74.12	0.71	34.6	0.22 (25 °C)	2.8
DIPE	$C_6H_{14}O$	102.18	0.725	69	0.30 (20 °C)	2.2
MEK	C_4H_8O	72.11	0.805	79.6	0.43 (20 °C)	4.5

2.7 Literature reviews

Boocock et al. (1996) [1] studied the use of a co-solvent such as tetrahydrofuran or methyl tertiary butyl ether speeds up methanolysis considerably. However, like one-phase butanolysis, one-phase methanolysis initially exhibits a rapid formation of ester, but then slows drastically. Experiments show that the half-life of the hydroxide catalyst is too long to explain the sudden slowing of the reaction. Similarly, lower rate constants for the methylation of the mono- and diglycerides are not a reasonable explanation. Instead the cause has been identified as the fall in polarity which results from the mixing of the nonpolar oil with the methanol. This lowers the effectiveness of both hydroxide and alkoxide catalysts. Increasing

the methanol/oil molar ratio to 27 in the one-phase system raises the polarity such that the methyl ester content of the ester product exceeds 99.4 wt% in 7 min. This has obvious implications for the size of new methyl ester plants as well as the capacity of existing facilities.

Guoqing, G. et al. (2009) [2] Studied the synthesis of biodiesel fuel (BDF) from sunflower oil by using a KOH catalyst at 25 ◦C in the presence of various co-solvents, was investigated in a closed batch reactor. The minimum co-solvent/methanol molar ratio required for the complete dissolution of methanol and sunflower oil was determined. Addition of a co-solvent enhanced the transesterification rate at the methanol/oil molar ratio of 6 at 25◦C, and sunflower oil was almost completely converted into BDF after 20 min reaction while only approximately 78% conversion was reached in the absence of a co-solvent. The oil conversion was influenced by the co-solvent/methanol molar ratio, methanol/oil molar ratio, and catalyst concentration. The maximum oil conversion for each co-solvent was obtained at the minimum co-solvent/methanol molar ratio. DME could be considered as an effective co-solvent in BDF production and was more easily recovered from the products after depressurization of the reaction system.

Ratree, P. (2008) [8] Biodiesel production by transesterification at the 6:1 methanol : oil molar ratio in the presence of a 1% by weight KOH catalyst addition of 1.25 volumes Co-solvent ,Tetrahydrofuran (THF) and Hexane Reaction times at 20,40 and 60 min, temperature 40 and 60 ^{0}C, speed of mixing 200,400 and 600 rpm respective. The effective of variation in temperature at 60 ^{0}C for all condition have methyl ester maximum and increasing

times too, speed of mixing increased for mass transfer of triglyceride from oil phase to methanol-oil faster than in non-mixing system. The effective of variation in co-solvent, THF produces an oil-methanol one phase system in which methanolysis speeds up dramatically and occurs faster than in hexane and co-solvent-free system.

Abraham, C. et al. (2009) [3] Studied the transesterification of sunflower oil with methanol was carried out using potassium hydroxide and methoxide as catalysts and MTBE as co-solvent. The aim of this work was to study and optimize the reaction parameters. Chosen parameters were reaction time, catalyst amount and methanol amount (expressed as catalyst-to-oil and methanol-to-oil molar ratios, respectively). The response variables were methyl ester content (ME) and acid value (AV) due to their relationship with the completion and yield reaction, respectively. A factorial plus composite design was developed to carry out the optimization. From this design, several quadratic models have been used to fit the experimental data. All the factors studied had a positive influence on methyl ester content and acid value, except the methanol amount on acid value.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Chemicals

1) Palm oil (Yok brand)
2) Methanol(CH_3OH), Analytical grade from Lab Scan Company
3) Anhydrous magnesium sulfate($MgSO_4$), Analytical grade from Carlo Erba Company
4) Ethanol(C_2H_5OH), Analytical grade from Carlo Erba Company
5) Potassium hydroxide(KOH), Analytical grade from Carlo Erba Company
6) Methyl ethyl ketone (C_4H_8O), Analytical grade from from Lab Scan Company
7) Diethyl ether($C_4H_{10}O$), Analytical grade from Carlo Erba Company
8) Diisopropyl ether ($C_6H_{14}O$), Analytical grade from Carlo Erba Company
9) Deionized water
10) Phenolphthalein
11) Paraffin oil

3.2 Apparatus and Instruments

1) Three necks round bottom flask	500 ml
2) Beaker	50 ml, 100 ml, 250 ml and 500 ml
3) Volumetric	100 ml
4) Erlenmeyer flask	250 ml
5) Pipette	10 ml

6) Burette 50 ml

7) Separatory funnel 500 ml

8) Condenser

9) Thermometer

10) Hot plate

11) Magnetic stirrer

12) Water bath

13) Balance

14) Litmus paper

15) Vacuum-filtrated

16) Fourier Transform Infrared Spectroscopy (FT-IR Spectrum GX, The Department of Chemistry, KMITL)

17) Fourier Transform Nuclear Magnetic Resonance Spectrometer (Advance DPX300, Bruker, the Department of Chemistry, KMITL)

18) Auto Flash point ISL FP935G2

19) Automatic Digital Kinematic Viscometer ERTCO CAV-2000

20) Adiabatic Bomb Calorimeter-PARR 1281

3.3 Experimental Procedure

3.3.1 **Part 1** : The minimum amount of co-solvent required for the complete dissolution of methanol and oil

1) Palm oil and methanol at given mole ratio were added to the erlenmeyer flask.

2) The co-solvent was slowly added from the burette to the oil and methanol while continuously shaking well, and mixture changed from turbid to transparent.

3) The volume of co-solvent dissolved in the oil and methanol system was recorded from the burette.

Part 2: Transesterification reaction

1) The reflux apparatus was set up which consists of three necks round Bottom flask immersed in paraffin oil bath, fitted with thermometer, Condenser and magnetic stirrer.

2) The reactor was initially charged with the palm oil and the co-solvent needed to obtain an initial single phase mixture and the mixture are heated by paraffin oil bath. The temperature of the mixture was controlled at 60±5 °C

3) The catalyst (KOH) was dissolved in the methanol and the resulting solution was added to the reactor under magnetic stirring.

4) The reaction was timed as soon as the catalyst and methanol solution was added to the reactor.

5) At the end of reaction time, the product solution was poured into the separatory funnel, it was separated into two layers, the upper one was biodiesel while the lower layer was formed out of glycerol and glycerol was drowning off.

6) Remove co-solvent by using rotational evaporator

7) Washing biodiesel with 10 ml of 0.01M HCl and followed by 10 ml of distilled water various times to remove catalyst basically until it became neural solution, tested by litmus paper.

8) Dried biodiesel over anhydrous magnesium sulfate and remove it out of the biodiesel by vacuum filtration.

9) Weighed product to determine yield of biodiesel.

10) Pour biodiesel into a bottle and keep for analyze physical and chemical properties.

3.3.2 Measure of acid value [20]

1) Each 10 ml of each ethanol and diethyl ether were mixed in the 250 ml Erlenmeyer flask then 3-4 drops of phenolphthalein indicator was added.

2) The mixture was titrated with 0.01 M KOH until the pale pink appeared.

3) 5 g of methyl ester was added into the flask then it was titrated with 0.01 M KOH until its end point which pale pink solution was observed.

Calculation

$$Moles\ of\ KOH\ used = \frac{MV}{1000}$$

$$Milligrams\ of\ KOH = \frac{0.01V}{1000} \times MW_{KOH} \times 1000$$

$$= 0.01V \times 56$$

$$Acid\ value = \frac{0.01V}{g} \times 56$$

Where g is grams of oil used

V is milliliters of KOH used for titration

3.3.3 Measure of physical properties and chemical characterization

1) Viscosities of biodiesel were measured by Viscometer ERTCO CAV-2000 as ASTM D445 standard.
2) Flash point of biodiesel was analyzed by Auto Flash point ISL FP935G2 as ASTM D93 standard.
3) Heating value of biodiesel was analyzed by Adiabatic Bomb Calorimeter-PARR 1281as ASTM 2015 standard
4) The chemical property of biodiesel product was determined by acid number.
5) The chemical characterizations of biodiesel were determined by Fourier Transform Infrared Spectrophotometer (FT-IR) and Fourier Transform Nuclear Magnetic Resonance Spectrometer (FT-NMR)

3.4 Experimental Design

From the experiment, methyl ester conversion was influenced by the methanol/oil mole ratio, type of co-solvent, catalyst concentration. The experimental runs of each factor were shown in table 3.4.1-3.4.3

Table 3.4.1 The experimental runs for study effect of mole ratio of methanol to oil on biodiesel yield.

Co-solvent	Mole of methanol	Mole of Palm oil	% of catalyst to oil (%wt)	Reaction Time (h)	Temperature (°C)
DEE	4	1	1	2	60±5
	6	1	1	2	
	10	1	1	2	
DIPE	4	1	1	2	60±5
	6	1	1	2	
	10	1	1	2	
MEK	4	1	1	2	60±5
	6	1	1	2	
	10	1	1	2	

Table 3.4.2 The experimental runs for study effect of mass ratio of catalyst to oil on biodiesel yield.

Co-solvent	% of catalyst to oil (%wt)	Mole ratio of methanol to oil	Reaction time (h)	Temperature (°C)
MEK	0.5	6:1	2	60±5
	1	6:1	2	
	2	6:1	2	

Table 3.4.3 The experimental runs for study effect of reaction time on biodiesel yield.

Co-solvent	Reaction time (h)	% of catalyst to oil (%wt)	Mole ratio of methanol to oil	Temperature (°C)
MEK	1	1	6:1	60±5
	2	1	6:1	
	3	1	6:1	

CHAPTER 4

RESULTS AND DISCUSSION

The synthesis of biodiesel from palm oil and methanol with homogeneous base catalysts, KOH in the presence of co-solvent were investigated. The results as described in this chapter were classified into four parts. First, the minimum amount of co-solvent required for the complete dissolution of methanol and oil was investigated. Next, the effect of operating variables on production of biodiesel such as type of co-solvent, amount of catalyst, mole ratio of methanol to palm oil, and reaction time were studied. In third part, the chemical characterization of biodiesel that obtained from transesterification reaction was determined by Fourier-Transform Infrared Spectrophotometer (FT-IR) and Fourier-Transform Nuclear Magnetic Resonance Spectrometer (FT-NMR). Finally, determination of physical properties of FAME such as viscosity, flash point, heating value, and acid value were discussed.

4.1 The minimum volume of co-solvent required for the complete dissolution of methanol and oil

The three types of co-solvent were used to investigate the minimum amount of co-solvent required for the complete dissolution of methanol and oil, there are diethyl ether (DEE), diisopropyl ether (DIPE), and methyl ethyl ketone (MEK). The minimum volume and mole of co-solvents at various mole ratios of methanol and palm oil were shown in Table 4.1 and Figure 4.1

Table 4.1 The minimum volume of co-solvent required for the complete dissolution of methanol and oil

Co-solvent	Mole of methanol	Mole of Palm oil	Volume of co-solvent required (cm^3)
DEE	4	1	5.0
	6	1	20.9
	10	1	53.2
DIPE	4	1	4.7
	6	1	16.9
	10	1	45.1
MEK	4	1	3.0
	6	1	9.0
	10	1	26.9

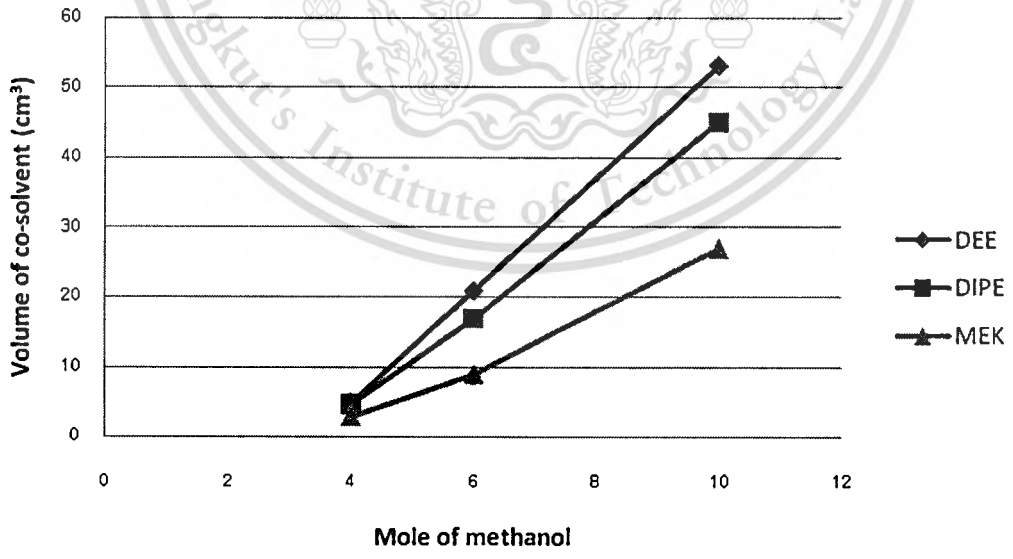

Figure 4.1 The minimum volume of co-solvent required for the complete dissolution of methanol and oil at various mole ratios of methanol to palm oil

From figure 4.1, when increasing mole ratio of methanol to oil from 4:1 to 10:1 the volume of co-solvents that required for complete dissolution were also increased. At the same mole ratio of methanol to oil, MEK was used at the least volume for dissolved oil and methanol homogeneously when compares with the others co-solvent while DEE was used at the highest volume for complete dissolution of methanol and oil.

The oil and alcohol phases in a transesterification system are immiscible, the mass transfer between the two phases becomes a significant factor that affects the reaction rate. The addition of a co-solvent could enhance the miscibility of the phases and speed up the reaction rate, because of the disappearance of interphase mass transfer resistance in the heterogeneous two-phase reaction system.

From the experimental results in Figure 4.1, it can be reported that the minimum volume of co-solvent required for homogeneous phase of oil and methanol was in order of DEE > DIPE > MEK. Because three types of co-solvent are different in polarity which MEK has highest polarity index (4.5) when compare with DEE (2.8) and DIPE (2.2) [21] therefore, MEK can dissolve in methanol which has polarity index 6.6 and led methanol to dissolve in oil better than others co-solvent.

4.2 Transesterification of palm oil and methanol with KOH as homogeneous catalyst base in presence of co-solvents

The transesterification reactions of palm oil with methanol to obtain biodiesel product were carried out by varying the co-solvent, mole ratio of methanol to palm oil, amount of catalyst, and reaction time to obtain the highest biodiesel yield. The factors affecting the yield of biodiesel were discussed as follows:

4.2.1 The effect of mole ratio of methanol to palm oil

The study of mole ratio of methanol to palm oil that affected to yield of biodiesel were varied from 4:1 to 10:1 with the constant of catalyst content at 1%wt, reaction temperature at 60 °C and reaction time 2 hr. The experimental results were reported in Table 4.2.1 and comparison of biodiesel yield was obtained from reactions that presence in various types of co-solvent as shown in Figure 4.2.1.

Table 4.2.1 The effect of mole ratio of methanol to palm oil

Co-solvent	Mole of Methanol to oil	% of catalyst (%wt)	Reaction Time (h)	%wt of biodiesel
DEE	4:1	1	2	41
	6:1	1	2	57
	10:1	1	2	53
DIPE	4:1	1	2	65
	6:1	1	2	83
	10:1	1	2	74
MEK	4:1	1	2	74
	6:1	1	2	86
	10:1	1	2	81

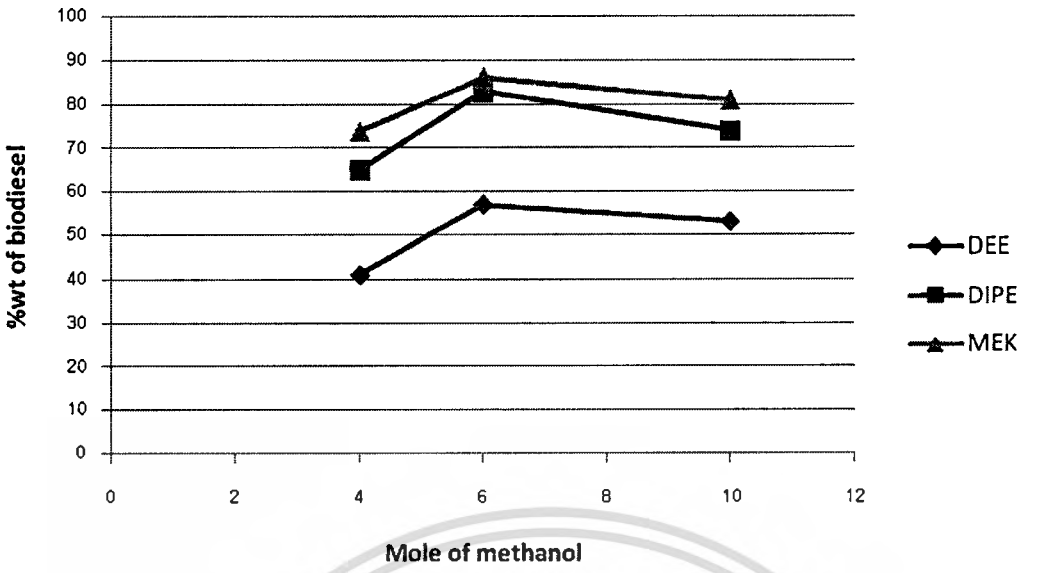

Figure 4.2.1 The effect of mole ratio of methanol to oil on %wt of biodiesel that that presence in various types of co-solvent

From figure 4.2.1, increasing mole ratio of methanol to oil from 4:1 to 6:1, it can be observed that the yield biodiesel was increased with the highest %wt of biodiesel was observed at 6:1 of mole ratio for all types of co-solvents. However, the %wt of biodiesel was decreased with mole ratio of methanol to oil over 6:1

The transesterification reactions of triglyceride and methanol catalyzed by basic catalyst was the reversible reaction as shown in equation (1)

Triglyceride + 3 Methanol $\rightleftharpoons$ 3 FAME + Glycerol (1)

Higher amount of FAME was generated by adding excess amount of methanol in the reaction, in the other hand, insufficient amount of methanol caused the low yield of biodiesel. According to Figure 4.2.1, low %wt of biodiesel was obtained when using mole ratio of

methanol to palm oil at 4:1. Then, it can be summarized that at 6:1 mole ratio of methanol to oil that showed the highest yield of biodiesel for all types of co-solvents. %wt of biodiesel, at 10:1 mole ratio of methanol to oil was decrease because of the dilution of catalyst concentration when added the large amount of methanol.

4.2.2 The effect of the amount of catalyst

In this research, the amount of catalyst was varied from 0.5%, 1%, and 2% wt with the constant of mole ratio of methanol to palm oil at 6:1, reaction temperature 60 °C, reaction time 2 hrs in the presents of MEK as co-solvent. The results were shown in Table 4.2.2 and Figure 4.2.2.

Table 4.2.2 The effect of the amount of KOH catalyst on biodiesel yield.

Co-solvent	% of catalyst (%wt)	Mole ratio of methanol to oil	Reaction time (h)	%wt of biodiesel
MEK	0.5	6:1	2	78
	1	6:1	2	86
	2	6:1	2	49

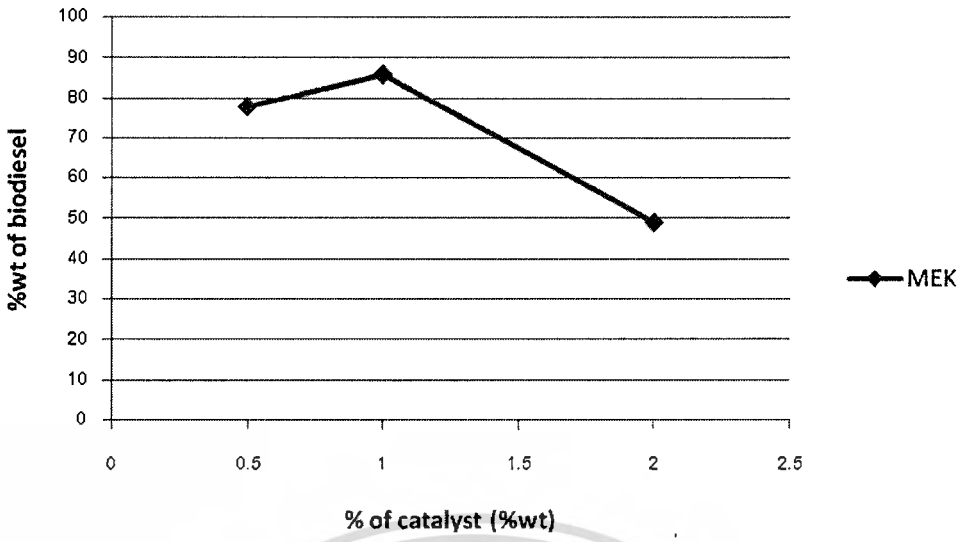

Figure 4.2.2 Effect of the amount of catalyst on %wt of biodiesel by using KOH as homogeneous base catalyst in presence of MEK co-solvent

From Figure 4.2.2, the increasing amount of KOH catalyst from 0.5 to 1 wt%, the yield of biodiesel increased from 78% to 86% but over 1%wt of KOH yield of biodiesel was decreased. The reason is that during the transesterification reaction, the amount of KOH catalyst was added is to complete transesterification reaction of triglyceride was reacted with methanol. Since, adding excess of KOH which catalyst could contains moisture that led to hydrolysis to the reaction which saponification reaction can be occurred that result in the decreasing of %wt of biodiesel.

4.2.3 Effect of reaction time

One of the most important variable affecting the %wt of biodiesel was the reaction time. The effect of reaction time was studied by fixing the reaction temperature at 60 °C, mole ratio of methanol to oil was 6:1, and amount of catalyst at 1%wt. The experimental

results were reported in Table 4.2.3 and comparison the effect of reaction time on biodiesel yield obtained from reaction that catalyzed by KOH in presence of MEK co-solvent was shown in Figure 4.2.3.

Table 4.2.3 Effect of reaction time to %wt of biodiesel

Co-solvent	Reaction time (h)	% of catalyst (%wt)	Mole ratio of methanol to oil	%wt of biodiesel
MEK	1	1	6:1	88
	2	1	6:1	86
	3	1	6:1	89

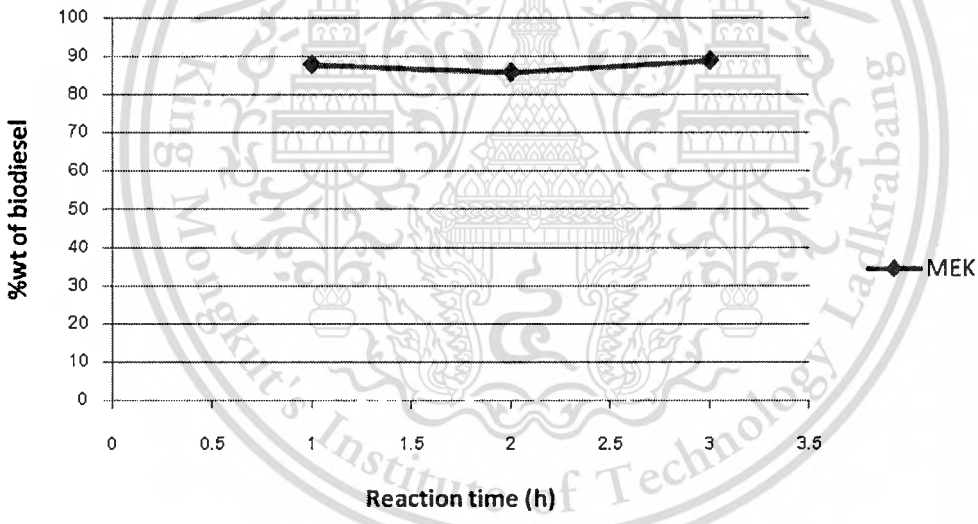

Figure 4.2.3 Effect of the reaction time on %wt of biodiesel by using KOH as homogeneous base catalyst in presence of MEK co-solvent.

From figure 4.2.3, shown changes in %wt of biodiesel with reaction time in the presence of MEK as co-solvent when the transesterification reactions were carried out under the condition of methanol to oil ratio was 6:1 with a 1%wt of KOH catalyst.

Transesterification of triglycerides with methanol is a reverse equilibrium reaction. Thus, a relative high methanol / oil is required to force the reaction to produce in the direction of methyl ester formation. At a relatively high methanol/oil molar ratio of 6.0, %wt of biodiesel increased to 88% within 1 hr, it was found that the relation reached an equilibrium point and the %wt of biodiesel stayed at a constant level when the reaction time over 1 hr.

It can be summarized that MEK was the most effective co-solvent that could overcome the immiscibility problem between oil and methanol. When MEK was added, the immiscible two phases system was changed to the homogeneous emulsion state.

4.3 Product Characterization by FT-IR and FT-NMR

4.3.1 Product Characterization by FT-IR

The functional groups of FAME synthesized from palm oil and methanol with homogeneous base catalysts in presence of co-solvent were determined by Fourier-Transform Infrared Spectrophotometer at the School of Chemistry, Faculty of Science, KMITL. The FT-IR spectrum of FAME was shown in Figure 4.3.1.

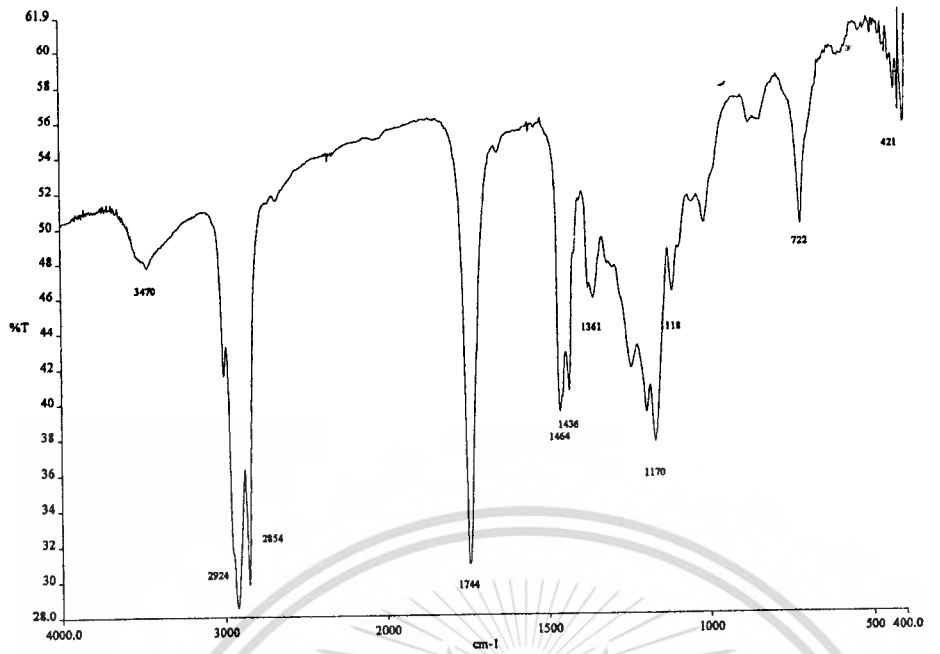

Figure 4.3.1 FT-IR spectrum of biodiesel from transesterification of palm oil with KOH as a homogeneous base catalyst.

Figure 4.3.1 showed FT-IR spectrum that the structure of biodiesel was confirmed at 1196 cm^{-1} for $-OCH_3$ stretching, 1245 cm^{-1} for C(=O)O stretching, 1744 cm^{-1} for C=O stretching, and 2854 cm^{-1} for alkane stretching.

4.3.2 Characterization of FAME by FT-NMR

The chemical structure of FAME synthesized from palm oil and methanol with homogeneous base catalysts in presence of co-solvent was measured by Fourier-Transform Nuclear Magnetic Resonance Spectrometer or called FT-NMR (Advance DPX300, Bruker, the Department of Chemistry, Faculty of Science, KMITL. The ^{1}H-NMR spectrum of palm oil and FAME was shown in Figure 4.3.2-4.3.3.

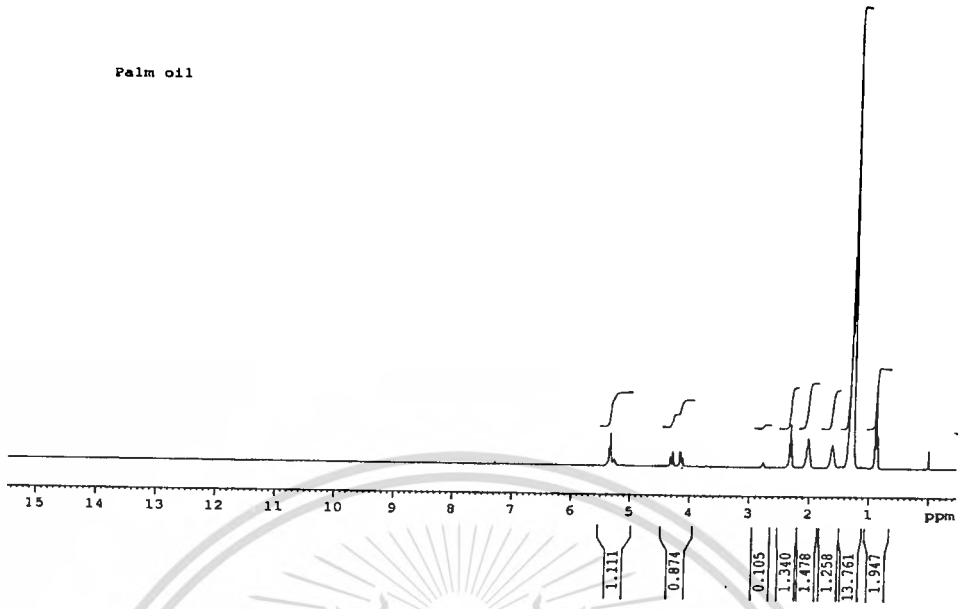

Figure 4.3.2 ^{1}H-NMR Spectrum of palm oil.

From Figure 4.3.2, ^{1}H-NMR spectrum of biodiesel showed the signals of methyl proton (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.85-0.88 and 1.25-1.30 ppm,. The signal of -CH_2-C-COO-C- appears at δ 1.61 ppm. The signal of –CH_2-C=C- appears at δ 2.01-2.05 ppm. The signal of -CH2-COO-C- appears at δ 2.28-2.33 ppm. The signal of –C=C-CH_2-C=C- appears at δ 2.74-2.76 ppm. The signal of –CH2-OOC-R and –CH-OOC-R appears at δ 4.11-4.17 and 4.27-4.32 ppm. The signal of –CH=CH- appears at δ 5.26-5.35 ppm.

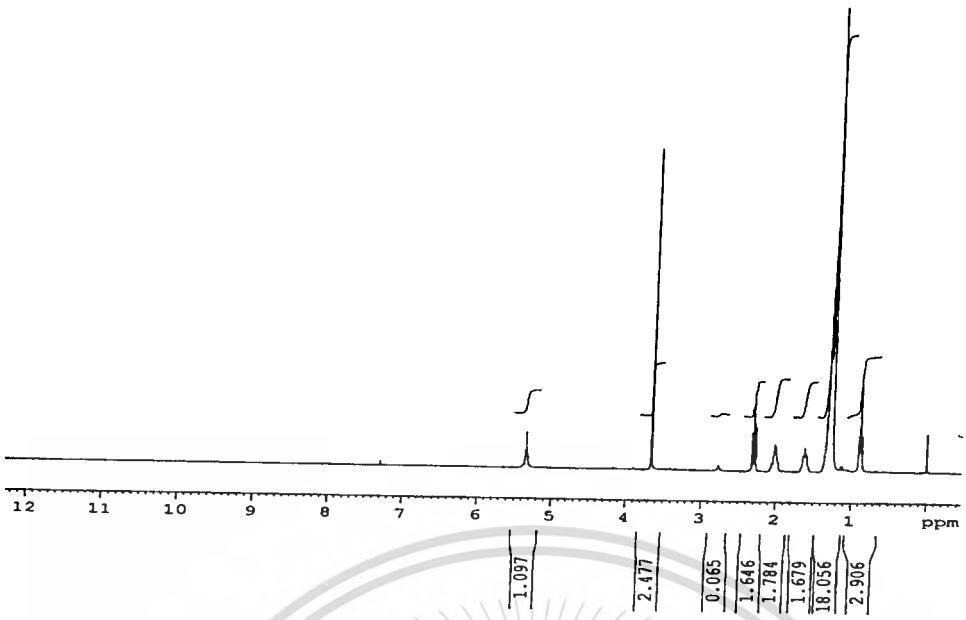

Figure 4.3.3 ^{1}H-NMR Spectrum of biodiesel.

From Figure 4.3.3 ^{1}H-NMR spectum of biodiesel showed the signals of methyl proton (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.85-0.88 and 1.25-1.30 ppm, respectively. The signal of -CH_2-C-COO-C- appears at δ 1.61 ppm. The signal of –CH_2-C=C- appears at δ 2.01-2.05 ppm. The signal of α–CH_2- appears at δ 2.4 ppm. The signal of –C=C-CH_2-C=C- appears at δ 2.74-2.76 ppm. The signal of -OCH_3 appears at δ 3.7 ppm. The signal of –CH=CH- appears at δ 5.26-5.35 ppm.

The yield of FAME calculated from area under peak of FT-NMR spectrum was shown in the example below;

Example

$$\% \text{ FAME} = \frac{100x2x\text{Area under peak of } -OCH_3}{3x\text{Area under peak of of } \alpha - CH_2}$$

$$= \frac{100x2x2.477}{3x1.646}$$

$$= 100\%$$

4.4 Determination of physical properties of biodiesel

The physical properties of biodiesel which consisted of viscosity, flash point, heating value and acid were investigated as a function of methanol/oil ratio ,catalyst amount, and reaction time. The results were shown in Table 4.4.1 – 4.4.3.

Table 4.4.1 The effect of mole ratio of methanol to oil on physical properties of FAME

Co-solvent	Mole of methanol to oil	Viscosity (cSt) at 40°C	Flash point (°C)	Heating value (Btu/lb)	Acid value (mg KOH/g oil)
MEK	6:1	4.63	130	16751	0.336
	10:1	4.76	127	16904	0.280

Table 4.4.2 The effect of catalyst amount on physical properties of FAME

Co-solvent	Catalyst amount (%wt)	Viscosity (cSt) at 40°C	Flash point (°C)	Heating value (Btu/lb)	Acid value (mg KOH/g oil)
MEK	0.5	4.12	135	16926	0.283
	1	4.63	130	16751	0.336
	2	4.48	131	16553	0.321

Table 4.4.3 The effect of reaction time on physical properties of FAME

Co-solvent	Reaction time (hr)	Viscosity (cSt) at 40°C	Flash point (°C)	Heating value (Btu/lb)	Acid value (mg KOH/g oil)
MEK	1	5.12	135	16765	0.323
	2	4.63	130	16751	0.336
	3	4.76	137	16432	0.331

From Table 4.4.1 – 4.4.3can be summarized that physical properties of biodiesel products are in range of fuel properties of the biodiesel according to the table 2.3

Table 2.3 Fuel properties of the biodiesel [17]

Biodiesel physical characteristics	
specific gravity	0.87–0.89
kinematic viscosity @ 40°C	3.7–5.8
cetane number	46–70
higher heating value (btu/lb)	16,928–17,996
sulfur by weightt (%)	0.0–0.0024
cloud point (°C)	-11 to 16
pour point (°C)	-15 to 13
iodine number	60–135
lower heating value (btu/lb)	15,700–16,735
flash point(°C)	>120
acid value (mg KOH/g oil)	<0.5

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Effect of co-sovent required for the complete dissolution of methanol and oil

The minimum volume of co-solvent required for homogeneous phase of oil and methanol was in order of DEE > DIPE > MEK. Because three types of co-solvent are different in polarity which MEK has highest polarity index (4.5) when compare with DEE (2.8) and DIPE (2.2) therefore, MEK can dissolve in methanol which has polarity index 6.6 and led methanol to dissolve in oil better than others co-solvent.

5.2 The effect of mole ratio of methanol to oil, mass ratio of catalyst to oil and reaction time on biodiesel yield.

This special project was intended to study the best condition of transesterification of palm oil to biodiesel with homogeneous base catalysts, KOH in the presence of co-solvent. The effects of the mole ratio of methanol to oil, mass ratio of catalyst to oil and reaction time were investigated.

According to the experimental designs, the results determined that the mole ratio of methanol to oil at 6:1, 1% by weight of KOH was used gave the highest %wt of biodiesel while the %wt of biodiesel at reaction time 1hr, 2hrs, and 3hrs are slightly different due to transesterification of triglycerides with methanol is a reverse equilibrium reaction. Thus, a relative high ratio of methanol to oil is required to force the reaction to produce in the direction of methyl ester formation. At a relatively mole ratio of methanol to oil molar at 6:1, %wt of biodiesel increased to 88% within 1 hr, it was found that the relation reached an

equilibrium point and the %wt of biodiesel stayed at a constant level when the reaction time over 1 hr.

5.3 Measurement of physical properties and chemical characterization

Flash point

The standard flash point of biodiesel should be higher than 120°C to be usable in engine. From experimental results, flash points of each sample were higher than 120°C, so it can be further used.

Acid Value

The acid value of the oils gives an indication of the quantity of fatty acids present in the sample. From experimental results, the acid values of each sample were not exceeding the standard value of 0.5mg KOH/g oil.

Viscosity

From the results, the viscosity of each sample were not exceeded the specific viscosity of biodiesel that ranges between 1.9 – 6.0 cSt at 40 °C.

Heating value

Heating value referred as heat of combustion. From experimental results, the heating values of each sample were not exceeding the ranges of standard value of higher heating value 16,928–17,996 Btu/lb and lower heating value 15,700–16,735 Btu/lb

Recommendations

1. Co-solvent should be evaporated before separate biodiesel from glycerol.
2. The heterogeneous catalyst could be used in tranesterification reaction in the presence of co-solvent for biodiesel production.
3. The temperature of water circulating in condenser was room temperature so co-solvent could be evaporated during the reaction. Therefore, cooling water should be used for circulating in condenser.
4. The experiment should perform at reaction time lower than 1 hr in order to know the conversion of palm oil to biodiesel

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Appendix A

PRODUCT DATA

Calculation of the viscosity of biodiesel by viscosmeter.

1. Find volume of Pycnometer.

$$V = \frac{Mw - m}{D}$$

V = Volume of pyknometer (cm^3)

Mw= Weight of pyknometer with deionized water (gram)

m = Weight of pyknometer blank (gram)

D = Density of deionized water at temperature of this experiment

2. Find density of bioeiesel.

$$V = \frac{Ms - m}{D}$$

Ms = Weight of pyknometer with biodiesel (gram)

3. FInd Absolute Viscosity.

$$\eta = t\rho$$

t = Time of fluid flow (s)

η = Absolute Viscosity (Poise)

ρ =Density (g/ml)

4. Unit conversion of Absolute Viscosity

1 poise = 100 centipoise

1 centistoke = $\frac{centipoise}{density}$