การทำไบโอดีเซลให้บริสุทธิ์โดยการดูดซับด้วยเบนทอไนต์ที่กระตุ้นด้วยกรด

นายเอกสิทธิ์ เทพวีระกุล

PURIFICATION OF BIODIESEL BY ADSORPTION WITH ACID ACTIVATED
BENTONITE

Mr. Ekkasit Tepveeragul

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

Chulalongkorn University

Academic Year 2012

Thesis Title   PURIFICATION OF BIODIESEL BY ADSORPTION WITH ACID ACTIVATED BENTONITE

By   Mr Ekkasit Tepveeragul

Field of study   Petrochemistry and Polymer science

Thesis Advisor   Associate Professor Somchai Pengprecha, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

…………………………………………Dean of the Faculty of Science

(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

……………………………………………….. Chairman

(Professor Pattarapan Prasassarakich, Ph.D.)

………………………………………….……. Thesis Advisor

(Associate Professor Somchai Pengprecha, Ph.D.)

……………………………………………….. Examiner

(Associate Professor Surachai Pornpakakul, Ph.D.)

……………………………………………….. Examiner

(Amarawan Intasiri, Ph.D.)

……………………………………………….. External examiner

(Suchada Butnark, Ph.D.)

เอกสิทธิ์ เทพวีระกุล : การทำให้ไบโอดีเซลบริสุทธิ์โดยการดูดซับด้วยเบนทอไนต์ที่กระตุ้น ด้วยกรด

(PURIFICATION OF BIODIESEL BY ADSORPTION WITH ACID ACTIVATED BENTONITE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.สมใจ เพ็งปรีชา, 91 หน้า.

จุดประสงค์ของงานวิจัยนี้คือการกระตุ้นเบนทอไนต์ด้วยกรดซัลฟิวริกสำหรับการทำให้ไบโอดีเซล บริสุทธิ์ ในการกระตุ้นเบนทอไนต์จะทำการศึกษาปัจจัยดังนี้ ความเข้มข้นของกรดซัลฟิวริก (0.1 0.3 และ 0.5 โมลาร์) อุณหภูมิที่ใช้ในการกระตุ้น(60 และ 100 องศาเซลเซียส) และ เวลาที่ใช้ในการ กระตุ้น (1 ถึง 24 ชั่วโมง) สภาวะที่เหมาะสมในการกระตุ้นเบนทอไนต์คือใช้กรดซัลฟิวริก 0.1 โมลาร์ ที่ อุณหภูมิ 60 องศาเซลเซียสเป็นเวลา 12 ชั่วโมง ทำการหาคุณลักษณะเฉพาะของเบนทอไนต์ที่ผ่าน การกระตุ้นโดยใช้เครื่องวิเคราะห์หาพื้นที่ผิวและรูพรุน เครื่องเอกซเรย์ดิฟแฟรกชันและเครื่องเอกซเรย์ ฟลูออเรสเซนต์ พบว่าพื้นที่ผิวจำเพาะและค่าเฉลี่ยเส้นผ่าศูนย์กลางของโพรงของเบนทอไนต์ที่กระตุ้น ด้วยกรดมีค่า 55.15 ตารางเมตรต่อกรัมและ 8 นาโนเมตรตามลำดับ ลักษณะโครงสร้างของเบนทอ ไนต์ที่ผ่านการกระตุ้นไม่มีการเปลี่ยนแปลง จากองค์ประกอบทางเคมีพบว่าร้อยละโดยน้ำหนักของ MgO CaO Na_2O และ K_2O ลดลงเล็กน้อยจาก 3.68 3.30 0.83 และ 0.75 เป็น 3.42 2.69 0.10 และ 0.65 ตามลำดับ ในการทำไบโอดีเซลให้บริสุทธิ์จะทำการศึกษาปัจจัยที่ดังนี้ ปริมาณเบนทอไนต์ที่ กระตุ้นด้วยกรด (ร้อยละ 1 ถึง 10 โดยน้ำหนัก) เวลาที่ใช้ในการกำจัดสบู่ (10 ถึง 30 นาที) และขนาด ของอนุภาคเบนทอไนต์ที่กระตุ้นด้วยกรด (60 ถึง 200 เมช) สภาวะที่เหมาะสมที่ใช้ในการกำจัดสบู่คือ ใช้เบนทอไนต์ที่ผ่านการกระตุ้นขนาดอนุภาค 80-100 เมช ปริมาณร้อยละ 10 โดยน้ำหนัก (น้ำหนัก เบนทอไนต์ที่ผ่านการกระตุ้นต่อน้ำหนักน้ำมัน) ทำการดูดซับที่อุณหภูมิห้องโดยใช้รอบการเขย่าเท่ากับ 150 รอบต่อนาที เป็นเวลา 20 นาที ซึ่งสามารถกำจัดสบู่ได้ร้อยละ 72.30 ไอโซเทอมการดูดซับตามไอ โซเทอมฟรุนลิช จากการทดลองพบว่าเบนทอไนต์ที่ผ่านการกระตุ้นสามารถใช้สำหรับการทำให้ไบโอ ดีเซลบริสุทธิ์ คุณภาพของไบโอดีเซลที่ได้หลังการทำให้บริสุทธิ์ด้วยเบนทอไนต์ที่ผ่านการกระตุ้นตาม ด้วยการล้างด้วยน้ำพบว่าตรงตามมาตรฐานของไบโอดีเซลที่กำหนดไว้

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต.....................................

ปีการศึกษา ....2555.................... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์..............

5272639523 : MAJOR   PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS : BENTONITE / ACTIVATION / ADSORBENTS

EKKASIT TEPVEERAGUL: PURIFICATION OF BIODIESEL BY ADSORPTION WITH ACID ACTIVATED BENTONITE. ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 91 pp.

The objective of this research is to activating bentonite with sulfuric acid for purification of biodiesel. In order to activating bentonite, the effects of sulfuric acid concentrations (0.1, 0.3 and 0.5 M), activating temperature (60 and 100 °C) and activating times (1-24 h) were studied. The optimal condition for activating bentonite was 0.1 M H_2SO_4 at 60 °C for 12 h. The characteristics of activated bentonite were characterized by BET, XRD and XRF methods. The specific surface area and average pore diameter of activated bentonite were 55.15 m^2/g and 8 nm, respectively. The morphology of activated bentonite was unchanged. The chemical composition: MgO, CaO, Na_2O and K_2O, were slightly decreased from 3.68, 3.30, 0.83 and 0.75 to 3.42, 2.69, 0.10 and 0.65 %wt., respectively. In order to purify biodiesel, the effects of amounts of activated bentonite (1-10 %wt. of activated bentonite per g oil), mesh sizes (60-200 mesh) and contact times (10-30 min.) on soap removal were also studied. The optimal condition for removal of soap in biodiesel was 10%wt. of activated bentonite (80-100 mesh) per g oil at room temperature with stirring rate of 150 rpm for 20 min. The removal of soap in biodiesel was 72.30%. The adsorption isotherm was fit to Freundlich isotherm. The results showed that activated bentonite can be used for purifying biodiesel. The quality of biodiesel after purified by activated bentonite followed by water washing could meet the major specification of biodiesel standards.

Field of Study: Petrochemistry and Polymer Science   Student's Signature………….
Academic Year: ………..2012……………….......... Advisor's Signature………....

ACKNOWLEDGEMENTS

CONTENTS

LIST OF TABLES

TABLE **PAGE**

LIST OF FIGURES

LIST OF ABBREVIATIONS

µl	=	Microliter
µm	=	Micrometer
Å	=	Angstrom
ASTM	=	American Standard Test Method
$^\circ$C	=	Degree Celsius
cSt	=	Centistroke
EN	=	European Standards
FFA	=	Free fatty acid
FID	=	Flame Ionization Detector
g	=	Gram
GC	=	Gas-liquid chromatography
h	=	Hour
m	=	Meter
min	=	Minute
mg	=	Miligram
ml	=	Milliliter
mm	=	Millimeter
No.	=	Number
ppm	=	parts per million
rpm	=	round per minute
TLC	=	Thin Layer Chromatography
v/v	=	Volume by volume
% conversion	=	Percent conversion
% wt	=	Percent by weight
% yield	=	Percent yield

CHAPTER I

INTRODUCTION

Presently the world's energy needs are met through non-renewable resources such as petrochemicals, natural gas and coal. The high energy demand in an industrialized world as well as in the domestic sector and pollution problem caused due to the widespread use of fossil fuels makes it necessary to develop the renewable energy sources/fuels with lower environmental impact than the conventional ones. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available [1]. Biodiesel is one of the most promising alternative fuels to meet these problems. It is renewable, biodegradable, non-toxic and has almost very close property to that of diesel fuel [2].

Biodiesel is a mixture of fatty acid alkyl esters, which are generally produced through transesterification using feedstocks containing triglycerides. The conventional method for biodiesel production is transesterification of fresh vegetable oil in the presence of homogeneous base catalysts such as sodium or potassium hydroxide [3]. The production of biodiesel using alkaline catalysts such as sodium and potassium hydroxides (NaOH and KOH), and sodium and potassium methoxides (CH$_3$ONa and CH$_3$OK), could provide higher biodiesel yield (>98%), but the process of biodiesel refining is complicated. This is due to soaps formation associated with alkaline catalyst. Further, the formation of soap decreases biodiesel yield obtained after the clarification and separation stages. As well, the dissolved soaps increase the biodiesel solubility in glycerol, an additional cause of yield loss [4].

To meet the requirements of biodiesel standards, removal of these impurities are especially important. Moreover, glycerol is especially undesired in the fuel because when heated it tends to polymerize by condensation with other molecules of glycerol or glycerides. The result is the formation of coke and tarnish on injectors and cylinders. Glycerides also increase the cloud point of biodiesel by forming small crystals at low temperatures [5]. In the usual industrial practice, water washing is

wildly used to purified biodiesel but it has been lately critically objected on an environmental basis because of the relatively large amounts of water that are issued as wastewater.

To eliminate these problems, the use of waterless process becomes the important role in removing biodiesel contaminants then conventional water washing could be replaced by using adsorption process. The study of adsorbents which adsorb impurities in biodiesel is needed. Activated bentonite is chosen to be adsorbents in this work because of their various applications such as water purification, winemaking filtration, building material and refining oil. Especially, these adsorbents are interesting because they are available in Thailand with their competitive cost.

1.1 Objectives of the research

The objective of this research is to study activating factors of bentonite and use activated bentonite to purify biodiesel impurities.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1   Background

Thailand is an agricultural country with high potential for energy crops which could contribute to reduce its reliance on import of fossil energy resources to satisfy its demand. In 2004, the country energy demand amounted to 61.080 ktoe (25 billion USD), with the transportation sector contribution the largest share (35%) of the total energy demand. In 2000, the cost of the imported oil was 258,172 million baht (1 USD=35 Thai Baht) out of which 12,133 million baht was paid for the importation of diesel oil, an important factor of production in the industrial, agricultural and transportation sectors. Biofuels–biodiesel and bioethanol are being promoted by the government of Thailand to partly address the above issues. The target is to have the 5% biodiesel blend (B5) by the year 2007 and B10 in 2012 [6].

There is considerable interest in biodiesel because of its domestic and renewable origin. Furthermore, there is a substantial body of evidence showing that use of biodiesel (and biodiesel blends) has a strong and consistent beneficial effect on emissions of hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM) [7]. There are some disadvantages too: high freezing point (between 0 and −5 ∘C); filter obstruction (due to solvent power); lower energy capacity than petrodiesel and storage problems (due to it is biodegradable) [8].

2.2   Biodiesel production [9]

Several methods have been established to modify vegetable oil and waste cooking oil to fuels which have physical properties such as viscosity comparable to fossil fuel. These include blending, cracking, micro emulsification, pyrolysis and tranesterification. Tranesterification is the most commonly used method for modify

vegetable oil and waste cooking oil to fuel. It has many advantages over other methods.

2.3 Transesterification [10, 11]

Vegetable oil or waste cooking oil is reacted with alcohol such as methyl alcohol and ethyl alcohol in presence of appropriate catalyst. Generally transesterification is divides into three consecutive steps. First, triglyceride is converted to diglyceride, then monoglyceride is produced from diglyceride and in the last step, glycerin is obtained from monoglycerides. The reactions consist of consecutive reversible processes as shows in Figure 2.1.

$$1.\ Triglyceride\ (TG) + R'OH \xrightarrow[\quad]{Catalyst} Diglyceride\ (DG) + R'COOR_1$$

$$2.\ Diglyceride\ (DG) + R'OH \xrightarrow[\quad]{Catalyst} Monoglyceride\ (MG) + R'COOR_2$$

$$3.\ Monoglyceride\ (MG) + R'OH \xrightarrow[\quad]{Catalyst} Glycerol\ (GL) + R'COOR_3$$
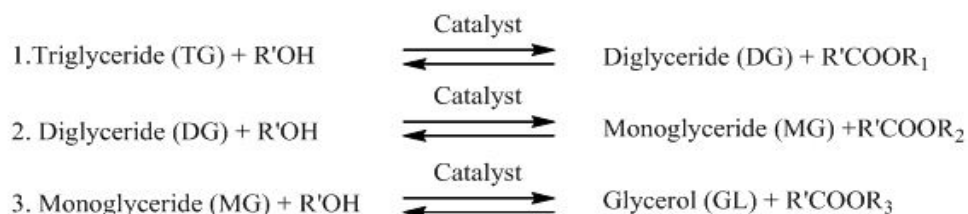
Figure 2.1 Three consecutive steps of transesterification

As you see in Figure 2.1, Fatty acid methyl ester (FAME) is produced. Theoretical, the ratio of oil and alcohol should be 1:3. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product. The reaction of transesterification was shown in figure 2.2.

$$\begin{array}{cccc}
CH_2\text{-}OOC\text{-}R_1 & & R_1\text{-}COO\text{-}R' & CH_2\text{-}OH \\
| & & & | \\
CH\text{-}OOC\text{-}R_2 + 3R'OH & \xleftrightarrow{catalyst} & R_2\text{-}COO\text{-}R' + & CH\text{-}OH \\
| & & & | \\
CH_2\text{-}OOC\text{-}R_3 & & R_3\text{-}COO\text{-}R' & CH_2\text{-}OH \\
Glyceride & Alcohol & Esters & Glycerol
\end{array}$$
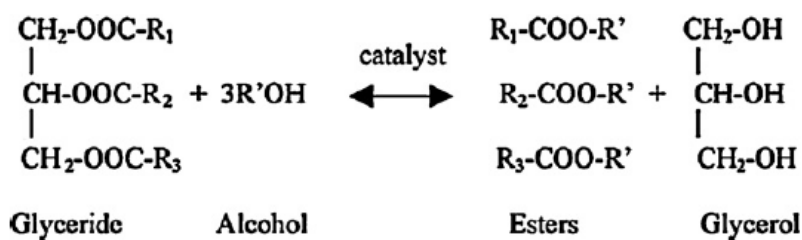
Figure 2.2 Transesterification of biodiesel

The byproduct of this reaction is the glycerol. High free glycerol content may result in decantation, storage, and engine fuel injection system problems. Free glycerol is also associated with fuel tank bottom deposits, which attract other contaminants, such as water, which in turn increases engine corrosion and reduces the engine's useful life. Burning glycerol together with biodiesel may also result in hazardous emissions [12].

Another byproduct is soap. Soap is produce by saponification reaction. The saponification reaction is highly undesirable, because it consumes catalyst and causes phase separation problems and emulsion formation during purification [13].

The type of catalyst that used in transesterification reaction is acid catalyst, alkaline catalyst, enzyme-catalyst, non-ionic based catalyst, heterogeneously catalyst and noncatalytic transesterification. The commonly catalyst in transterification is alkaline catalyst. The alkali-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Alkali catalyzed transeterification, the triglycerides should have lower free fatty acid (FFA) content, and the alcohol must be anhydrous to render soap formation. Soap formation lowers the yield of esters and renders the separation of esters and glycerol. Up to about 5% FFA, the reaction can be catalyzed using an alkali catalyst. The extent of transesterification and side reactions depends upon the type of feedstock, catalyst formulation, catalyst concentration, alcohol-to-oil ratio, reaction temperature and reaction time [14, 15]. The alkaline catalyst that commonly use is sodium hydroxide.

2.4   Biodiesel quality [16]

These standard specifications could either be the American standards for testing materials (ASTM 6751-3) or the European Union (EN 14214) for biodiesel fuel. The purity and quality of biodiesel fuel can be significantly influenced by numerous factors amongst others include: the quality of feedstock, fatty acid composition of the vegetable oils, animal fats and waste oils, type of production and refining process employed and post-production parameters. The international standards specification of biodiesel fuel is show in Table 2.3 and 2.4.

Table 2.1 Biodiesel (B100) specification (ASTM 6751-3)

Property	ASTM method	Limits	Units
Flash point	D93	130 min	°C
Water and sediment	D2709	0.050 max	vol.%
Kinematic viscosity, 40 °C	D445	1.9–6.0	mm²/s
Sulfated ash	D874	0.020 max	mass%
Sulfur	D5453	–	–
S 15 grade	–	15 max	ppm
S 500 grade	–	500 max	–
Copper strip corrosion	D130	No. 3 max	–
Cetane	D613	47 min	–
Cloud point	D2500	Report	°C
Carbon residue 100% sample	D4530[a]	0.050 max	mass%
Acid number	D664	0.50 max	mg KOH/g
Free glycerine	D6584	0.020 max	mass%
Total glycerine	D6584	0.240 max	mass%
Phosphorus content	D4951	0.001 max	mass%
Distillation temperature, atmospheric equivalent temperature, 90% recovered	D1160	360 max	°C
Sodium/potassium	UOP391	5 max combined	ppm

[a]The carbon residue shall be run on 100% sample

Table 2.2 International standard (EN14214) requirements for biodiesel

Property	Units	Lower limit	Upper limit	Test-method
Ester content	% (m/m)	96.5	–	Pr EN 14103 d
Density at 15 °C	kg/m³	860	900	EN ISO 3675/EN ISO 12185
Viscosity at 40 °C	mm²/s	3.5	5.0	EN ISO 3104
Flash point	C	>101	–	ISO CD 3679e
Sulfur content	mg/kg	–	10	–
Tar remnant (at 10% distillation remnant)	% (m/m)	–	0.3	EN ISO 10370
Cetane number	–	51.0	–	EN ISO 5165
Sulfated ash content	% (m/m)	–	0.02	ISO 3987
Water content	mg/kg	–	500	EN ISO 12937
Total contamination	mg/kg	–	24	EN 12662
Copper band corrosion (3 h at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability at 110 °C	h	6	–	pr EN 14112 k
Acid value	mg KOH/g	–	0.5	pr EN 14104
Iodine value	–	–	120	pr EN 14111
Linoleic acid methyl ester	% (m/m)	–	12	pr EN 14103d
Polyunsaturated (P4 double bonds) methylester	% (m/m)	–	1	–
Methanol content	% (m/m)	–	0.2	pr EN 141101
Monoglyceride content	% (m/m)	–	0.8	pr EN 14105m
Diglyceride content	% (m/m)	–	0.2	pr EN 14105m
Triglyceride content	% (m/m)	–	0.2	pr EN 14105m
Free glycerine	% (m/m)	–	0.02	pr EN 14105m/pr EN 14106
Total glycerine	% (m/m)	–	0.25	pr EN 14105m
Alkali metals (Na+K)	mg/kg	–	5	pr EN 14108/pr EN 14109
Phosphorus content	mg/kg	–	10	pr EN14107p

2.7   Biodiesel purification [17]

There are two generally accepted methods to purify biodiesel: wet and dry washing. The more traditional wet washing method is widely used to remove excess contaminants and leftover production chemical from biodiesel. However, the inclusion of additional water to the process offers many disadvantages, including increased cost and production time. Dry washing replaces water with an ion exchange resin or magnesium silicate powder to neutralize impurities. Both dry washing methods are being used in industrial plants.

2.7.1   Wet washing

Biodiesel wet washing technique involves addition of certain amount of water to crude biodiesel and agitating it gently to avoid formation of emulsion. The process is repeated until colorless wash water is obtained, indicating complete removal of impurities. Wet washing processes usually requires a lot of water, approximately water wash solution at the rate of 28% by volume of oil and 1 g of tannic acid per liter of water. The use of large quantity of water generates huge amount of wastewater and incur high energy cost.

2.7.2   Dry washing

The dry washing technique commonly employed to purify crude biodiesel is usually achieved through the use of silicates (Magnesol or Trisyl), ion exchange resins (Amberlite or purolite), cellulosics, activated clay, activated carbon, and activated fiber, etc. These Adsorbents consist of acidic and basic adsorption (binding) sites and have strong affinity for polar compounds such as methanol, glycerin, glycerides, metals and soap. This technique is followed with the use of a filter to enable the process to be more effective and efficient.

2.8   Adsorption [18, 19, 20]

Adsorption is used to describe the existence of a higher concentration of any particular substance at the surface of a liquid or solid than it present in the bulk. Molecules can stick to surfaces in two ways.

Physical adsorption is a van der Waals interaction between the surface of adsorbent and the adsorbed molecules. This is a long-range but weak interaction and the amount of energy released when molecules is physical adsorbed is of the order of the enthalpy of condensation. Van der Waals adsorption is characterized by relatively low heats of adsorption (about 20 kJmol^{-1}). These energies are insufficient to bond breaking, and so in physical adsorption the molecules retain its identity, although it might be stretched or bent on account of proximity of surface.

In chemical adsorption, the molecules stick to the surface of adsorbent as result of the formation of a chemical, and usually a covalent bond. The energy of attachment is very much greater than physical adsorption (about 200 kJmol^{-1}). A molecules undergoing chemical adsorption may be torn apart at the demand of the unsatisfied valencies of the surface atoms, and so its lose identity.

2.9   Adsorption isotherm [21, 22]

Classification of adsorption isotherm is important in theoretical modeling of adsorption phenomena. It also is important for practical reasons. As an illustration, consider surface area measurements using the BET method. There are international standards and a number of commercial devices for using this method in different applications. However, according to the IUPAC manual, the first step is 'to identify the isotherm type and hence the nature of the adsorption process'. The modern version of IUPAC classification scheme has six types of isotherms for gas-solid equilibrium as shown in Figure 2.3. It is based on an earlier classification by Brunauer which had five types of isotherms.
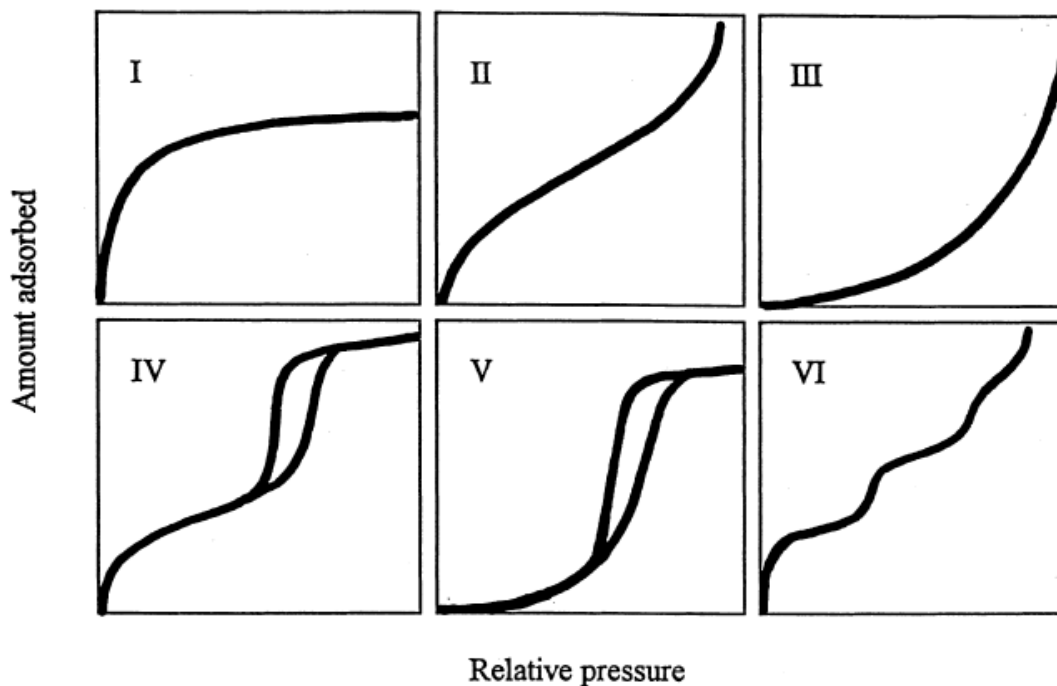
Figure 2.3 IUPAC standard adsorption isotherms.

Type I isotherm is used to describe adsorption on microporous adsorbents. Types II and III describe adsorption on macroporous adsorbents with strong and weak adsorbate-adsorbent interactions respectively. Types IV and V represent monolayer and multilayer adsorption plus capillary condensation. Type VI, which was not included in the Brunauer classification, illustrates that the adsorption isotherms can have one or more steps.

There are models describing process of adsorption such as Langmuir isotherm, Freundlich isotherm and BET isotherm.

2.9.1   Langmuir isotherm [23, 24, 25]

Langmuir model is the simplest theoretical model for monolayer adsorption onto a surface with finite number of identical sites. It is originally developed to represent chemisorption on a set of distinct, localized adsorption sites. Langmuir has developed a theoretical equilibrium isotherm relating the amount of gas adsorbed on a surface due to the pressure of the gas. The equation is applicable to homogeneous adsorption where adsorption process has equal activation energy, based on the following basic assumptions:

1. The surface of the adsorbent is uniform. All the adsorption sites are equal.

2. Adsorbed molecules do not interact.

3. All adsorption occurs through the same mechanism.

4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

$$\text{Langmuir equation:} \quad \frac{1}{(x/m)} = \frac{1}{nK_LCe} + \frac{1}{n}$$

Where: x/m   = the amount of soap adsorbed per unit of
                         adsorbent at equilibrium (mg/g)

           Ce   = the concentration of soap at equilibrium(mg/l)

           n   = the maximum amount of adsorption with
                         complete monolayer coverage on the
                         adsorbent surface (mg/g)

           K_L = Langmuir constant (l/mg)

The Langmuir constants, K_L and n can be determined from the linear plot of 1/Ce versus 1/(x/m).

The Langmuir isotherm is based on the assumption that a structure of adsorbent is homogeneous, where all sorption sites are identical and energetically equivalent. For the Langmuir model, the effect of isotherm shape is used to predict a favourability of an adsorption system under specific conditions. According to Hall et al. [26], the favourable adsorption of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L.

$$R_L = \frac{1}{1 + K_L C_i}$$

The values of the R_L are basically classified into four groups, indicating the shape of the isotherm as follows:

$R_L > 1$ Unfavourable

$R_L = 1$ Linear

$0 < R_L < 1$ Favourable

$R_L = 0$ Irreversible

2.9.2   Freundlich isotherm [27, 28]

The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases so too does the concentration of adsorbate on the adsorbent surface. Theoretically, using this expression, an infinite amount of adsorption can occur.

$$qe = K_F C_e^n$$

In this equation K_F and n are the Freundlich constants. This expression is characterised by the heterogeneity factor, n, and so the Freundlich isotherm may be used to describe heterogeneous systems. The linearized Freundlich adsorption isotherm by taking logarithms can be written:

$$\log(x/m) \quad = \quad \frac{1}{n} \log Ce \quad + \quad \log K_F$$

Where: $\quad x/m \quad$ = the amount of soap adsorbed per unit of

adsorbent at equilibrium (mg/g)

$Ce \quad$ = the concentration of soap at equilibrium(mg/l)

$n , K_F \quad$ = Freundlich constant

K_F and $1/n$ values can be calculated from intercept and slope of the linear plot between $\log Ce$ and $\log (x/m)$.

The favourable adsorption of the adsorption model can be determined from Freundlich constants. K_F is indicative of the adsorption capacity of the adsorbent, e.g., the greater K_F value, the greater adsorption capacity. The other Freundlich constant, n is a measure of the deviation from linearity of the adsorption and used to verify types of adsorption. It is suggested that if n is equal to unity, the adsorption is linear. Furthermore, n below unity indicates that adsorption is a chemical process; whereas, n above unity is associated with a favourable adsorption and a physical process.

2.9.3 Brunauer-Emmett-Teller isotherm [29]

Brunauer-Emmett-Teller (BET) modified Langmuir's theory to allow for multilayer adsorption. The BET isotherm, as it is known, allows for multilayer adsorption, but retains the other original assumptions. The assumption that gases behave ideally generally holds. However, the other assumptions are problematic: Not every site on the surface is equivalent, molecular interactions on the surface do occur, and molecules can move on the surface, especially if they are physisorbed. The BET isotherm works best at low pressures where only a few complete monolayers of adsorbate may have formed since highly porous or irregular solids, such as alumina, cannot form regular layers.

The BET model assumes that a number of layers of adsorbate molecules form at the surface and that the Langmuir equations applies to each layer. A further assumption of the BET model is that a given layer need not complete formation prior to initiation of subsequent layers, the equilibrium condition will therefore involve several types of surfaces in the sense of number of layers of molecules on each surface site. For adsorption from solution with the additional assumption that layers beyond the first have equal energies of adsorption, the BET equation takes the simplified form as in equation below:

$$q \quad = \quad \frac{BQC_f}{(C_s-C_f)[1+(B-1)(C_f/C_s)]}$$

where: C_s = the saturation constant of the solute

  B = constant relating to the energy of interaction with the surface

  Q = the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface

2.10   Adsorbent

Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapors. Most industrial adsorbents fall into one of three classes:

- Oxygen-containing compounds: Are typically hydrophilic and polar, including materials such as silica gel and zeolites.
- Carbon-based compounds: Are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.

- Polymer-based compounds: Are polar or non-polar functional groups in a porous polymer matrix.

2.11   Clay [30]

Clay minerals, a large family of alumino-silicate structures with a range of chemical composition, structure and surface properties, are very reactive materials due to their small grain size, large surface area, adsorption properties and chemical variability. Therefore, they are of considerable recognition in all the physical, chemical and environmental processes in soils and sediments, and frequently control them. The industrial application of clays is enormous and grows with our ability to engineer their properties and use them in the production of composite materials. In addition, clays are able to retain inorganic and organic pollutants, and to stop the circulation of contaminated fluids in both aquatic and soil environments.

2.12   Bentonite [31]

Bentonite belongs to the 2:1 clay family, the basic structural unit of which is composed of two sheets of silicon atoms tetrahedrally coordinated with oxygen sandwiching a sheet of aluminum atoms octahedrally coordinated with oxygen. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay basal surface. Compared with other clay types, bentonite has excellent sorption properties and possesses sorption sites available within its interlayer space as well as on its outer surface and edges.
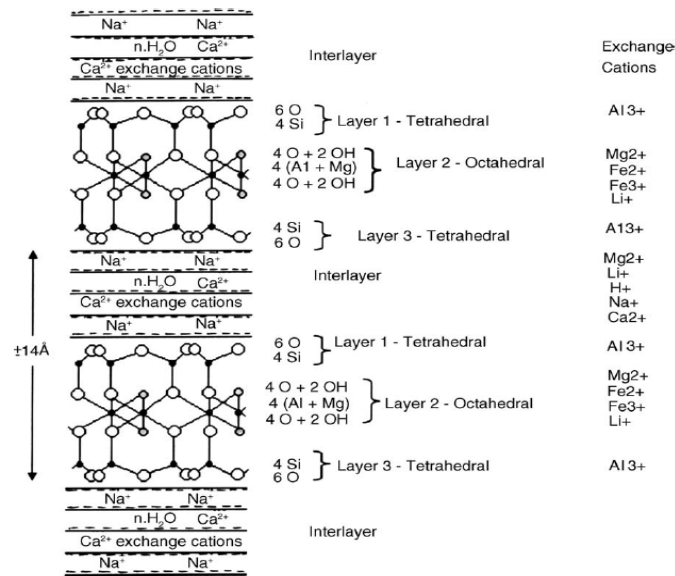
Figure 2.4 Structure of bentonite [32].

2.13 Type of bentonite.

- **Sodium bentonite.**

Sodium bentonite is widely used in chemical and oil industries such as catalyst beds, drilling mud and ceramic body compositions, due to their high specific surface area. This material is preferred to use in drilling mud composition because of its suitable rheological properties and maintaining ability of the cut pieces due to sufficient yield stress [33].

- **Calcium bentonite**

Calcium bentonite is a useful adsorbent of ions in solution, as well as fats and oils, being a main active ingredient of fuller's earth, probably one of the earliest industrial cleaning agents. Ca-bentonites are usually activated with soda using varying proportions of soda. Alkali or soda activation with sodium carbonate (Na_2CO_3) converts the calcium and/or magnesium bentonites into sodium–calcium forms [34].

2.14   Literature reviews

In 2006, Shailendra et al. [35] studied the various factor that effect transesterification such as reaction time, reaction temperature, molar ration of alcohol to oil and catalyst concentration for transesterification of rice bran oil. The result show that the optimum condition for transesterification was found to be 9:1 molar ratio of methanol to oil, 0.75% (w/w) NaOH, 55 °C reaction temperature and 1 h reaction time. The viscosity of rice bran oil reduces substantially after transesterification and becomes comparable to that of Diesel. The density, flash point and cloud and pour points of biodiesel from rice barn oil were higher than those of the mineral Diesel. Comparatively, the higher flash point of biodiesel from rice barn oil makes it a safer fuel to handle. The calorific value of biodiesel from rice barn oil was slightly lower than that of Diesel. All these tests for the characterization of biodiesel from rice barn oil demonstrated that almost all characteristics of biodiesel from rice barn oil are comparable to those of Diesel, and this makes it a potential substitute for Diesel fuel in compression ignition engines.

In 2012, Márcia et al. [36] studied the purification of biodiesel from waste frying oil using rice husk ash at concentrations of 1%, 2%, 3%, 4% and 5% (w/w) and compare it with two other different purification methods, the traditional acid solution (1% aqueous H_3PO_4) and with the commercial adsorbent Magnesol 1% (w/w). The structure and composition of the rice husk ash were studied to better understand its properties as an adsorbent. In a concentration of 4%, the rice husk ash showed excellent results for removal impurities from biodiesel. The high concentration of silica in its composition and the presence of meso and macropores can explain its high capacity of adsorption. Thus, the rice husk ash, that is a byproduct of the rice processing, can appear as an alternative material for biodiesel purification.

In 2009, Hajjaji and Arfaoui [37] studied the adsorption of methylene blue and zinc ions on raw and acid-activated Moroccan bentonite. The adsorption capacity of MB and Zn ions by raw bentonite were about 2.2 and 1.1 mmol/(g of bentonite) and the best-fit isotherm models were those of Harkins–Jura and Langmuir. Acid-activation of the bentonite reduced the maximum uptake of MB and Zn ions by 30 and 95% and the best-fit models of the isotherms were Freundlich and Dubinin–

Radushkevich for MB and Zn ions respectively. The reduced adsorption was associated with partial collapse of the montmorillonite particles and the formation of amorphous silica.

In 2012, Nilgün et al. [38] studied the ion exchanged and physically adsorbed methylene blue cations on ionic surfaces of acid activated bentonite. The result shows, acid activation was changed properties of bentonite depending on the acid content, contact time, process temperature and also mineralogy of the natural materials. The sorption of large organic ions such as methylene blue cations on the ionic surfaces takes place simultaneously by two different mechanisms.

The first is an ion exchange which has chemical nature and independent from the concentration of solution. The second is physical adsorption on the surface after ion exchange was completed, which is dependent to the concentration of solution. The optimum HCl/CaB ratio in acid activation at 90 ∘C for 16 h was found 45–50% to obtain a bentonite powder having maximum specific surface area value about 190 m^2 g^{-1}.

In 2004, Temuujin et al. [39] characterized acid-leached montmorillonite-containing clay from Tuulant (Mongolia). Montmorillonite were treated with 50 ml 2 M hydrochloric acid at 80 °C for various times. Leaching caused the surface area of the clay to increase 3-fold to 93.9 m$_2$/g reflecting the formation in the porous silica product of 3–5 nm micropores and 6–10 nm mesopores, the latter resulting from a delaminated card-house structure rather than from the condensation of the micropores.

In 2009, Steudel et al. [40] studied acid activation of bentonite. The bulk material of six dioctahedral and two trioctahedral swellable clay minerals was leached in sulfuric acid and hydrochloric acid at concentrations of 1.0, 5.0 and 10.0 M at 80 °C for several hours. Alteration of the clay mineral structures was dependent on the individual character of each mineral (chemical composition and initial particle size). Acid attack dissolved the octahedral sheets by interlayer and edge attack. The number of substitutions by Mg or Fe in the octahedral sheet of the clay minerals promoted the dissolution of these layers and the formation of a silica phase. The dissolution of the octahedral cations occurred in the following order: Mg>Fe>Al. The dioctahedral smectites were more stable than the trioctahedral smectites and vermiculites; the behavior of trioctahedral smectites against acid was similar to that of vermiculites.

The acid activated smectites displayed still the ability to exchange cations. The obtained materials had a lower layer charge, lower cation exchange capacity and higher specific surface area than the crude materials but still adsorbed very large organic cations like dodecylammonium ions. The reaction with the acid caused particle splitting within the octahedral sheet.

In 2009, Budsaya [41] studied the purification of biodiesel from palm oil by adsorption with clay. The result shows, glycerin in biodiesel was effectively eliminated by using 4%wt of adsorbents at 50°C for 10 min in presence of methanol. The removal of glycerin was improved up to 90% by using 1%wt of adsorbents for 1 min on the condition that methanol had been removed before treatement. Adsorption processes of activated clay were described by monolayer and multilayer. The quality of purified biodiesel could meet the major specification of biodiesel standards.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1. Chemicals and materials

1. Acetic acid: analytical grade; Merck
2. Activated clay: commercial grade; Siam Taiko Marketing CO., LTD.
3. Anhydrous sodium sulfate: analytical grade; Merck
4. Bentonite: commercial grade; Thai Nippon
5. Bromophenol blue: analytical grade; Carlo erba
6. Cyclohexane: analytical grade; Merck
7. EN 14105 standard and internal standard solution; Supelco
8. Ethanol: analytical grade; Merck
9. Ethyl acetate: analytical grade; Merck
10. Heptane: analytical grade; Merck
11. Hexane: analytical grade; Merck
12. Hydrochloric acid: analytical grade; Merck
13. Isopropyl alcohol: commercial grade; Merck
14. Methanol: analytical grade; Merck
15. N-methyl-N-(trimethylsilyl)-trifluoroacetamide: derivatization grade; Sigma-Aldrich
16. Phenolphthalein indicator: analytical grade; Merck
17. Phenol red: analytical grade; Carlo erba
18. Potassium hydrogen phthalate: analytical grade; Merck
19. Potassium hydroxide: analytical grade; Lab-Scan
20. p-Naphtholbenzein: Analytical grade; Carlo erba
21. Refined palm oil

22. Sodium hydroxide: analytical grade; ACS

23. Sulfuric acid: analytical grade; Carlo Erba

24. Toluene: analytical grade; Merck

25. Wijs solution: analytical grade; Merck

3.1.2   Equipments

- BET (using BELSORP analysis program); SA 3100 Coulter
- Cannon Automatic Viscometer: Model CAV-3; Cannon
- Gas-liquid Chromatography; Varian 3800
- Rotary evaporator; Buchi
- Magnetic stirrer
- Water bath and shaker; Mammert W350
- X-Ray Diffractometer (XRD); RigakuUltima+
- X-Ray Fluorescence (XRF); Phillip PW2400

3.2 Procedure

3.2.1   Activation of bentonite

One hundred grams of bentonite were added into 1000 milliliters of round bottom flask equipped with condenser. Five hundred milliliters of sulfuric acid solution (0.1, 0.3 and 0.5 M) were slowly added into the reaction and then the mixture was heated to 60 and 100 ^{o}C for 1-12 h. Then, the bentonite was separated from solution and washed with distilled water for several time, until pH 5 of washed water was achieved, and dried at 110°C for 48h. The activated bentonite was stored in tightly closed glass bottles.

3.2.2   Characterization of activated bentonite

The effect of acid activation on natural bentonite was characterized by, BET method, X-Ray Fluorescence (XRF) and X-Ray Diffractometer (XRD).

3.2.2.1 BET Method

The characterization of natural bentonite and activated bentonite according to BET method can be carried out into two steps: pretreatment and surface area analyzer.

Step1, Pretreatment; 40 milligrams of each adsorbent were accurately weighed (0.04xx g) into sample cell, then the sample cells were connected with connection tube to evacuate the air and then heat at $400^{o}C$ for 3h.

Step2, Surface area analyzer; sample cell was accurately weighed after complete pretreatment. Then, sample cell was connected on BELSORP instrument for calculated surface area, pore volume and average pore size.

3.2.2.2 X-Ray Diffractometer

The mineralogical composition of natural and activated bentonite was determined by X-ray diffraction analysis (RigakuUltima+, CuKα radiation, graphite secondary monochromator, 5 s counting time per 0.02° 2θ step, divergence and antiscatter slit at 1 mm, detector slit 0.1 mm and scanned from 5 to 60° 2θ step).

3.2.2.3 X-Ray Fluorescence

The chemical composition of the natural and acid treated bentonite was determined with X-ray fluorescence analysis (XRF). The analyses were performed on PW2400 (Phillips), equipped with a rhodium X-ray tube running at 3 kW.

3.2.3 Transesterification of refined palm oil

Five hundred grams of refined palm oil were added into 1000 milliliters of round bottom flask equipped with condenser. After the oil was heated to 65 °C, the solution of sodium hydroxide (5.0 g) in methanol (144.82 ml), 6:1 molar ratio of methanol to oil, was slowly added into the reaction and then the mixture was heated to $65^{o}C$ for 1.50h. The reaction was monitored by TLC developed

by hexane: ethyl acetate: acetic acid (90:10:1 v/v) and visualized by vanillin solution. The mixture was transferred to a separatory funnel and allowed glycerin to separate for 30 min. The methyl ester layer (crude biodiesel) was later brought to purification process.

3.2.4   Purification of crude biodiesel

3.2.4.1 Purification of crude biodiesel by using activated bentonite

- Effect of sulfuric acid concentration

Fifty grams of crude biodiesel were treated with 3%wt. of activated bentonite per g oil (120-200 mesh, treated with 0.1, 0.3 and 0.5M of sulfuric acid at 60 °C for 12h). The experiment was performed at room temperature for 10 min with stirring rate at 150 rpm. Then, an adsorbent were removed from biodiesel by using syringe filter nylon (0.45 µm). The amount of soap content in biodiesel was determined by titration method.

- Effect of activation temperature

Fifty grams of crude biodiesel were treated with 3%wt. of activated bentonite per g oil (120-200 mesh, treated with 0.1M of sulfuric acid at 60 and 100°C for 12h). The experiment was performed at room temperature for 10 min with stirring rate at 150 rpm. Then, an adsorbent were removed from biodiesel by using syringe filter nylon (0.45 µm). The amount of soap content in biodiesel was determined by titration method.

- Effect of activation time

Fifty grams of crude biodiesel were treated with 3%wt. of activated bentonite per g oil (120-200 mesh, treated with 0.1M of sulfuric acid at 60°C for 1-24h). The experiment was performed at room temperature for 10 min

with stirring rate at 150 rpm. Then, an adsorbent were removed from biodiesel by using syringe filter nylon (0.45 µm). The amount of soap content in biodiesel was determined by titration method.

- Effect of amount of activated bentonite on soap adsorption

Fifty grams of crude biodiesel were treated with four concentrations of activated bentonite: 1, 3, 5 and 10%wt. of activated bentonite per g oil (120-200 mesh, treated with 0.1M of sulfuric acid at 60°C for 12h). The experiment was performed at room temperature for 10 min with stirring rate at 150 rpm. Then, an adsorbent were removed from biodiesel by using syringe filter nylon (0.45 µm). The amount of soap content in biodiesel was determined by titration method.

- Effect of particle size on soap adsorption

Fifty grams of crude biodiesel were treated with 10%wt. of activated bentonite per g oil (60-80, 80-100, 100-120 and 120-200 mesh, treated with 0.1M of sulfuric acid at 60°C for 12h). The experiment was performed at room temperature for 10 min with stirring rate at 150 rpm. Then, an adsorbent were removed from biodiesel by using syringe filter nylon (0.45 µm). The amount of soap content in biodiesel was determined by titration method.

- Effect of contact time on soap adsorption

Fifty grams of crude biodiesel were treated with 10%wt. of activated bentonite per g oil (80-100 mesh, treated with 0.1M of sulfuric acid at 60°C for 12h) at room temperature with stirring rate at 150 rpm. The contact time between adsorbents and crude biodiesel was varied in the range of 10, 20 and 30 min. Then, an adsorbent were removed from biodiesel by using syringe filter nylon (0.45 µm). The amount of soap content in biodiesel was determined by titration method.

3.2.4.2 Purification of crude biodiesel by using natural, activated and commercial bentonite

Fifty grams of crude biodiesel were treated with 1, 3, 5 and 10%wt. of natural bentonite, activated bentontie (treated with 0.1M of sulfuric acid at 60°C for 12h) and commercial bentonite per g oil. The optimal parameters used in this experiment were as follows: 80-100 mesh of particle size, 20 min of contact time 150 rpm stirring rate at room temperature. Then, an adsorbent were removed from biodiesel by using syringe filter nylon (0.45 µm). The amount of soap content in biodiesel was determined by titration method.

3.2.4.3 Purification of crude biodiesel by water washing

After the glycerin layer at the bottom was removed, the crude biodiesel on the upper phase was washed several times with warm distilled water (50°C) in a separatory funnel until the washed water became clear. Then, the water in biodiesel was removed by using anhydrous sodium sulfate and evaporation under reduced pressure. The amount of soap content in biodiesel was determined by titration method

3.2.6   Biodiesel analysis

3.2.6.1 Determination of the amount of soap and unreacted catalyst by titration method

Five grams of biodiesel sample were dissolved in 100 milliliters of isopropyl alcohol with 2 milliliters of 1% phenol red (indicator). The mixture was titrated with 0.01N hydrochloric acid until the color of the solution changed from red to colorless. This amount of 0.01N hydrochloric acid solution is referred as "A".

Then, 1 milliliter of 0.04% bromophenol blue was added into the mixture solution and titrated with 0.01N hydrochloric acid until the color of the

solution changed from blue to yellow. This amount of 0.01N hydrochloric acid solution is referred as "B".

The amount of unreacted catalyst can be calculated by using equation 1:

$$g \ of \ catalyst \ / \ g \ of \ sample = \frac{A \times 0.01 \times 40.0}{W \times 1000} \qquad (1)$$

Where: A = volume of hydrochloric acid used in first step (ml)

W = weight of untreated biodiesel used (g)

40.0   = molecular weigh of sodium hydroxide

And the amount of soap in the biodiesel was calculated by using equation (2):

$$Soap \ content \ (ppm) = \frac{B \times 0.01 \times 303.4}{W \times 1000} \qquad (2)$$

Where: B = volume of hydrochloric acid used in second step (ml)

W = weight of untreated biodiesel (g)

303.4 = average molecular weigh of sodium oleate

3.2.6.2 Determination of free and total glycerin contents (EN14105)

The free glycerol and total glycerin contents including residual mono-, di-, and triglyceride contents in biodiesel were determined by means of the chromatographic method of EN14105. N-heptane was used as a solvent. 1,2,4-Butanetriol and tricaprin were added as internal standard 1 and 2, respectively. N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was used as derivatizing agent. Standard mixtures and internal standard solutions were prepared according to the method. Approximately 100 μL of homogenized biodiesel sample was accurately weighed (± 0.1 mg) in a 20 ml vial, then, using a micropipet, 80 μL of internal Standard 1, 100 μL of internal standard 2 and 100 μL MSTFA were added to the

sample vials. The vials were hermetically sealed and shaken vigorously. After storing the vials at room temperature for 15-20 min, approximately 8 ml of heptane were added to each. Then, 1 μLof the reaction mixture was injected into the gas chromatograph.

The analysis was performed with a CP-3800 Varian gas chromatograph equipped with an on-column injector and a flame ionization detector (FID). The column was a Glycerides Ultimetal (Varian), 10 m x 0.32 mm (ID) x 0.1 μm (film thickness) with retention gap 2 m x 0.53 mm (ID). The samples were injected manually at an oven temperature of 50 °C. After held for 1 min, the oven was heated at 15°C/min to 180°C, at 7°C/min to 230 °C, and at 10 °C/min to 370 °C (held for 5 min). Helium was used as a carrier gas at a flow rate of 4 mL/min. The detector temperature was set to 380°C. The total run time was 36 min.

3.2.7 Determination of the properties of biodiesel

The physical properties of biodiesel were determined according to the test methods shown in Table 3.1.

Table 3.1 Test method of biodiesel fuels

Properties	Method
Viscosity at 40 °C (mm^2/s)	ASTM D445
% Free fatty acid	ASTM D5555
Acid value (mg KOH/g)	ASTM D974

3.2.8 Adsorption isotherm

3.2.8.1 Adsorption isotherm with surface area analyzer.

The type of adsorption isotherm of natural bentonite and activated bentonite were determined using the nitrogen adsorption isotherm at 77K.

The determination method was performed the same as 3.2.2.1 Type of adsorption isotherm was obtained from this analysis.

3.2.8.2 Adsorption isotherm of soap

The adsorption isotherms were studied to describe how soap molecules interact with the activated bentonite surface. To perform the experiment, ten concentrations of activated bentonite (treated with 0.1M of sulfuric acid at 60°C for 12h) were studied in the range of 1-10%wt. of activated bentonite per g oil. In a 100 milliliters glass bottom, 50 grams of crude biodiesel was treated with activated bentonite at optimum condition (20 min at room temperature with stirring at 150 rpm). Then, an adsorbent were removed from biodiesel by using syringe filter nylon (0.45 µm) and the amount of soap was analysed according to titration method. The result obtained from the experiment was then calculated through two equations, Langmuir and Freundlich isotherms, for determination the nature of the adsorption.

$$\text{Langmuir equation:} \quad \frac{1}{(x/m)} = \frac{1}{nK_LC_e} + \frac{1}{n}$$

Where:

x/m = the amount of soap adsorbed per unit of adsorbent at equilibrium (mg/g)

C_e = the concentration of soap at equilibrium(mg/l)

n = the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg/g)

K_L = Langmuir constant (l/mg)

The Langmuir constants, K_L and n can be determined from the linear plot

of $1/C_e$ versus $1/(x/m)$.

$$\text{Freundlich equation:} \quad \log(x/m) \quad = \quad \frac{1}{n} \log C_e \; + \; \log K_F$$

Where: x/m = the amount of soap adsorbed per unit of

adsorbent at equilibrium (mg/g)

C_e = the concentration of soap at equilibrium(mg/l)

n , K_F = Freundlich constant

K_F and $1/n$ values can be calculated from intercept and slope of the linear plot between $\log C_e$ and $\log (x/m)$.

CHAPTER IV

RESULTS AND DISCUSSION

4.1　Transesterification of refined palm oil

The transesterification reaction was monitored by Thin Layer Chromatography (TLC). As shown in Figure 4.1, triglyceride was completely converted to methyl ester. There were traces of diglyceride and monoglyceride in crude biodiesel   due to three steps of conversion of triglyceride to biodiesel. First, triglyceride was converted to diglyceride followed by the conversion of diglyceride to monoglyceride and then the monoglyceride was converted to glycerol. Each step was given one molecule of methyl ester.

CPO   BD
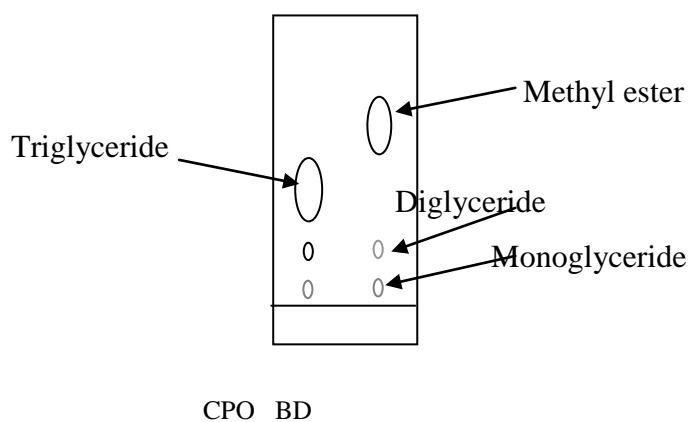
Figure 4.1 TLC of biodiesel which synthesized with base-catalyzed process when CPO: Crude palm oil, BD: Biodiesel and Mobile phase: a mixture of hexane, ethyl acetate and acetic acid (90:10:1 v/v).

4.2   Physical properties of bentonite and activated bentonite

4.2.1   BET analysis

The specific surface area (S_{BET}), average pore diameter (dp) and total pore volume (Vp) of natural and activated bentonite (treated with 0.1 M of sulfuric acid at 60 °C for 12 h) were calculated using the BET method. The obtained value was shown in Table 4.1. The value of specific surface area was 48.45 m^2/g for natural bentonite, this value was increased to 55.15 m^2/g after being activated by 0.1 M of sulfuric acid at 60 °C for 12 h whereas average pore diameter and total pore volume were decreased from 10 to 8 nm and 0.12 to 0.11 cm^{-1}/g, respectively. Results show that specific surface area was increased by acid activation which improves the adsorption capacity due to acid dissolved cations (Mg^{2+}) in the octahedral sheets by exchanging H^+ with Mg^{2+} leading to destruction of some montmorillonite layers and modification of the bentonite crystalline structure.

Table 4.1 The BET analysis of natural bentonite and activated bentonite (0.1 M of sulfuric acid at 60 °C for 12 h).

Adsorbent	Specific surface area (m^2/g)	Average Pore Diameter (nm)	Total pore volume (cm^{-3}/g)
NarutalBentonite	48.45	10	0.12
0.1M of sulfuric acid	55.15	8	0.11

4.2.2 Determination of the adsorption isotherm with surface area analyzer

The type of adsorption isotherm of natural bentonite and activated bentonite (treated with 0.1 M of sulfuric acid at 60 °C for 12 h) were determined by using the

nitrogen adsorption isotherm at 77K. The results are shown in Figure 4.2 and Figure 4.3.
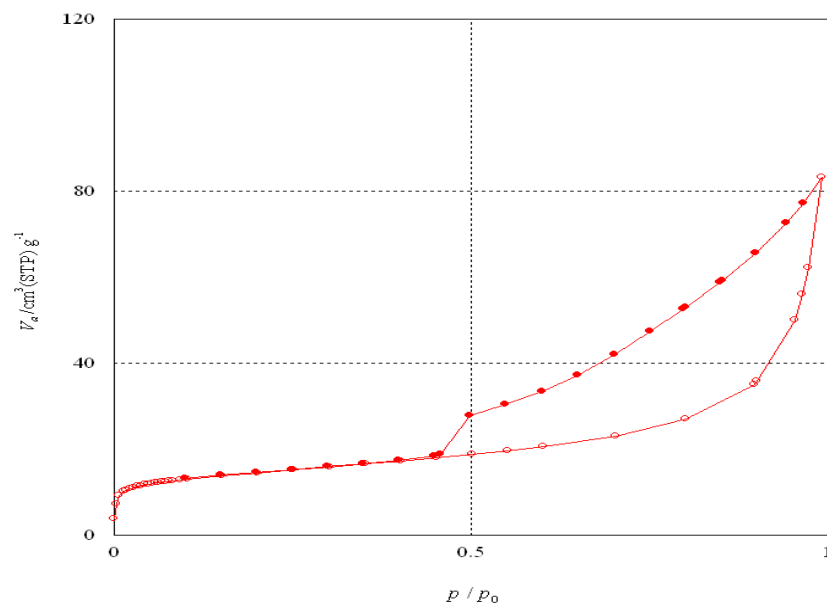
Figure 4.2 Adsorption isotherm of natural bentonite when P: Pressure, P_0: Pressure saturated.
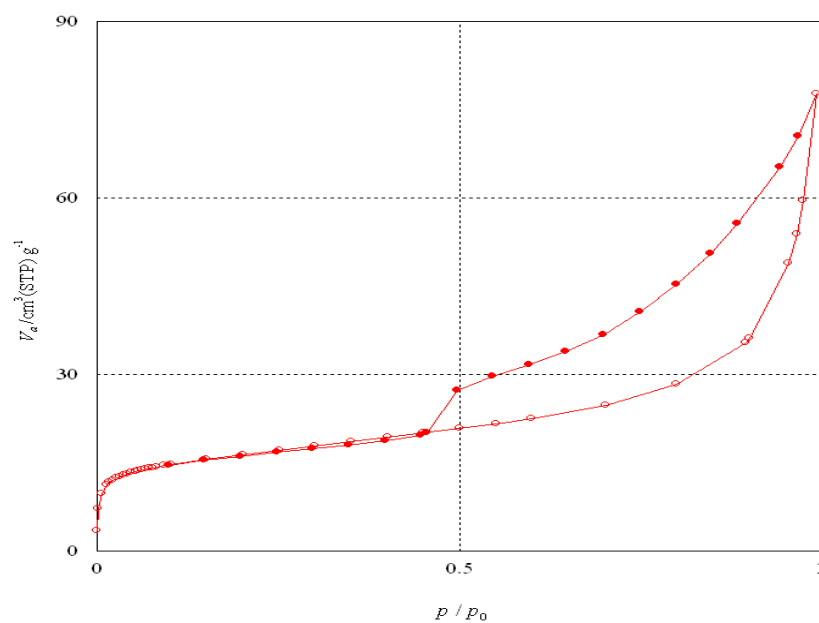
Figure 4.3 Adsorption isotherm of activated bentonite when P: Pressure, P_0: Pressure saturated.

Figures 4.2 and 4.3 shown that the adsorption isotherm of natural bentonite and activated bentonite were Type IV. It could be explained that the adsorption lower pressure region of graph was quite similar to Type II. The monolayer was initially formed at a pressure below the saturation vapor pressure (p/p_0= 4). When the pressure was increased to greater than 0.4, the adsorption would be limited accumulating causing multilayer formation. The hysteresis loop was occurred because of the desorption of nitrogen gas. According to the desorption, molecule of gas would be gradually desorbed from the surface of adsorbents leading to the increase of gas molecule in their pores. Then it had a possibility of gas getting condensed in the tiny capillary pores of adsorbents at pressure below the saturation pressure of the gas which caused the hysteresis loop. Finally, molecule of nitrogen gas could be desorbed and the desorption line was returned to the same line as adsorption. From these reasons above, it could be concluded that the adsorption of natural bentonite and activated bentonite were mesoporous.

4.2.3 XRD analysis

The XRD patterns of natural bentonite and activated bentonite (treated with 0.1 M of sulfuric acid at 60 °C for 12 h) were investigated with XRD. The results are shown in Figure 4.4.
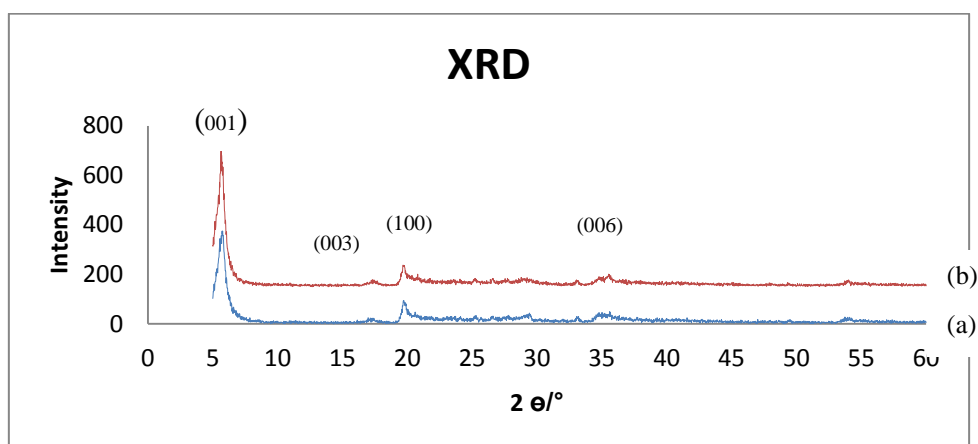
Figure 4.4 The XRD pattern of natural bentonite (a) and activated bentonite (0.1 M of sulfuric acid at 60 °C for 12 h) (b).

From Figure 4.4, The XRD patterns of natural bentonite and activated bentonite were not different. Due to sulfuric acid concentration that used to treated bentonite was 0.1 M which not enough to dissolve structure of bentonite.

4.2.4 XRF analysis

Chemical composition was analyzed using XRF (X-Ray Fluorescence). The adsorption efficiency results for the natural and the activated bentonite were given quantitatively in Table 4.2, as % wt. of metal oxide. Acid activation resulted in dissolving of cations from bentonite. Two groups of cations can be easily distinguished. First group contains Ca^{2+}, Na^+, K^+ and second group contains Mg^{2+}. The chemical composition of activated bentonite resulted in a material with higher silica oxide content (SiO_2 were 49.36%) and lower metal oxide (MgO, CaO, Na_2O and K_2O). Due to the quantity of Ca^{2+}, Na^+, and K^+ were removed by acid treatment. Consequently, first group was dissolved under mild condition. Second group contains Mg^{2+} which belonging to octahedral sheet. Dissolution of Mg^{2+} cations was increased by acid activation. However, the Si^{4+} cations at tetrahedral of bentonite was not dissolved by acid treatment. Increasing of Si^{4+} corresponds with quantity of these cations from the octahedral sheet and interlayer of the bentonite. The tetrahedral cations are normally resist to acid attack while the octahedral cations and exchangeable cations in interlayer were lower resistant than tetrahedral cations.

Table 4.2 Chemical composition of natural bentonite and activated bentonite (treated with 0.1M of sulfuric acid at 60°C for 12h) by using XRF

	% Natural Bentonite	% Activated Bentonite
SiO$_2$	47.47	49.36
Al$_2$O$_3$	11.86	12.48
Fe$_2$O$_3$	10.22	11.09
MgO	3.68	3.42
Na$_2$O	0.83	0.10
K$_2$O	0.75	0.65
CaO	3.30	2.69
TiO$_2$	1.78	1.89

4.3   Purification of crude biodiesel

4.3.1 Purification of crude biodiesel by using activated bentonite

.

- **Effect of sulfuric acid concentration on activating bentonite**

In order to investigate the influence of sulfuric acid concentration on activating bentonite, the benotnite (120-200 mesh) was treated with different concentration of sulfuric acid ranging from 0.1-0.5M. Then, activated bentonite was used to remove soap in crude biodiesel. The experiment was conducted at room temperature for 10 min. The results were shown in Figure 4.5 and Figure 4.6.
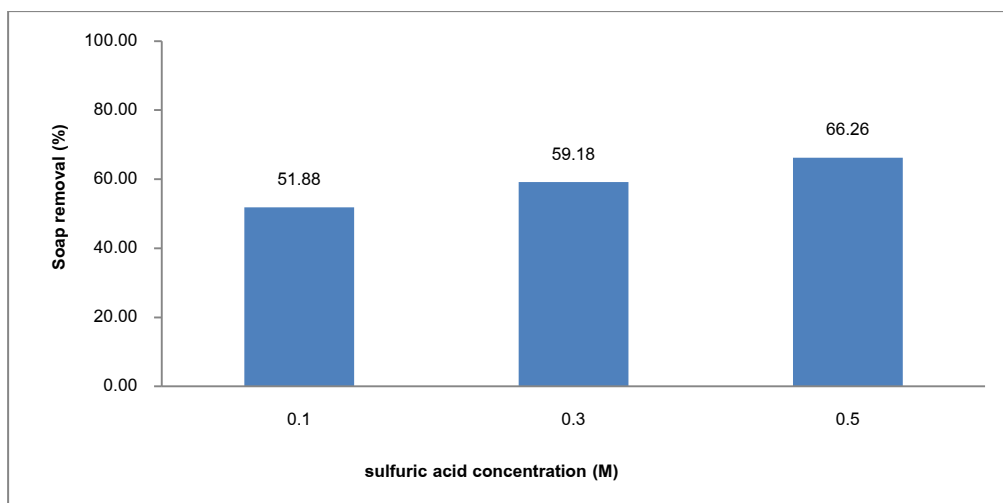
Figure 4.5 Effect of sulfuric acid concentration on soap removal (Activation condition: 0.1-0.5 M of sulfuric acid at 60°C for 12h. Removal condition: 3%wt. of activated bentonite per g oil at room temperature for 10 min)
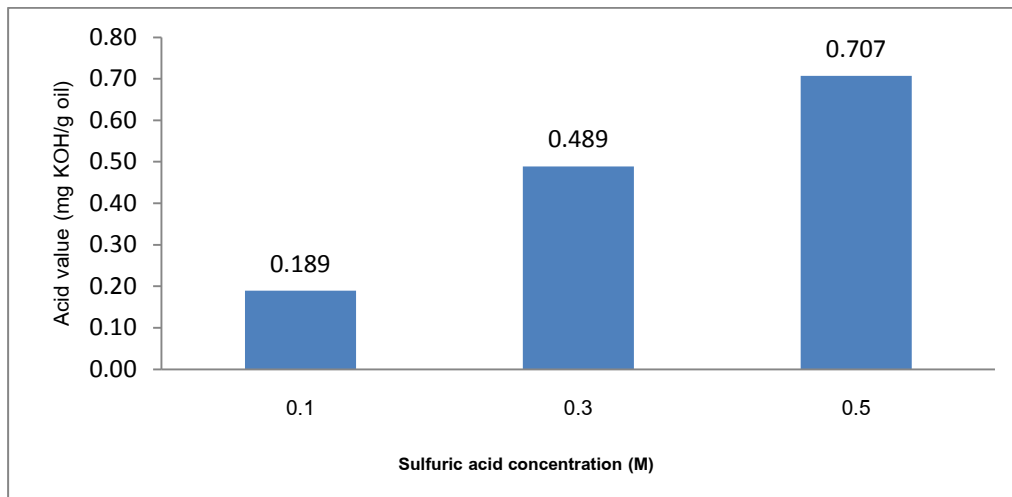
Figure 4.6 Effect of sulfuric acid concentration on acid value (Activation condition: 0.1-0.5 M of sulfuric acid at 60°C for 12h. Removal condition: 3%wt. of activated bentonite per g oil at room temperature for 10 min)

The results in Figure 4.5 showed that bentonite, which was treated with 0.1, 0.3 and 0.5 M of sulfuric acid, could remove 51.88, 59.18 and 66.26% of soap,

respectively. The percentage of soap removal was increased with increase of sulfuric acid concentration. The highest percentage of soap removal was obtained by using bentonite, which was treated with 0.5 M of sulfuric acid. However, the acid value of biodiesel was dramatically increased with the increase of sulfuric acid concentration (Figure 4.6) and it almost reached to the limit of biodiesel standard (0.5 mg KOH/g oil). Due to the greater amount of proton on surface of activated bentonite, sodium ion of soap was greatly exchanged, which resulted in a massive transformation of soap to free fatty acid. Therefore, 0.1 M of sulfuric acid was selected to activate bentonite for further examination.

- **Effect of temperature on activating bentonite**

In order to investigate the influence of temperature on activating bentonite, the bentonite (120-200 mesh) was treated with different temperature (60 and 100°C). Then, activated bentonite was used to remove soap in crude biodiesel. The experiment was conducted at room temperature for 10 min. The results were shown in Figure 4.7 and Figure 4.8.
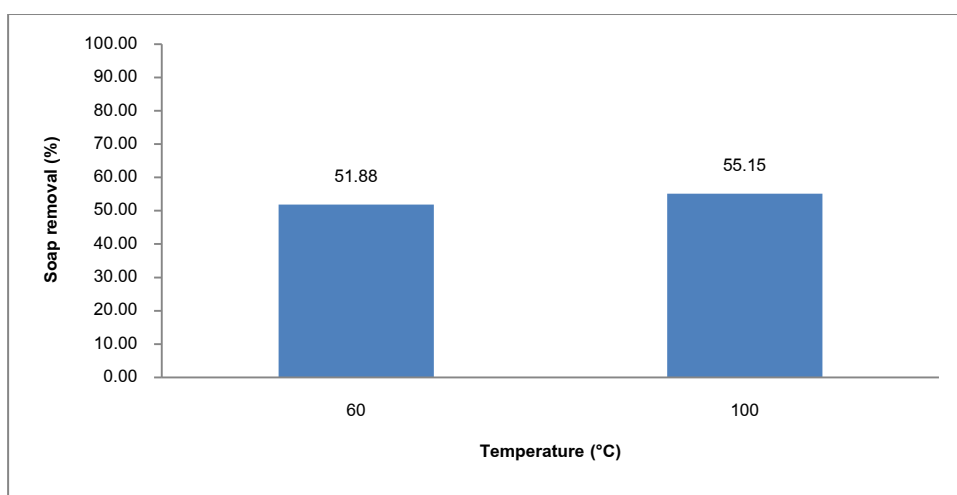
Figure 4.7 Effect of temperature on soap removal (Activation condition: 0.1 M of sulfuric acid at 60 and 100°C for 12h. Removal condition: 3%wt. of activated bentonite per g oil at room temperature for 10 min)
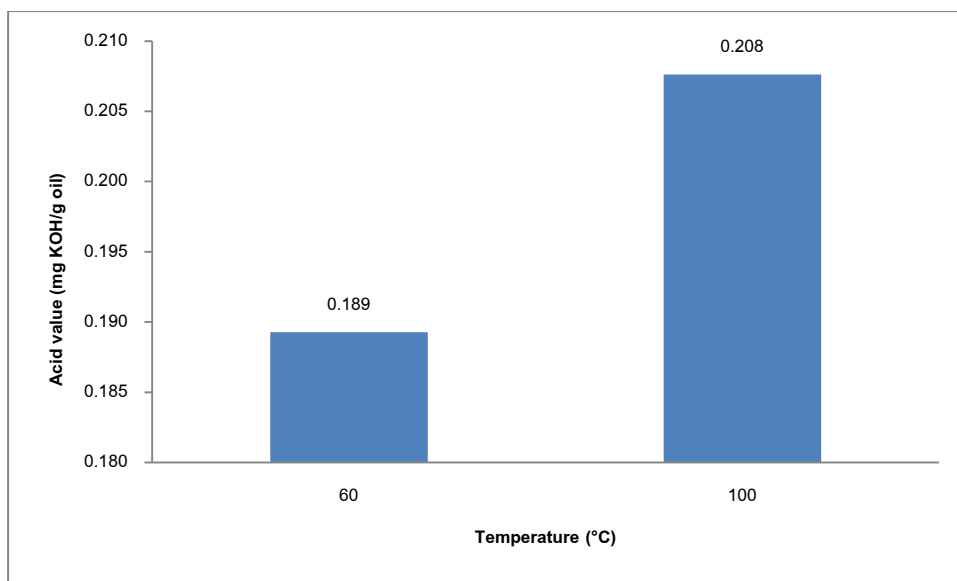
Figure 4.8 Effect of temperature on acid value (Activation condition: 0.1 M of sulfuric acid at 60 and 100°C for 12h. Removal condition: 3%wt. of activated bentonite per g oil at room temperature for 10 min)

The results in Figure 4.7 showed that bentonite, which was treated with sulfuric acid at 60 and 100°C, could remove 51.88 and 55.15% of soap, respectively. The percentage of soap removal was slightly increased with increase of activating temperature. This is due to the greater amount of proton entering into the layer to remove soap. From Figure 4.8, the activating temperature of activated bentonite doesn't affect acid value of biodiesel significantly. From the result, it can be concluded that the activating temperature has slight effect on activating bentonite. Therefore, the optimum temperature should be a lower temperature, which is 60°C.

- **Effect of time on activating bentonite**

In order to investigate the influence of time on activating bentonite, the bentonite (120-200 mesh) was treated with different time ranging from 1-24 hr. Then, activated bentonite was used to remove soap in crude biodiesel. The experiment was conducted at room temperature for 10 min. The results were shown in Figure 4.9 and Figure 4.10.
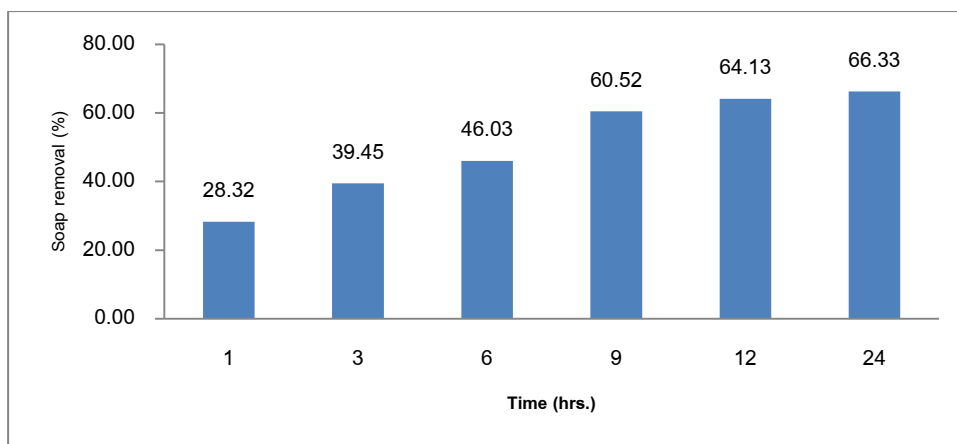
Figure 4.9 Effect of activation time on soap removal (Activation condition: 0.1 M of sulfuric acid at 60°C for 1-24h. Removal condition: 3%wt. of activated bentonite per g oil at room temperature for 10 min)
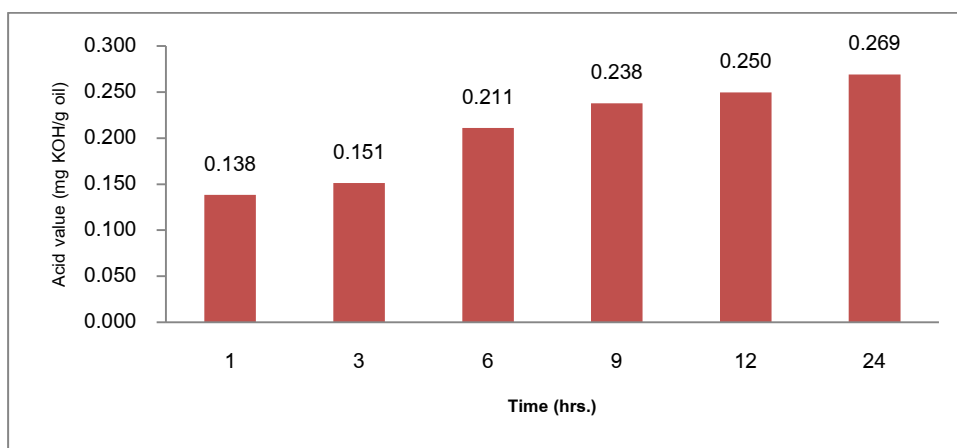
Figure 4.10 Effect of activation time on acid value (Activation condition: 0.1 M of sulfuric acid at 60°C for 1-24h. Removal condition: 3%wt. of activated bentonite per g oil at room temperature for 10 min)

The results in Figure 4.9 showed that bentonite, which was treated with sulfuric acid for 1, 3, 6, 9, 12 and 24h, could remove 28.32, 39.45, 46.03, 60.52, 64.13 and 66.33% of soap, respectively. The percentage of soap removal was increased with increase of activation time. The highest percentage of soap removal was bentonite that treated with 0.1 M of sulfuric for 24 h (66.33%). From Figure 4.10, the acid value of

biodiesel was increased with increase of activating time. However, there is not significant different of percentage of soap removal for activating time at 12 h and 24 h. Therefore the optimum activating time should be a lower one, which is 12 h.

- **Effect of amount of activated bentonite**

In order to investigate the influence of amount of activated bentonite, crude biodiesel was treated with different amount of activated bentonite ranging from 1-10%wt. of activated bentonite per g oil (120-200 mesh). The experiment was conducted at room temperature for 10 min. The results were shown in Figure 4.11 and Figure 4.12.
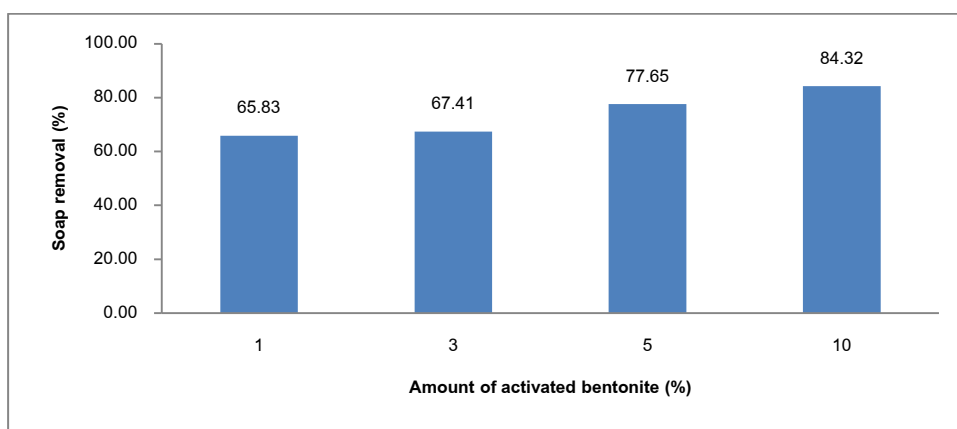
Figure 4.11 Effect of amount of activated bentonite on soap removal (Activation condition: 0.1 M of sulfuric acid at 60°C for 12h. Removal condition: 1-10%wt. of activated bentonite per g oil at room temperature for 10 min)
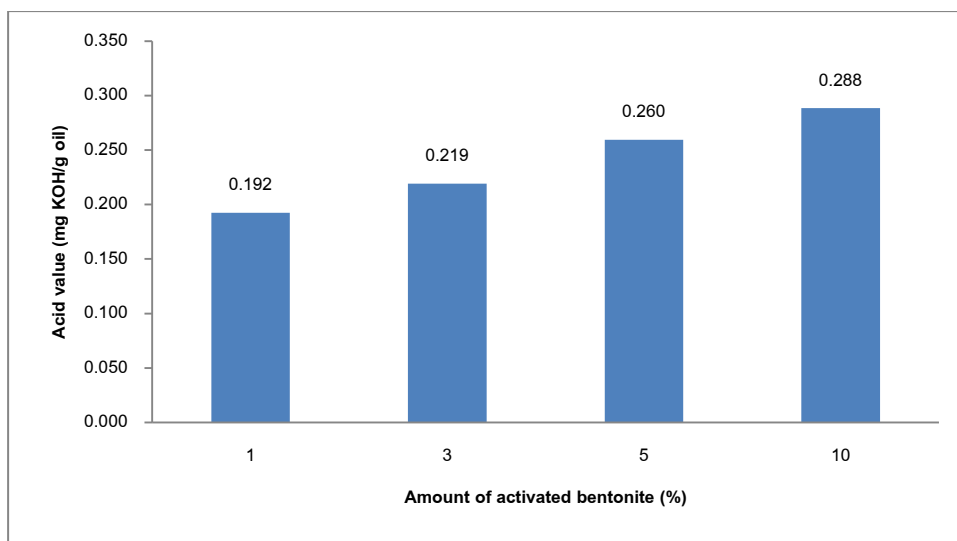
Figure 4.12 Effect of amount of activated bentonite on acid value (Activation condition: 0.1 M of sulfuric acid at 60°C for 12h. Removal condition: 1-10%wt. of activated bentonite per g oil at room temperature for 10 min)

The results in Figure 4.11 showed that soap removal was slightly increased with increase of amount of activated bentonite from 1-10%wt. of activated bentonite per g oil. As seen in Figure 4.12, the acid value also increased. However, the acid value was lower than biodiesel standard (not exceeded 0.5 mg KOH/g oil). Therefore, the optimum amount of activated bentonite was 10%wt. of activated bentonite per g oil.

- **Effect of particle size of activated bentonite**

In order to investigate the influence of particle size of activated bentonite, crude biodiesel was treated with different particle sizes of activated bentonite ranging from 60-200 mesh. The experiment was conducted at room temperature for 10 min. The amount of activated bentonite, which was used in this

process, was 10%wt. of activated bentonite per g oil. The results were shown in Figure 4.13 and Figure 4.14.
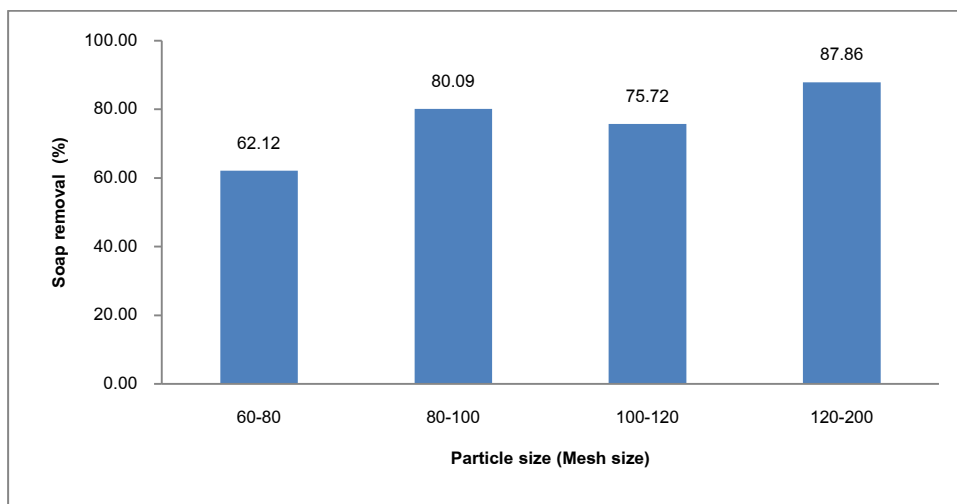
Figure 4.13 Effect of particle size on soap removal (Activation condition: 0.1 M of sulfuric acid at 60°C for 12h. Removal condition: 10%wt. of activated bentonite per g oil at room temperature for 10 min)
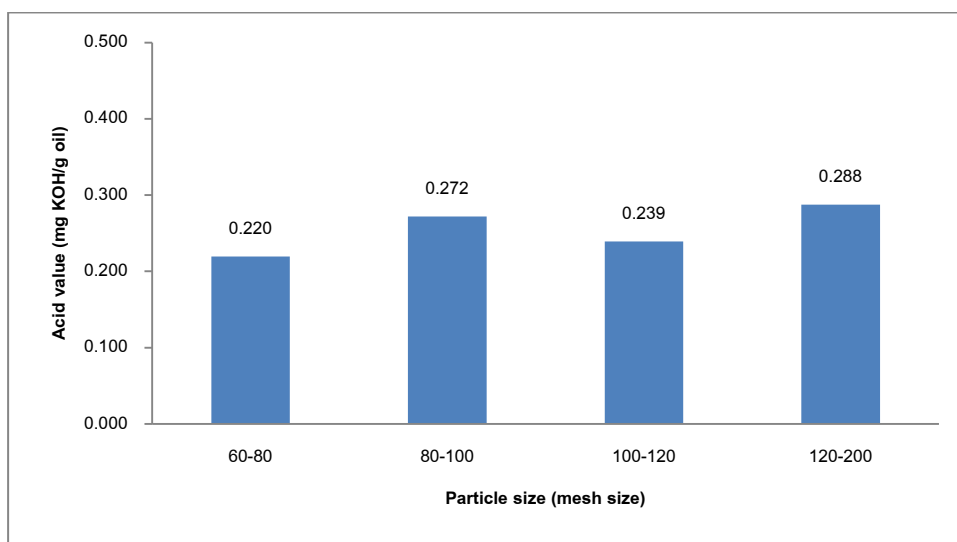
Figure 4.14 Effect of particle size on acid value (Activation condition: 0.1 M of sulfuric acid at 60°C for 12h. Removal condition: 10%wt. of activated bentonite per g oil at room temperature for 10 min)

The result in Figure 4.13, the particle size of activated bentonite, which was 60-80, 80-100, 100-120 and 120-200 mesh, could remove 62.12%, 80.09%, 75.72% and 87.86% of soap, respectively. The highest percentage of soap removal was obtained by using activated bentonite with particle size of 120-200 mesh. However, the usage of too small particle size (120-200 mesh) of activated bentonite cause a problem in purification process, which bentonite particle could not be removed from biodiesel. Therefore, the optimum particle size of activated bentonite was 80-100 mesh. The acid value was increased with increase of particle size of activated bentonite. However, the acid value was lower than biodiesel standard (not exceeded 0.5 mg KOH/g oil), as seen in Figure 4.14.

- **Effect of contact time**

The time-dependent behavior of the adsorption was measured by varying the equilibrium time between adsorbents and crude biodiesel in the range of 10–30 min. The experiment was conducted at room temperature with 10%wt. of activated bentonite per g oil (80-100 mesh, treated with 0.1M of sulfuric acid at 60 °C for 12h) and stirring rate at 150 rpm. The results were shown in Figure 4.15 and Figure 4.16.
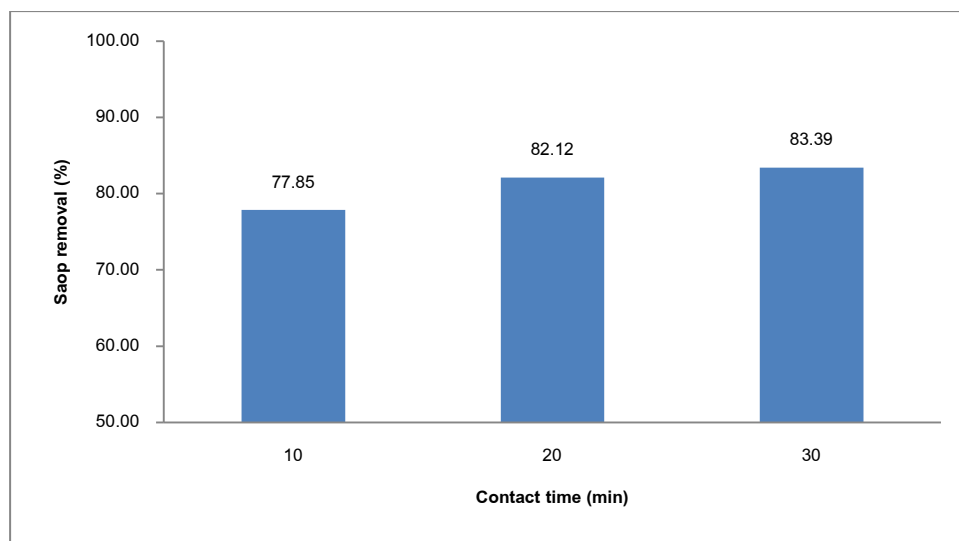
Figure 4.15 Effect of contact time on soap removal (Activation condition: 0.1 M of sulfuric acid at 60°C for 12h. Removal condition: 10%wt. of activated bentonite per g oil at room temperature for 10-30 min)
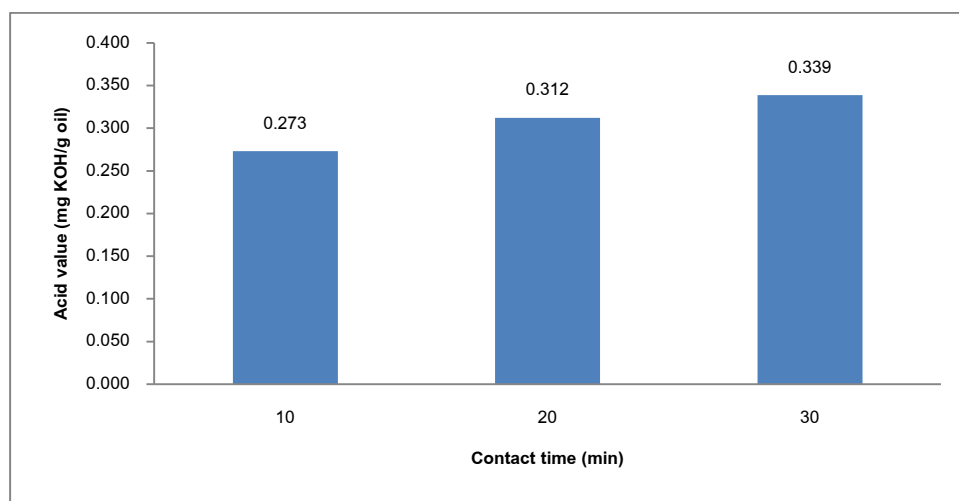
Figure 4.16 Effect of contact time on acid value (Activation condition: 0.1 M of sulfuric acid at 60°C for 12h. Removal condition: 10%wt. of activated bentonite per g oil at room temperature for 10-30 min)

As seen in Figure 4.15, at contact time of 20 min, the soap removal was increased to 82.12 %. Afterwards, the content of soap removal remains constant. From Figure 4.16, at contact time of 20 min, the acid value of biodiesel was 0.312 mg KOH/g oil and it was lower than biodiesel standard (not exceeded 0.5 mg KOH/g oil). Therefore, a 20 min contact time was found to be appropriate for soap removal.

4.3.2 Purification of crude biodiesel by using commercial bentonite and activated bentonite

In order to compares soap removal ability, crude biodiesel was treated with natural bentonite, activated bentonite (treated with 0.1M of sulfuric acid at 60 °C for 12h) and commercial bentonite. The results were shown in Figure 4.17 and Figure 4.18.
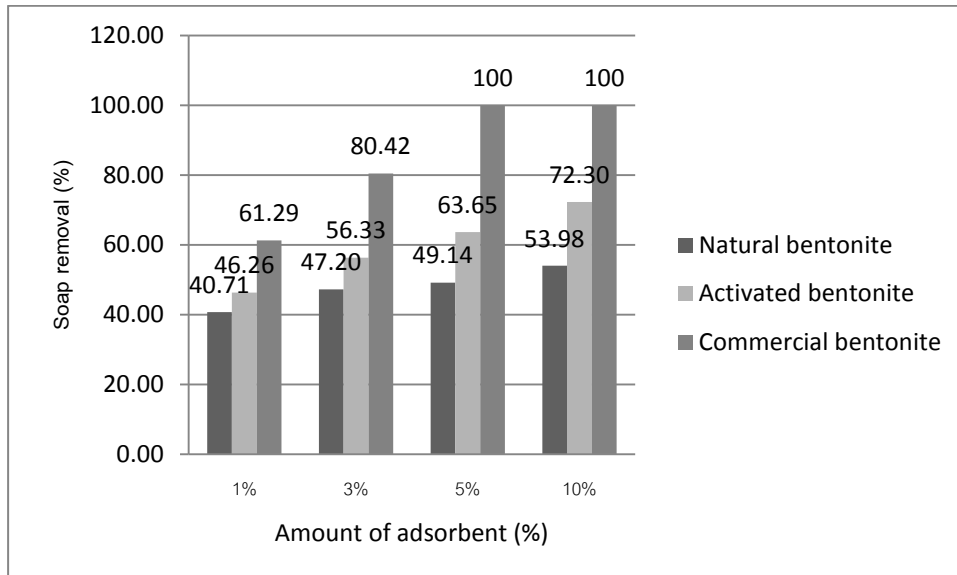
Figure 4.17 Comparison of soap removal ability (80-100 mesh at room temperature for 20 min)
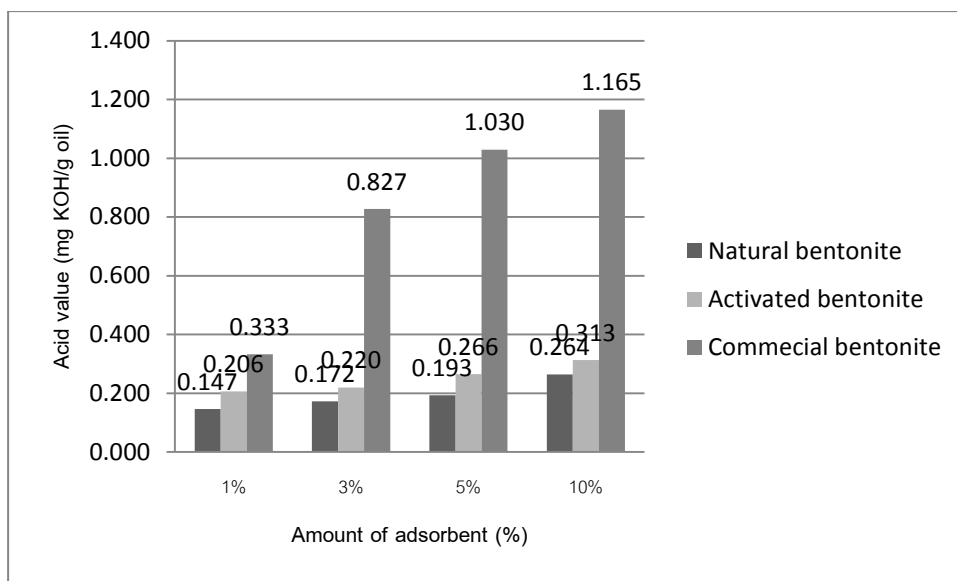
Figure 4.18 Comparison of acid value (80-100 mesh at room temperature for 20 min)

The results in Figure 4.17 and Figure 4.18 showed that commercial bentonite has highest percentage soap removal comparing with natural bentonite and activated bentonite with same amount of adsorbent usage. However, biodiesel that treated with commercial bentonite also has the highest acid value. At 1%wt. of adsorbent per g oil, commercial bentonite could remove 61.29% of soap and the acid value was 0.333 mg KOH/g oil, which almost reached to the limit of biodiesel standard (0.5 mg KOH/g oil). Therefore, 1%wt. of commercial bentonite per g oil was chosen to compare with natural bentonite and activated bentonite. At 10%wt. of natural bentonite per g oil, soap removal was 53.98% of soap and acid value was 0.264 mg KOH/g oil. At 10%wt. of activated bentonite per g oil, soap removal was 72.30% of soap and acid value was 0.313 mg KOH/g oil. Therefore, 10%wt. of activated bentonite per g oil could remove soap more than 1%wt. of commercial bentonite per g oil and 10%wt. of natural bentonite per g oil.

4.3.3 Purification of crude biodiesel by water washing

The properties of biodiesel that purified with water washing and dry-water washing by using 10%wt. of activated bentonite per g oil (80-100 mesh, 0.1M of sulfuric acid at 60°C for 12h) were showed in Table 4.3. Acid value of biodiesel that purified with water washing was 0.41 KOH/g oil. Acid value of biodiesel that purified with dry washing by using activated bentonite and water washing were 0.33 mg KOH/g oil. Viscosity of biodiesel that purified with water washing was 4.22 cSt. Viscosity of biodiesel that purified with dry washing by using activated bentonite and water washing was 3.83 cSt. Biodiesel that treated with activated bentonite was met the biodiesel standard.

Table 4.3 Comparison of biodiesel properties between water washing and dry washing by using activated bentonite (0.1M of sulfuric acid at 60°C for 12h).

Biodiesel properties	Biodiesel standard	Water washing	Dry-water washing
Acid value	< 0.5 mg KOH/g oil	0.41	0.33
Viscosity	3.0-5.0 cSt	4.22	3.83
Free glycerol	<0.02	-	0.0017
Mono glycerol	<0.80	0.1892	0.3077
Di glycerol	<0.20	0.0179	-
Tri glycerol	<0.20	-	-
Total Glycerol	<0.25	0.0509	0.0802

4.4   Determination of the properties of biodiesel

The quality of biodiesel could be estimated by investigated the properties of biodiesel such as viscosity and % free fatty acid.

4.4.1 Viscosity (ASTM D445)

The viscosity of crude biodiesel and purified biodiesel (with natural bentonite and bentonite that treated with 0.1M of sulfuric acid at 60°Cfor 12h) were showed in Table 4.4.

Table 4.4 Viscosity of crude biodiesel and purified biodiesels (treated with natural bentonite and bentonite that treated with 0.1M of sulfuric acid at 60°C for 12h)

Sample	Viscosity (cSt)
Crude biodiesel	6.18
Biodiesel that treat with natural bentonite	4.39
Biodiesel that treat with activated bentonite	3.83

From Table 4.4, Natural bentonite and activated bentonite could reduce viscosity of crude biodiesel from 6.18 to 4.39 and 3.83cSt, respectively. As observed, the viscosity of biodiesel that treated with natural bentonite and activated bentonite was in good agreement with biodiesel standard requirement (3.0-5.0 cSt).

4.4.2 % free fatty acid(ASTM 5555)

% free fatty acid of crude biodiesel and purified biodiesel (treated with natural bentonite and bentonite that treated with 0.1M of sulfuric acid at 60°C for 12h) were shown in Table 4.5.

Table 4.5 %free fatty acid of crude biodiesel and purified biodiesel (treated with natural bentonite and bentonite that treated with 0.1M of sulfuric acid at 60°C for 12h)

Sample	% free fatty acid
Crude biodiesel	4.16
Biodiesel that treat with natural bentonite	0.98
Biodiesel that treat with activated bentonite	1.28

From Table 4.5, Removal process with natural bentonite and activated bentonite could reduce free fatty acid from 4.16 to 0.98 and 1.28 %, respectively. As observed, Acid activation of bentonite increased free fatty acid of purified biodiesel from 0.98 to 1.28 %. Due to the greater amount of proton on surface of activated bentonite, sodium ion of soap was greatly exchanged, which resulted in a massive transformation of soap to free fatty acid.

4.5   Adsorption isotherm of soap

To simulate the adsorption isotherm, two commonly used models, the Freundlich and Langmuir isotherms, were selected to explain the adsorption. Ten concentrations of activated bentonite (80-100 mesh, treated with 0.1M of sulfuric acid at 60 °C for 12h) were studied in the range of 1-10%wt. of activated bentonite per g oil. In a 100 milliliters glass bottom, 50 grams of crude biodiesel was treated with activated bentonite at room temperature with stirring at 150 rpm for 20 min. The results were shown in Figure 4.19.

(a)   (b)
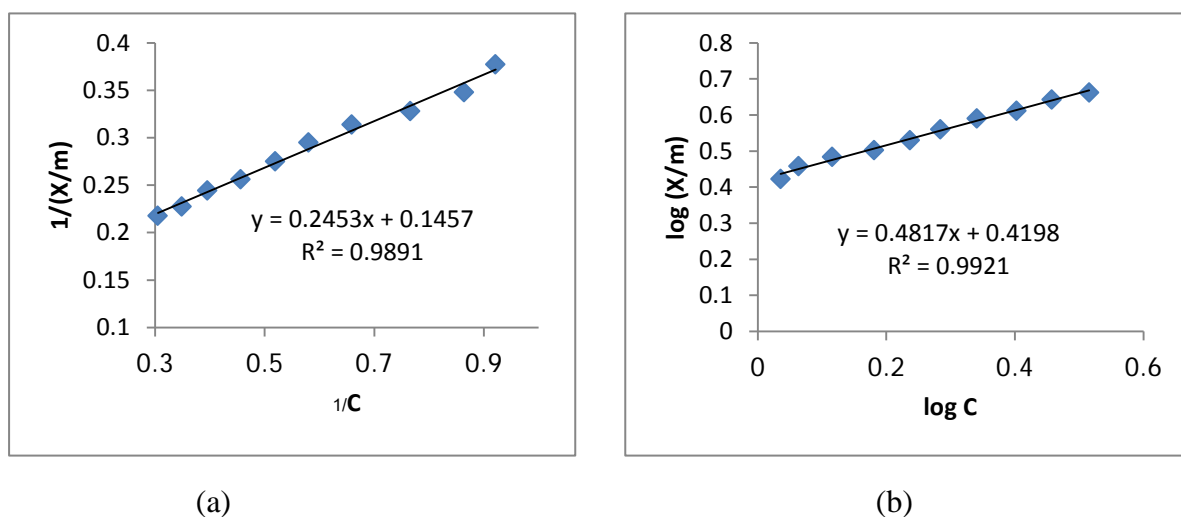
Figure 4.19 Adsorption isotherms of activated bentonite Langmuir isotherm (a) and Freundlich isotherm (b).

Table 4.6 Adsorption parameters of isotherm for the adsorption of soap molecule on activated bentonite.

Adsorbent	Freundlich			Langmuir	
	K_F	n	r^2	K_L	r^2
Activated clay	2.63	2.08	0.9921	0.59	0.9891

The calculated values of Freundlich and Langmuir model's parameters were shown in Table 4.6. From Figure 4.19, activated bentonite was better fit to Freundlich model than Langmuir because the r^2 value (0.9921) was closer to 1. K_F was indicated of the adsorption capacity of the adsorbent, the result showed that K_F of activated bentonite was 2.63. The other Freundlich constant, n was a measurment of the deviation from linearity of the adsorption and used to verify types of adsorption. It is suggested that if n below 1, the adsorption is a chemical process; whereas, n above 1 is associated with a physical process. The result shows that n of activated bentonite was 2.08. Therefore, the adsorption type of activated bentonite tended to be a physical adsorption.

CHAPTER V

CONCLUSION AND SUGGESTION

In the study of acid activation of bentonite for purification of biodiesel, the optimal condition for activating bentonite was 0.1 M H_2SO_4 at 60 ^{0}C for 12 h. The results showed that the specific surface area of activated bentonite was increased from 48.45 to 55.15 m^2 g^{-1}, calculated by BET method. The morphology of activated bentonite was unchanged compared with natural bentonite because sulfuric acid concentration that used to activating bentonite was too low to dissolve montmorillonite structure, described by XRD. The chemical composition of natural and activated bentonite showed that MgO, CaO, Na_2O and K_2O, were slightly decreased from 3.68, 3.30, 0.83 and 0.75 to 3.42, 2.69, 0.10 and 0.65 %wt., respectively, as described by XRF. The biodiesel was synthesized via transesterfication using based-catalyzed process then crude biodiesel was purified by activated bentonite. The optimal condition for soap removal was 10%wt. of activated bentonite (80-100 mesh) per g oil at room temperature with stirring rate of 150 rpm for 20 min. The efficiency of activated bentonite was subjected to compare with efficiency of natural bentonite. The removal of soap in biodiesel was increased from 53.98 to 72.30%. The acid value of biodiesel was also increased from 0.264 to 0.313 mg KOH/g oil, due to proton in interlayer of activated bentonite was exchanged with sodium ion of soap in biodiesel and converted to free fatty acid. The quality of biodiesel after purified by activated bentonite followed by water washing could meet the major specification of biodiesel standards. The adsorption isotherm was fit to Freundlich isotherm because the r^2 value (0.9921) was closed to 1.

Suggestion

Using base such as sodium hydroxide or potassium hydroxide to activate bentonite.

REFERENCES

[1]   Shishir M., Hingu, Parag R. and Gogate, Virendra K. Rathod. Synthesis of biodiesel from waste cooking oil using sonochemical reactors. Ultrasonics Sonochemistry 17 (2010): 827–832.

[2]   Fazal M.A., Haseeb A.S.M.A.and Masjuki H.H. Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability. Renewable and Sustainable Energy Reviews. 15 (2011): 1314–1324.

[3]   Lee S., Posarac D.and Ellis N. An experimental investigation of biodiesel synthesis from waste canola oil using supercritical methanol. Fuel. 91 (2012): 229–237.

[4]   Atadashi I.M., Aroua M.K., Abdul Aziz A.R. and Sulaiman N.M.N. Refining technologies for the purification of crude biodiesel. Applied Energy. 88 (2011): 4239–4251.

[5]   EPPO Department Operation Centre. Ministry of Energy, Thailand. Energy Statistics [online]. 2003. Available from : http://www.eppo.go.th [2009, August 19]

[6]   Kritana P., Shabbir H. G., Pomthong M. and Sébastien B. Energy analysis of Jatropha plantation systems for biodiesel production in Thailand. Energy for Sustainable Development. 14 (2010): 1–5.

[7]   Hoekman S. K. and Robbins C. Review of the effects of biodiesel on NOx emissions. Fuel Processing Technology. 96 (2012): 237–249.

[8]   Berrios M. and Skelton R.L. Comparison of purification methods for biodiesel. Chemical Engineering Journal. 144 (2008): 459–465.

[9]   Hideki F., Akihiko K. AND Hideo N. Biodiesel Fuel Production by Transesterification of Oils. Journal of Bioscience and Bioengineering. 92 (2001) 405-416.

[10]   Borugadda V. B. and Goud V. V. Biodiesel production from renewable feedstocks: Status and opportunities. Renewable and Sustainable Energy Reviews 16 (2012): 4763–4784.

[11]   Shahid E. M., Jamal Y. Production of biodiesel: A technical review. Renewable and Sustainable Energy Reviews. 15 (2011): 4732– 4745.

[12] Maria C. S. G., Nehemias C. P. and Sueli T. D. B. Separation of biodiesel and glycerol using ceramic membranes. Journal of Membrane Science. 352 (2010): 271–276.

[13] Mendow G., Veizaga N.S., Sanchez B.S. and Querini C.A. Biodiesel production by two-stage transesterification with ethanol by washing with neutral water and water saturated with carbon dioxide. Bioresource Technology. 118 (2012): 598–602.

[14] Joon C. J., Damayani A. K., Ta Y. W. and Taufiq-Yap Y. H. Biodiesel production from jatropha oil by catalytic and non-catalytic approaches: An overview. Bioresource Technology. 102 (2011): 452–460.

[15] Keera S.T., Sabagh E. S.M. and Taman A.R. Transesterification of vegetable oil to biodiesel fuel using alkaline catalyst. Fuel. 90 (2011): 42–47.

[16] Atadashi I.M., Aroua M.K., Abdul A. A.R. and Sulaiman N.M.N. Production of biodiesel using high free fatty acid feedstocks. Renewable and Sustainable Energy Reviews 16 (2012): 3275– 3285.

[17] Zlatica J. Predojevic. The production of biodiesel from waste frying oils: A comparison of different purification steps. Fuel. 87 (2008): 3522–3528.

[18] Kopecký F., Kaclík P., Fazekaš T. Laboratory manual for physical chemistry, Pharmaceutical faculty of Comenius University, Bratislava, 1996.

[19] Maria L. S., Andres M., Herminia D. and Juan C. P. Recovery, concentration and purification of phenolic compounds by adsorption: A review. Journal of Food Engineering. 105 (2011): 1–27.

[20] Mohd R., Othman S, Rokiah H. and Anees A. Adsorption of methylene blue on low-cost adsorbents: A review. Journal of Hazardous Materials. 177 (2010): 70–80.

[21] Grigoriy A. and Marc D. Analysis of Adsorption Isotherms: Lattice Theory Predictions, Classification of Isotherms for Gas–Solid Equilibria, and Similarities in Gas and Liquid Adsorption Behavior. Journal of Colloid and Interface Science. 200 (1998): 273–290.

[22]   Donohue M.D. and Aranovich G.L. Classification of Gibbs adsorption isotherms. <u>Advances in Colloid and Interface Science</u>. 76-77 (1998). 137-152.

[23]   Yuksel B. Application of Langmuir isotherm to saturated fatty acid adsorption. <u>Microporous and Mesoporous Materials</u> 87 (2006): 203–206.

[24]   Abdullah M.A., Chiang L. and Nadeem M. Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents. <u>Chemical Engineering Journal</u>. 146 (2009): 370–376.

[25]   Garnier Ch., Finqueneisel G., Zimny T., Pokryszka Z., Lafortune S., Défossez P.D.C. and Gaucher E.C. Selection of coals of different maturities for CO_2 Storage by modelling of CH_4 and CO_2 adsorption isotherms. <u>International Journal of Coal Geology</u>. 87 (2011): 80–86.

[26]   Korkuna O., Leboda R., Skubiszewska-Zieba J., Vrublevs'ka T., Gun'ko V.M., and Ryczkowski J. Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite. <u>Micropore and Mesopore Material</u> 87 (2006) 243–254.

[27]   Cynthia A. C. and Raymond N. Y. Use of equilibrium and initial metal concentrations in determining Freundlich isotherms for soils and sediments. <u>Engineering Geology</u> 85 (2006): 19– 25.

[28]   Stephen J. A., Quan G., Ronan M. and Pauline A. J. Comparison of optimised isotherm models for basic dye adsorption by kudzu. <u>Bioresource Technology</u>. 88 (2003): 143–152.

[29]   Brunauer, S., Emmet, P.H. and Teller, E. Adsorption of gases in multimolecular layers. <u>Journal of American Chemistry Society</u> 60 (1938): 309-319.

[30]   Caglar B., Afsin B., Tabak A. and Eren E. Characterization of the cation-exchanged bentonites by XRPD, ATR, DTA/TG analyses and BET measurement. <u>Chemical Engineering Journal</u>. 149 (2009): 242–248.

[31]   Nalan T. and Yurdanur A. Adsorption of poly(vinylimidazole) from aqueous solutions onto Na-bentonite. <u>International Journal of Mineral Processing</u>. 112–113 (2012): 49–54.

[32]   Beena T., Chintan D. C. and Raksh V. J. Determination of structural modification in acid activated montmorillonite clay by FT-IR spectroscopy. Spectrochmica Part A. 64 (2006): 273-278.

[33]   Karimi L. and Salem A. Analysis of bentonite specific surface area by kinetic model during activation process in presence of sodium carbonate. Microporous and Mesoporous Materials. 141 (2011): 81–87.

[34]   Feridun B. Optimization of foundry sand characteristics of soda-activated calcium bentonite. Applied Clay Science. 52 (2011): 104–108.

[35]   Shailendra S., Avinash K. A. and Sanjeev G. Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. Energy Conversion and Management. 49 (2008): 1248–1257.

[36]   Márcia C. M., Candice S. F., Bruna O., Edilson V. B. and Elina B. C. Rice husk ash as an adsorbent for purifying biodiesel from waste frying oil. Fuel. 92 (2012): 56–61.

[37]   Hajjaji M. and Arfaoui H. E. Adsorption of methylene blue and zinc ions on raw and acid-activated bentonite from Morocco. Applied Clay Science. 46 (2009): 418–421.

[38]   Nilgün Y., Cengiz B., Müserref O. and Yüksel S. Simultaneous determination of cation exchange capacity and surface area of acid activated bentonite powders by methylene blue sorption. Applied Surface Science. 258 (2012): 2534–2539.

[39]   Temuujin J., Jadambaa Ts., Burmaa G., Erdenechimeg Sh., Amarsanaa J. and MacKenzie K.J.D. Characterisation of acid activated montmorillonite clay from Tuulant (Mongolia). Ceramics International. 30 (2004): 251–255.

[40]   Steudel A., Batenburg L.F., Fischer H.R., Weidler P.G. and Emmerich K. Alteration of swelling clay minerals by acid activation. Applied Clay Science. 44 (2009): 105–115.

[41]   Budsaya S. Purification of biodiesel from palm oil by adsorption with clays. Thesis of Chulalongkorn University. 2009.

APPENDICES

APPENDIX A

GC CHROMATOGRAM OF BIODIESEL

Appendix A

GC chromatogram

Data File: c:\star\joe\std1.1 11;30;40 am.run   Operator (Calc):   jo
Channel: Front = FID RESULTS   Calc Date: 26/03/2010 17:36:25
Sample ID: std.1.1   Times Calculated: 4
Operator (Inj):   io   Calculation Method: std1.1 11;30;40 am-front.mth
Injection Date: 26/2/2010 11:30:40   Instrument (Calc):   gc
Injection Method: c:\star\en14105.mth   Run Mode: Analysis
Run Time (min):   35.775   Peak Measurement: Peak Area
Workstation: Calculation Type: Percent
Instrument (Inj):   gc   Calibration Level: N/A
                                                                  Verification Tolerance: N/A
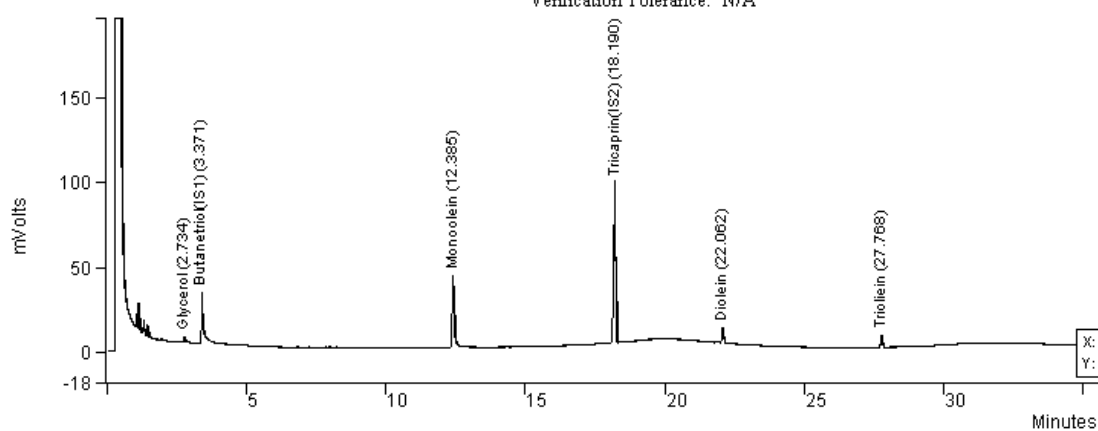
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.2179	2.734	-0.000	10554	0.00	BB	2.6		0
2	Butanetriol(IS1)	11.9895	3.371	0.004	103900	0.00	BB	2.6		0
3	Monoolein	24.8616	12.385	-0.016	215449	0.00	BB	4.5		0
4	Tricaprin(IS2)	53.6904	18.190	0.003	465277	0.00	BB	4.6		0
5	Diolein	4.4390	22.062	-0.001	38468	0.00	BB	4.1		0
6	Triolein	3.8016	27.768	-0.000	32944	0.00	BB	4.4		0
	Totals	**100.0000**		**-0.010**	**866592**					

Figure A1 GC chromatogram of EN 14105 standard solution 1 (1).

Data File: c:\star\joe\std1.2   12;21;39 pm.run   Operator (Calc):   jo
Channel: Front = FID RESULTS   Calc Date: 26/03/2010 17:36:25
Sample ID: std1.2   Times Calculated: 4
Operator (Inj):   io   Calculation Method: std1.1 11;30;40 am-front.mth
Injection Date: 26/2/2010 12:21:39   Instrument (Calc):   gc
Injection Method: c:\star\en14105.mth   Run Mode: Analysis
Run Time (min):   35.775   Peak Measurement: Peak Area
Workstation: Calculation Type: Percent
Instrument (Inj):   gc   Calibration Level: N/A
                                                                Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.2542	2.731	-0.003	11190	0.00	BB	2.5		0
2	Butanetriol(IS1)	12.2305	3.369	0.002	109112	0.00	BB	2.5		0
3	Monoolein	24.8375	12.383	-0.018	221583	0.00	BB	4.4		0
4	Tricaprin(IS2)	53.9499	18.190	0.003	481304	0.00	BB	4.5		0
5	Diolein	4.4034	22.061	-0.002	39284	0.00	BB	4.0		0
6	Trioliein	3.3244	27.763	-0.005	29658	0.00	BB	4.5		0
	Totals	**99.9999**		**-0.023**	**892131**					

Figure A2 GC chromatogram of EN 14105 standard solution 1 (2).

Data File:	c:\star\joe\std2.1 1;12;09 pm.run
Channel:	Front = FID RESULTS
Sample ID:	std2.1
Operator (Inj):	io
Injection Date:	26/2/2010 13:12:09
Injection Method:	c:\star\en14105.mth
Run Time (min):	35.773
Workstation:	
Instrument (Inj):	gc

Operator (Calc):	jo
Calc Date:	26/03/2010 17:29:48
Times Calculated:	5
Calculation Method:	std2.1 1;12;09 pm-front.mth
Instrument (Calc):	gc
Run Mode:	Analysis
Peak Measurement:	Peak Area
Calculation Type:	Percent
Calibration Level:	N/A
Verification Tolerance:	N/A
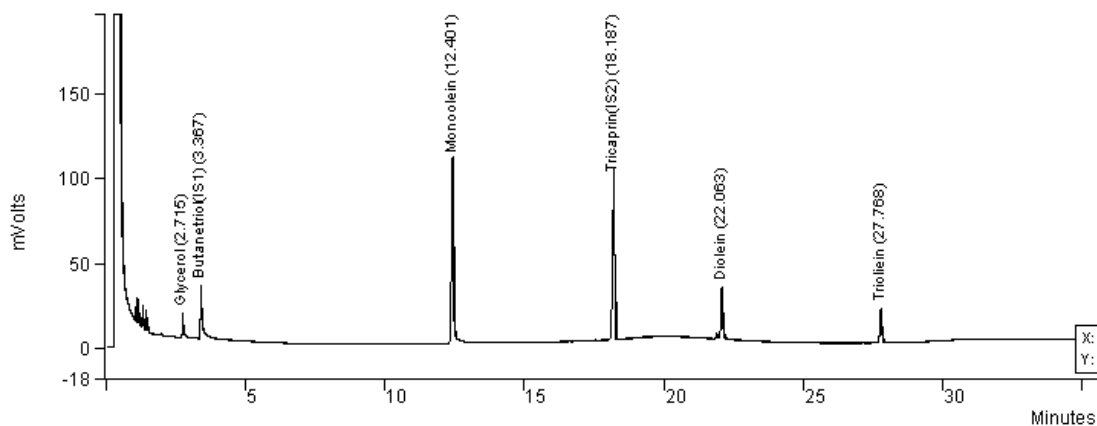
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	2.6591	2.715	-0.020	36824	0.00	BB	2.1		0
2	Butanetriol(IS1)	7.6435	3.367	-0.000	105847	0.00	BB	2.5		0
3	Monoolein	38.1843	12.401	-0.000	528776	0.00	BB	4.3		0
4	Tricaprin(IS2)	35.0148	18.187	-0.000	484885	0.00	BB	4.5		0
5	Diolein	9.6562	22.063	-0.000	133719	0.00	VB	4.1		0
6	Trioliein	6.8422	27.768	0.000	94750	0.00	BB	4.4		0
	Totals	100.0001		-0.020	1384801					

Figure A3 GC chromatogram of EN 14105 standard solution 2 (1).

Data File: c:\star\joe\std2.2 2;02;20 pm.run   Operator (Calc):   jo
Channel: Front = FID RESULTS   Calc Date: 26/03/2010 17:28:04
Sample ID: std2.2   Times Calculated: 3
Operator (Inj):   io   Calculation Method: std2.1 1;12;09 pm-front.mth
Injection Date: 26/2/2010 14:02:20   Instrument (Calc):   gc
Injection Method: c:\star\en14105.mth   Run Mode: Analysis
Run Time (min):   35.773   Peak Measurement: Peak Area
Workstation: Calculation Type: Percent
Instrument (Inj):   gc   Calibration Level: N/A
                                                                 Verification Tolerance: N/A
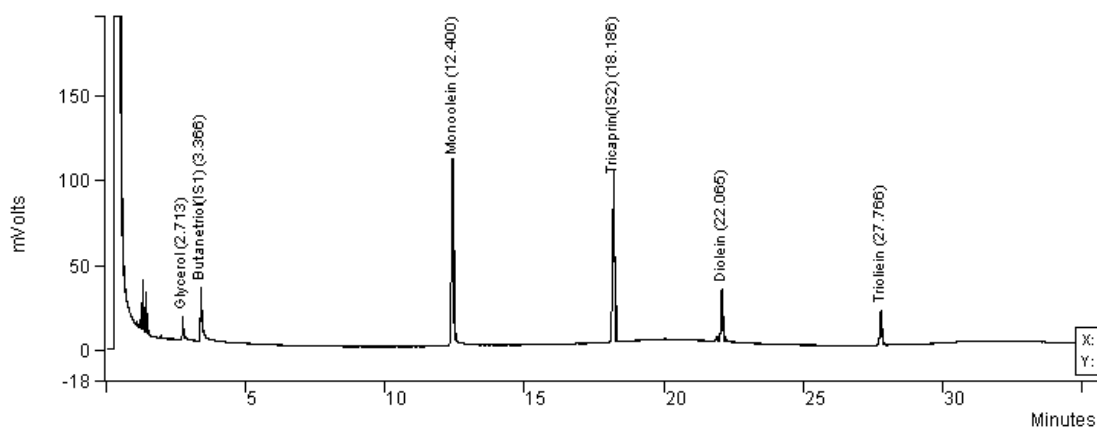
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	2.7003	2.713	-0.002	37959	0.00	BB	2.1		0
2	Butanetriol(IS1)	7.8658	3.366	-0.001	110574	0.00	BB	2.5		0
3	Monoolein	38.1313	12.400	-0.001	536031	0.00	BB	4.4		0
4	Tricaprin(IS2)	34.9182	18.186	-0.001	490864	0.00	BB	4.5		0
5	Diolein	9.6609	22.065	0.002	135809	0.00	VB	4.1		0
6	Trioliein	6.7235	27.766	-0.002	94516	0.00	BB	4.4		0
	Totals	100.0000		-0.005	1405753					

Figure A4 GC chromatogram of EN 14105 standard solution 2 (2).

Data File: c:\star\joe\std3.1 2;52;37 pm.run
Channel: Front = FID RESULTS
Sample ID: std3.1
Operator (Inj): io
Injection Date: 26/2/2010 14:52:37
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 26/03/2010 17:28:05
Times Calculated: 3
Calculation Method: std2.1 1;12;09 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A
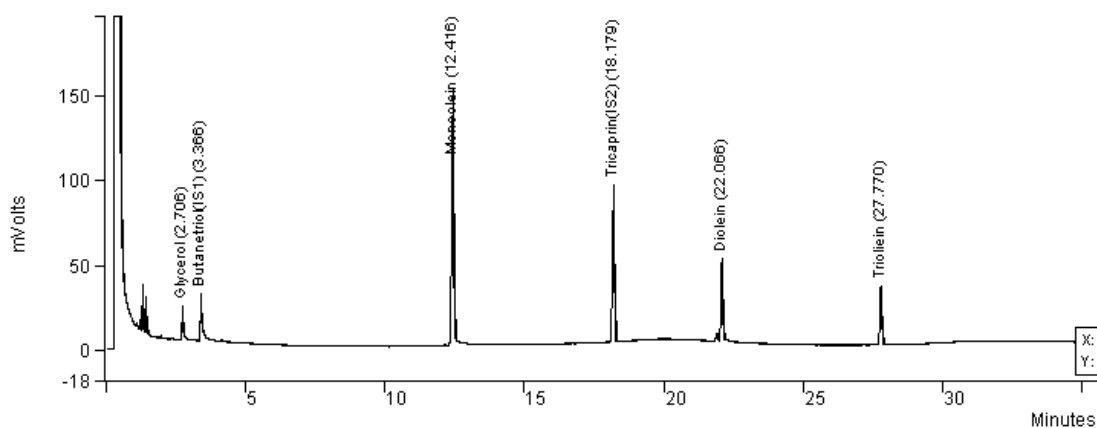
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.2580	2.706	-0.009	56688	0.00	BB	2.4		0
2	Butanetriol(IS1)	5.9095	3.366	-0.001	102822	0.00	BB	2.6		0
3	Monoolein	43.5769	12.416	0.015	758214	0.00	BB	4.6		0
4	Tricaprin(IS2)	25.5245	18.179	-0.008	444111	0.00	BB	4.5		0
5	Diolein	12.1463	22.066	0.003	211338	0.00	VB	4.1		0
6	Triolein	9.5848	27.770	0.002	166770	0.00	BB	4.4		0
	Totals	**100.0000**		**0.002**	**1739943**					

Figure A5 GC chromatogram of EN 14105 standard solution 3 (1).

Data File: c:\star\joe\std3.2 3;42;48 pm.run   Operator (Calc):   jo
Channel: Front = FID RESULTS   Calc Date: 26/03/2010 17:29:48
Sample ID: std3.2   Times Calculated: 4
Operator (Inj):   io   Calculation Method: std2.1 1;12;09 pm-front.mth
Injection Date: 26/2/2010 15:42:48   Instrument (Calc):   gc
Injection Method: c:\star\en14105.mth   Run Mode: Analysis
Run Time (min):   35.773   Peak Measurement: Peak Area
Workstation: Calculation Type: Percent
Instrument (Inj):   gc   Calibration Level: N/A
                                                               Verification Tolerance: N/A
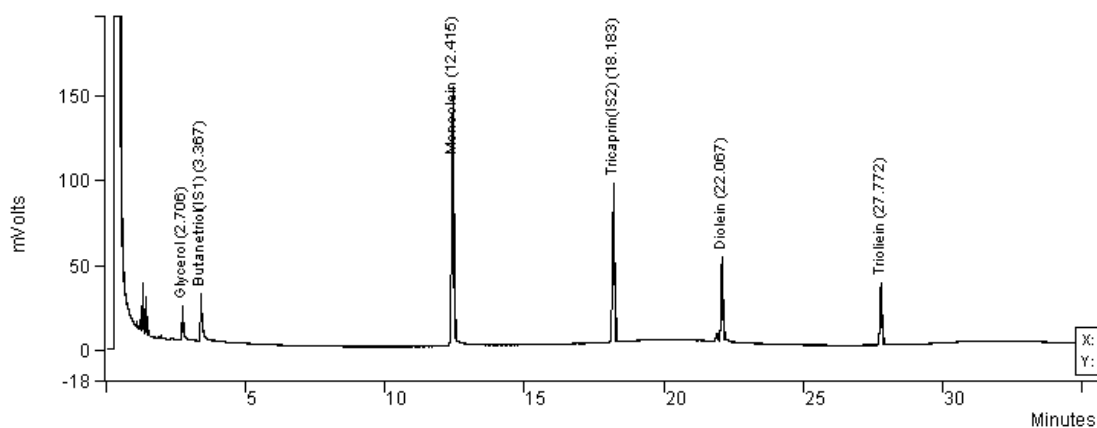
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.2183	2.706	-0.029	56811	0.00	BB	2.4		0
2	Butanetriol(IS1)	5.8378	3.367	0.000	103051	0.00	BB	2.6		0
3	Monoolein	43.4559	12.415	0.014	767103	0.00	BB	4.6		0
4	Tricaprin(IS2)	25.4945	18.183	-0.004	450041	0.00	BB	4.5		0
5	Diolein	12.1960	22.067	0.004	215288	0.00	VB	4.1		0
6	Trioliein	9.7975	27.772	0.004	172950	0.00	BB	4.4		0
	Totals	100.0000		-0.011	1765244					

Figure A6 GC chromatogram of EN 14105 standard solution 3 (2).

Data File: c:\star\joe\std4.1   4;38;32 pm.run   Operator (Calc):   jo
Channel: Front = FID RESULTS   Calc Date: 26/03/2010 17:29:48
Sample ID: std4.1   Times Calculated: 5
Operator (Inj):   io   Calculation Method: std2.1   1;12;09 pm-front.mth
Injection Date: 26/2/2010 16:38:32   Instrument (Calc):   gc
Injection Method: c:\star\en14105.mth   Run Mode: Analysis
Run Time (min):   35.775   Peak Measurement: Peak Area
Workstation: Calculation Type: Percent
Instrument (Inj):   gc   Calibration Level: N/A
                                                                      Verification Tolerance: N/A
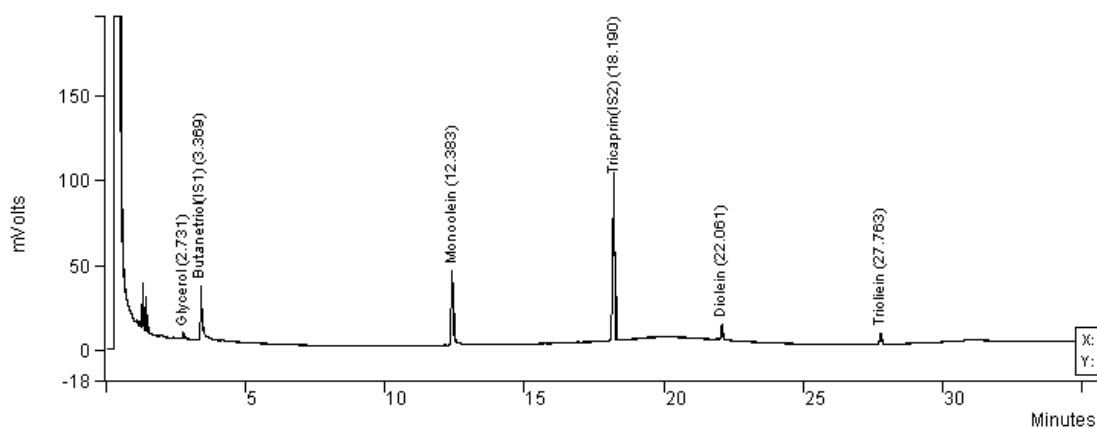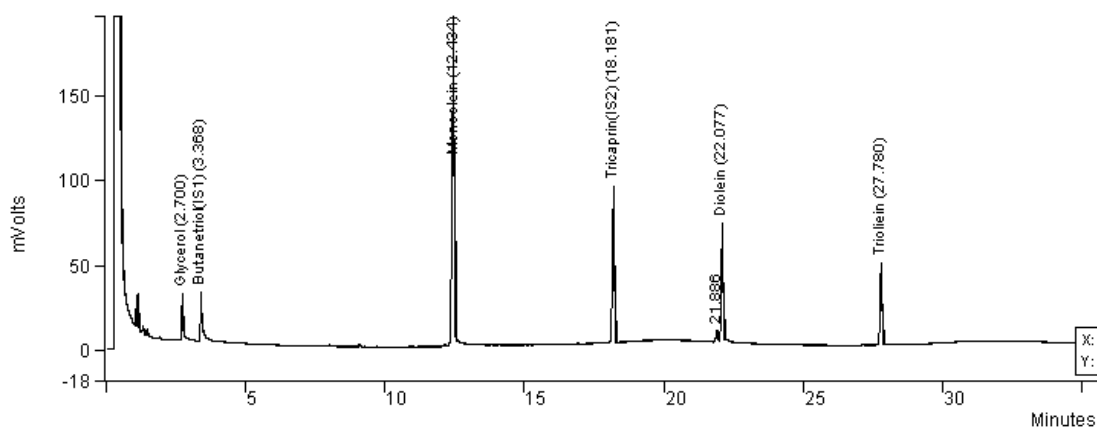

Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.5958	2.700	-0.035	79563	0.00	BB	2.5		0
2	Butanetriol(IS1)	4.5792	3.368	0.001	101322	0.00	BB	2.5		0
3	Monoolein	45.8442	12.434	0.033	1014370	0.00	BB	4.9		0
4	Tricaprin(IS2)	20.4509	18.181	-0.006	452505	0.00	BB	4.6		0
5		1.2314	21.886	0.000	27246	0.00	BV	4.2		0
6	Diolein	13.7652	22.077	0.014	304575	0.00	VB	4.2		0
7	Trioliein	10.5332	27.780	0.012	233063	0.00	BB	4.6		0
	Totals	**99.9999**		**0.019**	**2212644**					

Figure A7 GC chromatogram of EN 14105 standard solution 4 (1).

Data File:	c:\star\joe\std4.2 5;29;02 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 17:29:49
Sample ID:	std4.2	Times Calculated:	4
Operator (Inj):	io	Calculation Method:	std2.1 1;12;09 pm-front.mth
Injection Date:	26/2/2010 17:29:02	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A
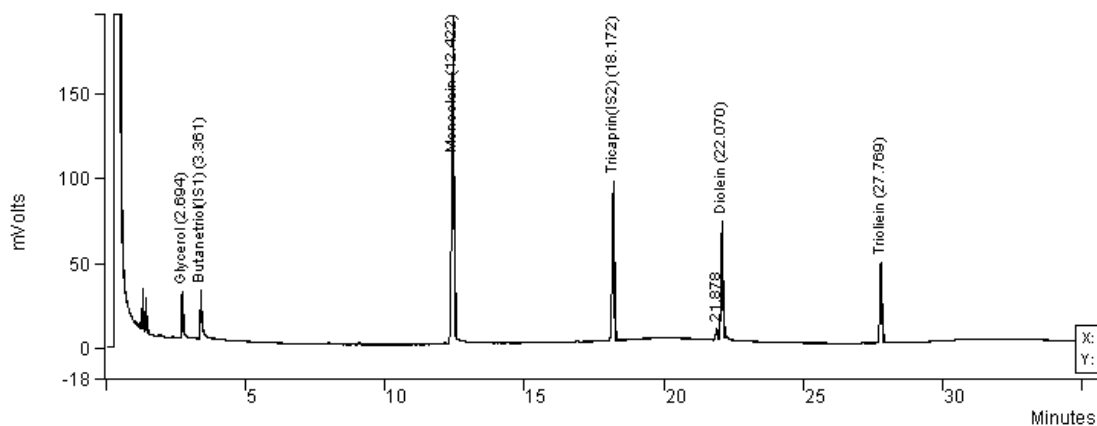
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.6985	2.694	-0.041	81836	0.00	BB	2.5		0
2	Butanetriol(IS1)	4.6654	3.361	-0.006	103228	0.00	BB	2.5		0
3	Monoolein	45.9462	12.422	0.021	1016626	0.00	BB	4.9		0
4	Tricaprin(IS2)	20.4388	18.172	-0.015	452238	0.00	BB	4.5		0
5		1.2199	21.878	0.000	26993	0.00	BV	4.1		0
6	Diolein	13.7870	22.070	0.007	305058	0.00	VB	4.1		0
7	Triolein	10.2441	27.769	0.001	226666	0.00	BB	4.5		0
	Totals	**99.9999**		**-0.033**	**2212645**					

Figure A8 GC chromatogram of EN 14105 standard solution 4 (2).
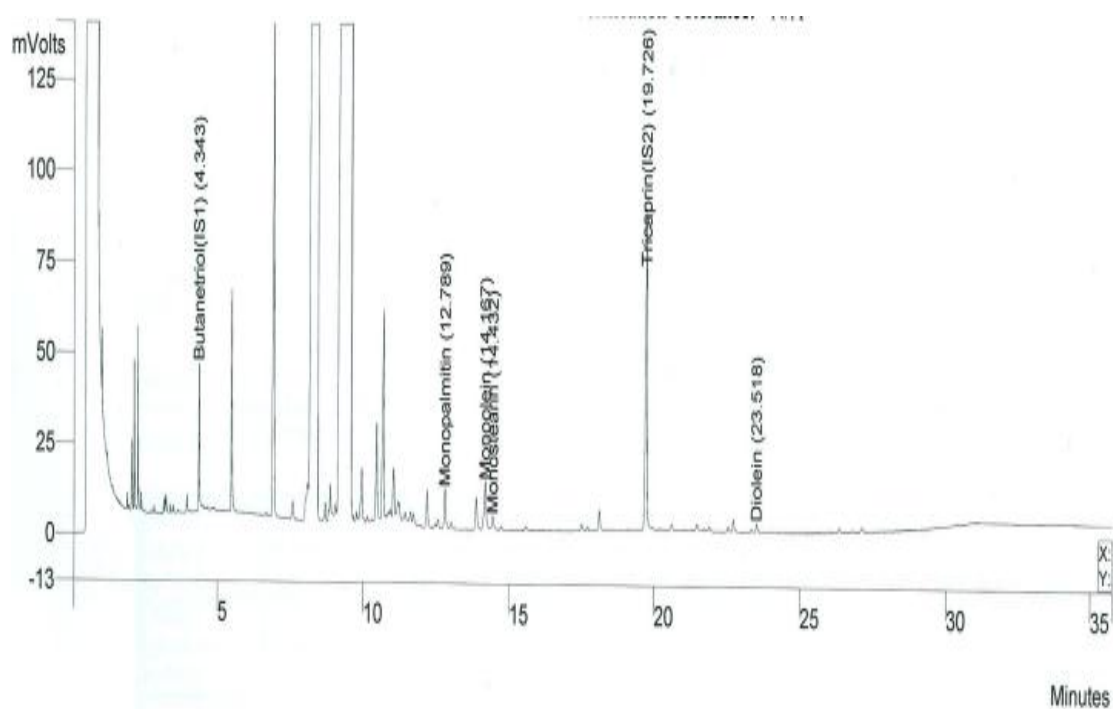
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	12.1478	4.343	-0.047	73989	0.00	BB	1.6		0
2	Monopalmitin	6.6788	12.789	-0.098	40679	0.00	BB	3.3		0
3	Monoolein	10.3896	14.167	-0.106	63280	0.00	BB	3.9		0
4	Monostearin	2.3730	14.432	-0.103	14453	0.00	BB	3.4		0
5	Tricaprin(IS2)	54.7093	19.726	-0.076	333219	0.00	BB	3.4		0
6	Diolein	1.4303	23.518	-0.242	8711	0.00	BB	3.0		0
	Totals	87.7288		-0.672	534331					

Figure A9 GC chromatogram of water washing biodiesel.
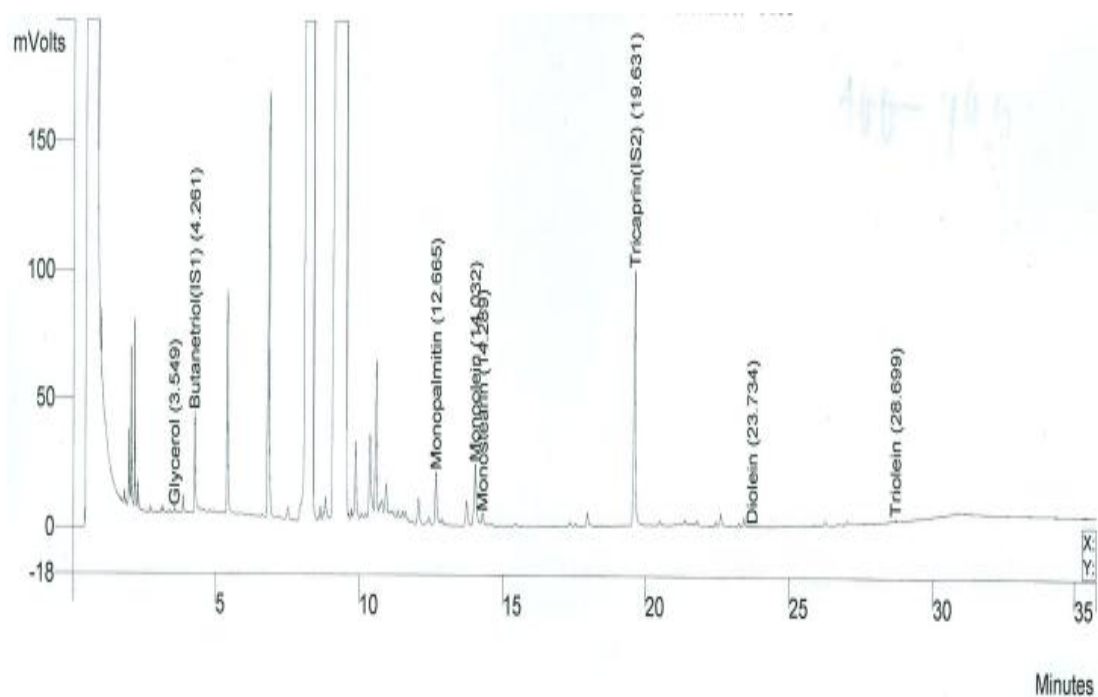
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	0.6363	3.549	0.049	5642	0.00	VB	2.2		0
2	Butanetriol(IS1)	11.1770	4.261	-0.039	99115	0.00	BB	1.9		0
3	Monopalmitin	8.6011	12.665	-0.035	76272	0.00	BB	3.4		0
4	Monoolein	14.7237	14.032	-0.118	130566	0.00	VV	4.1		0
5	Monostearin	3.1909	14.289	-0.061	28296	0.00	VV	4.3		0
6	Tricaprin(IS2)	47.0571	19.631	-0.171	417290	0.00	BB	3.8		0
7	Diolein	0.0356	23.734	-0.026	315	0.00	BB	0.9		0
8	Triolein	0.0948	28.699	-0.553	841	0.00	BB	0.7		0
	Totals	85.5165		-0.954	758337					

Figure A10 GC chromatogram of biodiesel that treated with activated bentonite (0.1 M of sulfuric acid at 60°C for 12h)

APPENDIX B

CALCULATIONS

Appendix B

CALCULATIONS

1. Calculation of soap content

The soap content in the biodiesel was calculated by using the equation:

$$Soap\ content\ (ppm) = \frac{B \times 0.01 \times 303.4}{W \times 1000}$$

Where: B = volume of hydrochloric acid used in second step (ml)

W = weight of untreated biodiesel (g)

303.4   = average molecular weight of sodium oleate

Table B1 Soap content of biodiesel purified by bentonite that stimulated with sulfuric acid in range 0.1-0.5M at 60°C for 12h (adsorption condition: 3%wt of adsorbent stir 10 min at room temperature)

Sulfuric acid concentration	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before purified	1	5.02	6.35	5303.88	5330.10
	2	5.01	6.40	5356.31	
0.1 M	1	5.17	3.15	2554.72	2565.03
	2	5.21	3.2	2575.35	
0.3 M	1	5.14	2.65	2161.75	2175.76
	2	5.17	2.7	2189.76	
0.5 M	1	5.38	2.3	1792.54	1798.20
	2	5.23	2.25	1803.87	

Table B2 Soap content of biodiesel purified by bentonite that stimulated with 0.1 M of sulfuric acid at 60 and 100°C for 12h (adsorption condition: 3%wt of adsorbent stir 10 min at room temperature)

Temperature	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before purified	1	5.02	6.35	5303.88	5330.10
	2	5.01	6.40	5356.31	
60	1	5.17	3.15	2554.72	2565.03
	2	5.21	3.2	2575.35	
100	1	5.17	2.95	2392.52	2390.72
	2	5.09	2.9	2388.93	

Table B3 Soap content of biodiesel purified by bentonite that stimulated with 0.1 M of sulfuric acid at 60°C for 1-12h (adsorption condition: 3%wt of adsorbent stir 10 min at room temperature)

Time	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before purification	1	5.00	7.00	3878.06	3886.28
	2	5.00	7.10	3894.51	
1	1	5.00	5.25	2902.74	2891.79
	2	5.00	5.20	2880.84	
3	1	5.03	4.65	2560.77	2549.53
	2	5.02	4.60	2538.28	
6	1	5.00	4.15	2299.13	2310.58
	2	5.07	4.25	2322.03	
9	1	5.02	4.00	2207.20	2197.77
	2	5.00	3.95	2188.33	
12	1	5.01	3.55	1962.80	1935.16
	2	5.01	3.45	1907.51	
24	1	5.01	3.00	1658.71	1617.24
	2	5.01	2.85	1575.77	

Table B4 Soap content of biodiesel treated with 1-10%wt of activated bentonite.

% wt adsorbent	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before purification	1	5.05	9.75	8095.37	8064.92
	2	5.01	9.6	8034.47	
1 %	1	5.02	3.45	2798.11	2755.61
	2	5.1	3.55	2713.11	
3 %	1	5.08	2.50	2641.25	2628.34
	2	5.05	2.40	2615.43	
5 %	1	5.12	2.20	1760.73	1802.82
	2	5	2.30	1844.91	
10 %	1	5.06	1.90	1284.41	1264.93
	2	5.05	1.80	1245.44	

Table B5 Soap content of biodiesel treated with various particle size of activated bentonite.

Particle size (Mesh)	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before purification	1	5.03	7.15	5882.58	5894.32
	2	5.01	7.15	5906.07	
60-80	1	5.06	2.75	2249.12	2233.05
	2	5.04	2.7	2216.99	
80-100	1	5.03	1.4	1151.83	1173.59
	2	5.02	1.45	1195.35	
100-120	1	5.08	1.8	1466.35	1431.12
	2	5.04	1.7	1395.88	
120-200	1	5.09	0.85	691.08	715.77
	2	5.03	0.9	740.46	

Table B6 Soap content of biodiesel purified by activated bentonite with various of contact time (10-30 min)

Contact time (min)	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before purification	1	5.06	12	9814.33	9815.38
	2	5.08	12.1	9816.42	
10	1	5.02	2.65	2184.60	2173.83
	2	5.07	2.65	2163.06	
20	1	5.01	2.15	1775.95	1755.30
	2	5.01	2.1	1734.65	
30	1	5	2	1655.35	1629.85
	2	5.03	1.95	1604.34	

Table B7 Soap content of biodiesel purified by natural bentonite, activated bentonite and commercial bentonite.

% wt adsorbent	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Natural bentonite					
Before purification	1	5.03	7.85	6458.50	6411.04
	2	5.04	7.75	6363.57	
1 %	1	5.06	4.65	3803.05	4422.20
	2	5.01	4.6	3799.71	
3 %	1	5.15	4.2	3374.99	3384.87
	2	5.12	4.2	3394.76	
5 %	1	5.04	4.05	3325.48	3260.57
	2	5.18	4	3195.66	
10 %	1	5.11	3.6	2915.49	2950.14
	2	5.13	3.7	2984.79	

Activated bentonite				
1 %	1	5.12	4.3	3475.59	3445.18
	2	5.09	4.2	3414.77	
3 %	1	5.09	3.4	2764.34	2799.42
	2	5.11	3.5	2834.50	
5 %	1	5.19	2.95	2352.26	2330.26
	2	5.02	2.8	2308.26	
10 %	1	5.02	2.1	1731.19	1776.04
	2	5	2.2	1820.89	
Commercial bentonite				
1 %	1	5.01	3.05	2519.37	2481.65
	2	5.08	3	2443.92	
3 %	1	5.14	1.6	1288.21	1255.09
	2	5.08	1.5	1221.96	
5 %	1	5.07	0	0	0
	2	5	0	0	
10 %	1	5.07	0	0	0
	2	5.03	0	0	

2. Calculation of free and total glycerin calibration functions (Linear regression)

2.1 Free Glycerol

Table B8 Calculation of glycerol calibration function.

M_g	M_{is1}	M_g/M_{is1}	A_g	A_{is1}	A_g/A_{is1}
0.005	0.08	0.063	10554	103900	0.102
0.005	0.08	0.063	11190	109112	0.103
0.020	0.08	0.250	36824	105847	0.348
0.020	0.08	0.250	37959	110574	0.343
0.035	0.08	0.438	56688	102822	0.551
0.035	0.08	0.438	56811	103051	0.551
0.050	0.08	0.625	79563	101322	0.785
0.050	0.08	0.625	81836	103228	0.793

Where: M_g is the mass of glycerol (milligrams);

M_{is1} is the mass of IS1 (milligrams);

A_g is the area of glycerol peak.

A_{is1} is the area of IS1 peak.

In regression function X is represented by the term A_g/A_{is1}, while Y is M_g/M_{is1}.

Table B9 Calculation of glycerol calibration function (continued).

X	Y	X²	Y²	XY
0.102	0.063	0.010	0.004	0.006
0.103	0.063	0.011	0.004	0.006
0.348	0.250	0.121	0.063	0.087
0.343	0.250	0.119	0.063	0.086
0.551	0.438	0.304	0.191	0.241
0.551	0.438	0.304	0.191	0.241
0.785	0.625	0.617	0.391	0.491
0.793	0.625	0.628	0.391	0.495
$\Sigma X = 3.576$	$\Sigma Y = 2.750$	$\Sigma X^2 = 2.113$	$\Sigma Y^2 = 1.297$	$\Sigma XY = 1.654$

$(\Sigma X)^2 = 12.787$ $\qquad$ $(\Sigma Y)^2 = 7.563$ $\qquad$ N = number of measure = 8

From obtained data can calculate:

$$a_g = \frac{(N \times \Sigma XY) - (\Sigma X \times \Sigma Y)}{(N \times \Sigma X^2) - (\Sigma Y)^2} = \frac{(8 \times 1.654) - (3.576 \times 2.750)}{(8 \times 2.113) - 1.297} = 0.8264$$

$$b_g = \frac{\Sigma Y - (a_g \times \Sigma X)}{N} = \frac{2.750 - (0.8264 \times 3.576)}{8} = -0.0256$$

The correlation coefficient (r) can be calculated from the following equation:

$$r = \frac{(N \times \Sigma XY) - (\Sigma X \times \Sigma Y)}{\sqrt{(N \times \Sigma X^2 - (\Sigma X)^2)(N \times \Sigma Y^2 - (\Sigma Y)^2)}}$$

$$= \frac{(8 \times 1.654) - (3.576 \times 2.750)}{\sqrt{(8 \times 2.113 - 12.787)(8 \times 1.297 - 7.563)}} = 0.9995$$

2.2 Monoglyceride

Table B10 Calculation of monoglyceride calibration function.

M_m	M_{is2}	M_m/M_{is2}	A_m	A_{is2}	A_m/A_{is2}
0.25	0.80	0.313	215449	465277	0.463
0.25	0.80	0.313	221583	481304	0.460
0.60	0.80	0.750	528776	484885	1.091
0.60	0.80	0.750	536031	490864	1.092
0.95	0.80	1.188	758214	444111	1.707
0.95	0.80	1.188	767103	450041	1.705
1.25	0.80	1.563	1014370	452505	2.242
1.25	0.80	1.563	1016626	452238	2.248

Table B11 Calculation of monoglyceride calibration function (continued).

X	Y	X^2	Y^2	XY
0.463	0.313	0.214	0.098	0.145
0.460	0.313	0.212	0.098	0.144
1.091	0.750	1.189	0.563	0.818
1.092	0.750	1.192	0.563	0.819
1.707	1.188	2.915	1.410	2.027
1.705	1.188	2.905	1.410	2.024
2.242	1.563	5.025	2.441	3.503
2.248	1.563	5.053	2.441	3.512
$\Sigma X = 11.007$	$\Sigma Y = 7.625$	$\Sigma X^2 = 18.707$	$\Sigma Y^2 = 9.023$	$\Sigma XY = 12.992$

$(\Sigma X)^2 = 121.163$ $\qquad$ $(\Sigma Y)^2 = 58.141$ $\qquad$ $N = 8$

$$a_m = \frac{(8 \times 12.992) - (11.007 \times 7.625)}{(8 \times 18.707) - 58.141} = 0.7021$$

$$b_m = \frac{7.625 - (0.7021 \times 11.007)}{8} = -0.1298$$

$$r = \frac{(8 \times 12.992) - (11.007 \times 7.625)}{\sqrt{(8 \times 18.707 - 121.163)(8 \times 9.023 - 58.141)}} = 0.9999$$

2.3 Diglyceride

Table B12 Calculation of diglyceride calibration function.

M_d	M_{is2}	M_d/M_{is2}	A_d	A_{is2}	A_d/A_{is2}
0.05	0.80	0.0625	38468	465277	0.083
0.05	0.80	0.0625	39284	481304	0.082
0.20	0.80	0.250	133719	484885	0.276
0.20	0.80	0.250	135809	490864	0.277
0.35	0.80	0.438	211338	444111	0.476
0.35	0.80	0.438	215288	450041	0.478
0.50	0.80	0.625	304575	452505	0.673
0.50	0.80	0.625	305058	452238	0.675

Table B13 Calculation of diglyceride calibration function (continued).

X	Y	X^2	Y^2	XY
0.083	0.063	0.007	0.004	0.005
0.082	0.063	0.007	0.004	0.005
0.276	0.250	0.076	0.063	0.069
0.277	0.250	0.077	0.063	0.069
0.476	0.438	0.226	0.191	0.208
0.478	0.438	0.229	0.191	0.209
0.673	0.625	0.453	0.391	0.421
0.675	0.625	0.455	0.391	0.422
$\Sigma X = 3.019$	$\Sigma Y = 2.750$	$\Sigma X^2 = 1.529$	$\Sigma Y^2 = 1.297$	$\Sigma XY = 1.408$

$$(\Sigma X)^2 = 9.112 \qquad (\Sigma Y)^2 = 7.563 \qquad N = 8$$

$$a_d = \frac{(8 \times 1.408) - (3.019 \times 2.750)}{(8 \times 1.529) - 7.563} \qquad = 0.9489$$

$$b_d = \frac{2.750 - (0.9489 \times 3.019)}{8} \qquad = -0.1429$$

$$r = \frac{(8 \times 1.408) - (3.019 \times 2.750)}{\sqrt{(8 \times 1.529 - 9.112)(8 \times 1.297 - 7.563)}} = 0.9999$$

2.4 Triglyceride

Table B14 Calculation of triglyceride calibration function.

M_t	M_{is2}	M_t/M_{is2}	A_t	A_{is2}	A_t/A_{is2}
0.05	0.80	0.063	32944	465277	0.071
0.05	0.80	0.063	29658	481304	0.062
0.15	0.80	0.188	94750	484885	0.195
0.15	0.80	0.188	94516	490864	0.193
0.30	0.80	0.375	166770	444111	0.376
0.30	0.80	0.375	172950	450041	0.384
0.40	0.80	0.500	233063	452505	0.515
0.40	0.80	0.500	226666	452238	0.501

Table B15 Calculation of triglyceride calibration function (continue).

X	Y	X^2	Y^2	XY
0.071	0.063	0.005013	0.004	0.004
0.062	0.063	0.003797	0.004	0.004
0.195	0.188	0.038184	0.035	0.037
0.193	0.188	0.037076	0.035	0.036
0.376	0.375	0.141011	0.141	0.141
0.384	0.375	0.147685	0.141	0.144
0.515	0.500	0.265277	0.250	0.258
0.501	0.500	0.251211	0.250	0.251
$\Sigma X = 2.296$	$\Sigma Y = 2.250$	$\Sigma X^2 = 0.889$	$\Sigma Y^2 = 0.859$	$\Sigma XY = 0.874$

$(\Sigma X)^2 = 5.274$ $\qquad$ $(\Sigma Y)^2 = 5.063$ $\qquad$ $N = 8$

$$a_t = \frac{(8 \times 0.874) - (2.296 \times 2.250)}{(8 \times 0.889) - 5.063} \quad = 0.9920$$

$$b_t = \frac{2.250 - (0.9920 \times 2.296)}{8} \quad = -0.0035$$

$$r = \frac{(8 \times 0.874) - (2.296 \times 2.250)}{\sqrt{(8 \times 0.889 - 5.274)(8 \times 0.859 - 5.063)}} = 0.9996$$

3. Calculation of the percentage of free and total glycerin

The percentage (*m/m*) of free glycerol in the sample was calculated by the following equation:

$$G = [a_g (A_g / A_{eil}) + b_g] \times (M_{eil} / m) \times 100$$

Where: G = percentage (*m/m*) of free glycerol

      A_g = peak area of the glycerol

      A_{eil} = peak area of internal standard No. 1

      M_{eil} = mass of internal standard No. 1 (milligrams)

      m = mass of sample (milligrams)

      a_g and b_g = constants coming from regression method for glycerol

The percentage (*m/m*) of mono-, di- and triglycerides in the sample were calculated by the following equation:

$$M = [a_m (\Sigma A_{mi}/A_{ei2}) + b_m] \text{ x } (M_{ei2}/m) \times 100$$

$$D = [a_d (\Sigma A_{di}/A_{ei2}) + b_d] \times (M_{ei2}/m) \times 100$$

$$T = [a_t (\Sigma A_{ti}/A_{ei2}) + b_t] \times (M_{ei2}/m) \times 100$$

Where: M, D, T = percentage (*m/m*) of mono-, di- and triglyceride

      $\Sigma A_{mi}, \Sigma A_{di}, \Sigma A_{ti}$ = sums of the peak areas of the mono-, di- and

            triglycerides

      A_{ei2} = peak area of internal standard No 2

      M_{ei2} = mass of internal standard No 2 (milligrams)

      m = mass of sample (milligrams)

      a_m and b_m = constants coming from regression method for monoglyceride

      a_d and b_d = constants coming from regression method for diglyceride

      a_t and b_t = constants coming from regression method for triglyceride

The percentage (*m/m*) of total glycerin in the sample was calculated by the following equation:

$$GT = G + 0.255\,M + 0.146\,D + 0.103\,T$$

Where: GT   = percentage (*m/m*) of total glycerin (free and bound)

           G = percentage (*m/m*) of free glycerol in the sample

           M = percentage (*m/m*) of monoglycerides in the sample

           D = percentage (*m/m*) of diglycerides in the sample

           T = percentage (*m/m*) of triglycerides in the sample

Table B16 The percentage of free glycerol of biodiesel.

Samples		Peak area (Sample)	Peak area (IS1)	Weight of sample (mg)	%Free
Water washing biodiesel	1	-	73989	100	-
10% of activated bentonite	1	5642	99115	99.5	0.0017

Table B17 The percentage of monoglyceride of biodiesel.

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Mono
Water washing biodiesel	1	118412	333219	100	0.1892
10% of activated bentonite	1	235135	99115	99.5	0.3077

Table B18 The percentage of diglyceride of biodiesel.

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Di
Water washing biodiesel	1	8711	333219	100	0.0179
10% of activated bentonite	1	-	99115	99.5	-

Table B19 The percentage of triglyceride of biodiesel.

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Tri
Water washing biodiesel	1	-	333219	100	-
10% of activated bentonite	1	-	99115	99.5	-

Table B20 The percentage of total glycerin of biodiesel.

Samples		Free glycerol	Mono	Di	Tri	Total glycerin
Water washing biodiesel	1	-	0.1892	0.0179	-	0.0509
10% of activated bentonite	1	0.0017	0.3077	-	-	0.0803

4. Calculation of the % free fatty acid (ASTM D5555)

Reagent

     1.   Ethanol

     2.   Phenolphthalein

     3.   0.25 N NaOH

To the 250 ml of Erlenmeyer flask, oil sample (1 g), ethanol (75 ml) and 2ml of 1% phenolphthalein were added. The mixture was subject to titrate with 0.25 N sodium hydroxide solutions until the pink color was occurred. The ml of alkali solution used was recorded.

The percentage of free fatty acids was calculated as follows:

% free fatty acids = (ml of alkali x N x 28.2) / weight of sample

N = normality of alkaline solution

ml of alkali = ml of sodium hydroxide solution

Table B21   Value of free fatty acids contain in crude oil.

Sample	Weight of sample (g)	Volume of titrant (ml)	Concentration of NaOH (N)	% FFA
Refined palm oil	1.0531	0.10	0.2354	0.64
	1.0361	0.10	0.2354	
Crude biodiesel	1.0534	0.65	0.2354	4.16
	1.0238	0.65	0.2354	
Biodiesel purified by natural bentonite	1.0320	0.15	0.2354	0.98
	1.0102	0.15	0.2354	
Biodiesel purified by activated bentonite	1.0232	0.2	0.2354	1.28
	1.0431	0.2	0.2354	

5. Determination of the acid value (ASTM D974)

Reagent

1.   p-naphtholbenzein indicator solution
2.   0.1 M Alcoholic KOH solution
3.   Titration solvent (250 ml toluene + 250 ml isopropyl alcohol)

To the 250 ml of Erlenmeyer flask, oil sample (2 g), titration solvent (25 ml) and 0.125 ml of 1% p-naphtholbenzein indicator solution were added. The mixture was subject to titrate with 0.1 M of alcoholic KOH until the green color was occured. Prepare a blank determination and carried out same with the sample. The ml of acid solution used was recorded.

The acid value was calculated as follows:

$$\text{Acid value} = [(A - B) \times N \times 56.1] / \text{weight of sample}$$

A = titration of sample

B = titration of blank

N = normality of alcoholic KOH solution

Alcoholic KOH = 0.6 g of potassium hydroxide

dissolved in 100 ml of isopropyl alcohol

Table B22 Acid value of biodiesel purified by bentonite that stimulated with sulfuric acid in range 0.1-0.5M at 60°C for 12h (adsorption condition: 3%wt of adsorbent stir 10 min at room temperature)

Sulfuric acid concentration	Experiment	Weight of sample (g)	Titrant (mL)	Volume of blank (ml)	Acid value
0.1 M	1	2.0013	0.145	0.07	0.189
	2	2.0134	0.14	0.07	
0.3 M	1	2.0126	0.255	0.07	0.489
	2	2.0093	0.26	0.07	
0.5 M	1	1.9993	0.335	0.07	0.707
	2	2.0012	0.345	0.07	

Table B23 Acid value of biodiesel purified by bentonite that stimulated with 0.1 M of sulfuric acid at 60 and 100°C for 12h (adsorption condition: 3%wt of adsorbent stir 10 min at room temperature)

Temperature	Experiment	Weight of sample (g)	Titrant (mL)	Volume of blank (ml)	Acid value
60	1	2.0013	0.145	0.07	0.189
	2	2.0134	0.14	0.07	
100	1	2.0258	0.15	0.07	0.208
	2	2.0121	0.15	0.07	

Table B24 Acid value of biodiesel purified by bentonite that stimulated with 0.1 M of sulfuric acid at 60°C for 1-12h (adsorption condition: 3%wt of adsorbent stir 10 min at room temperature)

Time	Experiment	Weight of sample (g)	Titrant (mL)	Volume of blank (ml)	Acid value
1	1	2.0107	0.125	0.07	0.138
	2	2.0233	0.12	0.07	
3	1	2.0165	0.13	0.07	0.151
	2	2.0192	0.125	0.07	
6	1	2.0208	0.15	0.07	0.211
	2	2.0056	0.15	0.07	
9	1	2.0128	0.16	0.07	0.238
	2	2.0043	0.16	0.07	
12	1	2.016	0.165	0.07	0.250
	2	2.0253	0.165	0.07	
24	1	2.0343	0.175	0.07	0.269
	2	2.0124	0.17	0.07	

Table B25 Acid value of biodiesel treated with 1-10%wt of activated bentonite.

% wt adsorbent	Experiment	Weight of sample (g)	Titrant (mL)	Volume of blank (ml)	Acid value
1 %	1	2.0029	0.1	0.07	0.192
	2	2.0123	0.105	0.07	
3 %	1	2.0052	0.11	0.07	0.219
	2	2.0065	0.115	0.07	
5 %	1	2.0007	0.125	0.07	0.260
	2	2.0032	0.13	0.07	
10 %	1	2.0493	0.145	0.07	0.288
	2	2.0152	0.135	0.07	

Table B26 Acid value of biodiesel treated with various particle size of activated bentonite.

Particle size (Mesh)	Experiment	Weight of sample (g)	Titrant (mL)	Volume of blank (ml)	Acid value
60-80	1	2.0136	0.115	0.07	0.220
	2	2.0063	0.11	0.07	
80-100	1	2.0243	0.13	0.07	0.272
	2	2.0124	0.135	0.07	
100-120	1	2.0191	0.12	0.07	0.239
	2	2.0048	0.12	0.07	
120-200	1	2.0694	0.145	0.07	0.288
	2	2.0231	0.135	0.07	

Table B27 Acid value of biodiesel purified by activated bentonite with various of contact time (10-30 min)

Contact time (min)	Experiment	Weight of sample (g)	Titrant (mL)	Volume of blank (ml)	Acid value
10	1	2.0118	0.135	0.07	0.273
	2	2.0065	0.13	0.07	
20	1	2.0151	0.15	0.07	0.312
	2	2.0121	0.145	0.07	
30	1	2.0155	0.16	0.07	0.339
	2	2.0109	0.155	0.07	

Table B28 Acid value of biodiesel purified by natural bentonite, activated bentonite and commercial bentonite.

% wt adsorbent	Experiment	Weight of sample (g)	Titrant (mL)	Volume of blank (ml)	Acid value
Natural bentonite					
1 %	1	2.0045	0.075	0.07	0.147
	2	2.013	0.075	0.07	
3 %	1	2.0252	0.09	0.07	0.172
	2	2.0075	0.08	0.07	
5 %	1	2.0092	0.095	0.07	0.193
	2	2.0145	0.09	0.07	
10 %	1	2.0302	0.12	0.07	0.264
	2	2.0181	0.12	0.07	

Activated bentonite					
1 %	1	2.0243	0.095	0.07	0.206
	2	2.0053	0.1	0.07	
3 %	1	2.0103	0.1	0.07	0.220
	2	2.0112	0.105	0.07	
5 %	1	2.0168	0.115	0.07	0.266
	2	2.0123	0.125	0.07	
10 %	1	2.0068	0.14	0.07	0.313
	2	2.0114	0.135	0.07	
Commercial bentonite					
1 %	1	2.0123	0.15	0.07	0.333
	2	2.0042	0.14	0.07	
3 %	1	2.0063	0.325	0.07	0.827
	2	2.0057	0.335	0.07	
5 %	1	2.0003	0.4	0.07	1.030
	2	2.0025	0.41	0.07	
10 %	1	2.0022	0.45	0.07	1.165
	2	2.0156	0.465	0.07	

6. Determination of viscosity (ASTM D445)

Viscosity is the unit specifying the resistance to flow; therefore viscosity is normally a specific value.

7 ml of each sample were added into the Viscometer tube, and insert the viscometer into the bath. After insertion, allow the viscometer to reach bath temperature, Use suction to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark. With the sample flowing freely, measure, in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second timing mark. The time of sample used was recorded.

The viscosity was calculated as follows:

$$viscosity \quad = \quad Ct$$
$$C \quad = \quad \text{Constant of viscometer tube (mm}^2/\text{s}^2)$$
$$time \quad = \quad \text{measured flow times for } t1 \text{ and } t2,$$
$$\text{respectively(s)}$$

Table B29 Viscosity of biodiesel.

Sample	Time 1 (s)	Time 2 (s)	Constants of tube	Viscosiy (cSt)
Water washing	294.28	294.75	0.01434[a]	4.22
Crude biodiesel	430.96	431.03	0.01434[a]	6.18
Biodiesel purified by natural bentonite	306.14	306.29	0.01434[a]	4.39
Biodiesel purified by activated bentonite	267.08	267.32	0.01434[a]	3.83

VITA

Mr. Ekkasit Tepveeragul was born on September 20, 1986 in Bangkok, Thailand. He graduated at Debsirin School in 2004. He received the Bachelor Degree of Science in chemistry, Chulalongkorn University in 2009. He continued his Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkom University in 2009 and completed the program in 2012.

Conference

12-13 March 2012   "Biodiesel purification with activated bentonite"

The 4th Science Research Conference

NARESUAN UNIVERSITY