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PURIFICATION OF BIODIESEL FROM PALM OIL BY ADSORPTION
WITH CLAYS

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The objective of this research is to purify biodiesel using activated charcoal, bentonite, diatomite and activated clay as adsorbents. Biodiesel obtained from transesterification via alkali-catalyzed process was purified by using four adsorbents compared with water washing process. In the presence of methanol, glycerin in biodiesel could be effectively eliminated by using 4% wt of adsorbents at 50°C for 10 min. In addition, 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 treatment. The result showed that activated clay was found to be the most effective adsorbent against the other adsorbents. Adsorption processes of activated clay were described by monolayer and multilayer. The quality of purified biodiesel could meet the major specification of biodiesel standards. Therefore, the adsorption process using adsorbent could be used to purify biodiesel in place of water washing process with the advantage that no wastewater generated.

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LIST OF ABBREVIATIONS

Å	=	Angstrom
µl	=	Microliter
µm	=	Micrometer
ASTM	=	American Standard Test Method
°C	=	Degree Celsius
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	=	Revolution per minute
TLC	=	Thin Layer Chromatography
v/v	=	Volume by volume
% conversion	=	Percent conversion
% wt	=	Percent by weight
% yield	=	Percent yield

CHAPTER I

INTRODUCTION

Rapid growth in population coupled with industrial and technological developments is leading towards the depletion of limited fossil fuel resources of the world. Currently, research is progressively more directed towards exploration of alternative renewable fuels. Biodiesel, an alternative diesel fuel, is a promising, non-toxic and eco-friendly clean fuel [1]. It could be regarded as petroleum-derived diesel substitute with many advantages including reduction of most exhaust emissions, biodegradability, high flash point, inherent lubricity, and domestic origin [2].

Biodiesel (fatty acid alkyl ester) is produced by transesterifying triglycerides, the main constituents of vegetable oils or animal fats with an excess alcohol, usually methanol, in the presence of a catalyst, usually a strong base such as sodium or potassium hydroxide [3]. The resulting product therefore can contain not only the desired alkyl ester product but also unreacted starting material (mono-, di- and triglycerides), residual alcohol, residual catalyst and soap. Glycerol is formed as a by-product and separated from the biodiesel in the production process, however, traces thereof can be found in the final biodiesel product [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 widely 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 charcoal, bentonite, diatomite and activated clay are chosen to be adsorbents in this work because of their various applications such as water purification, winemaking filtration, building material and refining oil, respectively. 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 purify biodiesel impurities by using activated charcoal, diatomite, bentonite and activated clay as adsorbents.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Background

Over the past twenty years, Thailand has had one of the fastest growing economies in the world. The demand for energy was also increased because of the industrial expansion. In 2006, imported energy was increased 16% year on year to a total US\$ 21.5 billion. Rising global fuel prices in combination with rising domestic demand led to a 92% increase in the cost of imported refined fuel from 2004-2005. Depend on its massive agricultural base, alternative energy such as biodiesel will play an increasingly important role in Thailand's domestic energy supplies. The government has a target of 4.25 million litres/day of biodiesel, for a 7% consumption substitute of diesel by the year 2011. Palm oil, one of the most readily available inputs for biodiesel production can be found in abundant quantities in Thailand. Its cultivation can produce 5,800 liters of the fuel per hectare (US 580 gallons/acre), making agricultural cultivation of biodiesel incredibly efficient. The government is promoting palm oil cultivation to reach 400,000 hectares by 2012[6].

Biodiesel, a clean-burning alternative fuel, is produced from renewable resources making it biodegradable, nontoxic and essentially free of sulfur and aromatics. Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed, sunflower, coconut) or animal fats (usually tallow) as well as waste oils (e.g., used frying oils). Depending on the origin and quality of the feedstock, the production process may be necessary. Biodiesel is miscible with petrodiesel in all ratios so it can be blended at any level with petroleum-based diesel or can be used one hundred percent biodiesel with little or no modifications[7].

Biodiesel has several distinct advantages compared with petroleum-based diesel because it is derived from a renewable domestic resource. It can be reduced

most exhaust emissions (with the exception of nitrogen oxides, NO_x) and it also has a higher flash point, leading to safer handling and storage. Furthermore, adding biodiesel at low levels (1–2%) can restore the lubricity with the fact that is steadily gaining importance with the advent of low-sulfur petroleum diesel, which has greatly reduced lubricity[8]. However, biodiesel also has disadvantages because it has storage problems (due to it is biodegradable), high freezing point (between 0 and -5°C) and less oxidatively stable than petroleum diesel fuel, hence, old fuel can become acidic and form sediments and varnish. It can cause filter plugging (at low temps, due to polymers, fuel tank deposits, other contaminants). In addition to their feedstock prices, production and processing cost still more expensive than petroleum diesel[9].

2.2 Biodiesel production [10,11,12,13]

Vegetable oils have to be modified before using with diesel engines to bring their combustion-related properties closer to those of mineral diesel. To diminish the flow and combustion problems, the fuel is modified for reducing its viscosity. Production of biodiesel can be performed four different ways including direct use and blending, micro-emulsion, pyrolysis and transesterification.

2.2.1 Direct use and blending

Direct use of vegetable oils or the use of blends of the oils has generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines. In 1980, a mixture of 10% vegetable oil was used to maintain total power without adjustments the engine by Caterpillar Brazil. The result showed that it was not practical to substitute 100% vegetable oil for diesel fuel while a blend of 20% vegetable oil and 80% diesel fuel was successful. Pramanik et al. [14] found that 50% blend of *Jatropha* oil could be used in diesel engine without any major operational difficulties. However, blended vegetable oil with diesel fuel was not appropriated for long-term use in the direct injection diesel engines because it could be high viscosity, acid composition, free fatty acid content, as well as gum formation

due to oxidation and polymerization during storage. Moreover, the combustion, carbon deposits and lubricating oil formation and thickening are distinct problems.

2.2.2 Micro-emulsions

Micro-emulsion is designed to solve the problem of the high viscosity of vegetable oils by reducing the viscosity of oils with solvents such as simple alcohols e.g., methanol, ethanol and 1-butanol. It is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1–150 nm, formed spontaneously from two normally immiscible liquids. The performances of ionic and non-ionic micro-emulsions were found to be similar to diesel fuel. Over short term testing, they can improve spray characteristics by explosive vaporization which improved the combustion characteristics of the low boiling constituents in the micelles. The performance of micro-emulsions of aqueous ethanol in soybean oil was nearly as good as that of no. 2 diesel, despite lower cetane number and energy content.

2.2.3 Pyrolysis [15]

Pyrolysis is the conversion of one substance into another by heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules with the aid of a catalyst. Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted to synthesize petroleum from vegetable oil. Since World War I, many investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel. However, the equipment for pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produced some low value materials and, sometimes, more gasoline than diesel fuel.

2.2.4 Transesterification

The most common way to produce biodiesel is by transesterification. In this reaction, vegetable oil or animal fat is reacted with an alcohol in the presence of a catalyst to produce fatty acid mono-alkyl esters and glycerol. The overall process is normally a sequence of three consecutive steps, which are reversible reactions. First, triglyceride is converted to diglyceride, then monoglyceride is produced from diglyceride and in the last step, glycerin is obtained from monoglycerides. In all these reactions, esters are produced. The relation between alcohol and oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product.

2.3 Transesterification of vegetable oils

Transesterification is a process of reacting a triglyceride such as one of the vegetable oils with an alcohol in the presence of catalyst to produce fatty acid esters (biodiesel) and glycerol [16-18]. This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the equation as seen in Figure 2.1.

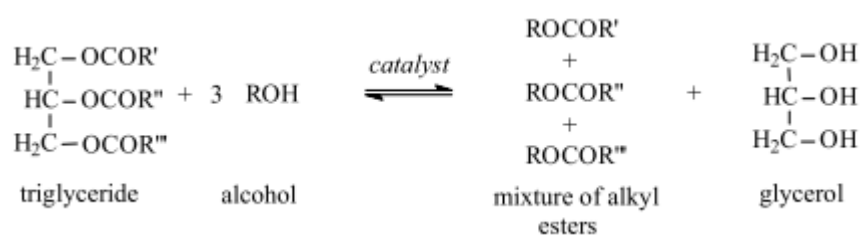


Figure 2.1 Equation for transesterification of vegetable oil.

After the reaction has been completed and glycerol has been removed by gravity settling or centrifugation, some impurities still remain in the fuel. These impurities are glycerol itself, soaps, catalyst, water, methanol, and mono-, di-, and triglycerides. In the usual industrial practice, the impurities are removed by washing

with water. Packed washing towers, mixers-settlers, and centrifuges are commonly used with this purpose.

Glycerol, co-product from transesterification, is especially undesired in the biodiesel because when heated it tends to polymerize by condensation with other molecules of glycerol or glycerides. The result is the formation of coke which can also generate deposits of carbonaceous compounds on the injector nozzles, pistons and valves in standard engines, reducing the efficiency of the engines [19]. Glycerides also increase the cloud point of biodiesel by forming small crystals at low temperatures.

Alcohol that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). Furthermore, it can quickly react with triglycerides. To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. However, in practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol to oil ratio has to be established empirically, considering each individual process.

A catalyst is usually used to improve the reaction and yield transesterification. The reaction can be catalyzed by alkalis, acids, enzymes, non-ionic base and heterogeneous catalyst. Moreover, noncatalytic process was readily developed to transesterification without using any catalyst.

2.4 Type of catalysts in transesterification

2.4.1 Acid-catalyzed processes [15]

Acid-catalyzed transesterification is more suitable for glycerides that have relatively high free fatty acid contents. The transesterification process is catalyzed by Bronsted acids, sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically,

temperatures above 100°C and more than 3 h to reach complete conversion. In general, a 1 mol% of sulfuric acid is a good amount for a final conversion of 99% in a time around 50 h. The mechanism of the acid-catalyzed transesterification of vegetable oils was shown in Figure 2.2. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+ . According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

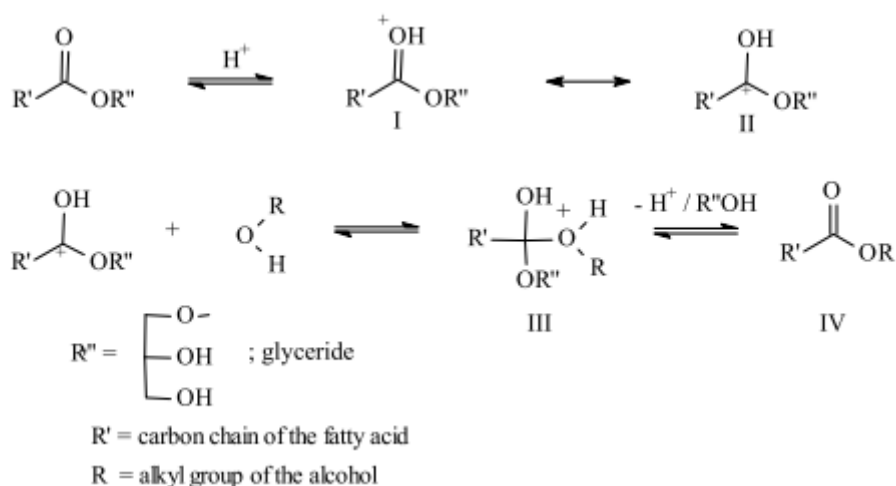


Figure 2.2 Mechanism of the acid-catalyzed transesterification of vegetable oil.

2.4.2 Alkaline-catalyzed processes

Alkaline-catalyzed transesterification process is normally adopted for biodiesel production because alkaline metal alkoxides and hydroxides are the most effective transesterification catalysts compared to the acid catalysts, although for economic reasons hydroxides are more often used. Transesterification occurs at a faster rate in the presence of an alkaline catalyst than in the presence of the same

amount of acid catalyst. Alkaline metal hydroxides (NaOH and KOH) are widely used for alkaline-catalyzed process but it is better to produce the alkoxy before the reaction to obtain a better global efficiency. They are a good alternative alkaline catalyst since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. However, even if a water-free alcohol to oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation (Figure 2.3). This undesirable saponification reaction reduces the ester yields and considerably complicates the recovery of the glycerol due to the formation of emulsions.

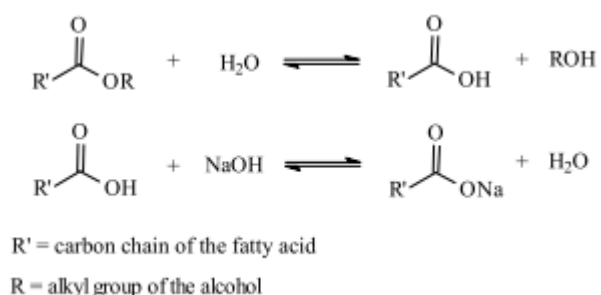


Figure 2.3 Saponification reaction of the produced fatty acid alkyl esters.

2.4.3 Enzyme-catalyzed processes

Eventhough using alkaline as catalyst for transesterification is widely used, there are several drawbacks such as recovery of glycerol is difficult, alkaline wastewater requires treatment and free fatty acids and water interfere with the reaction. Enzymatic transesterification process can overcome the problems mentioned above, particularly, glycerol can be easily recovered without any complex process and free fatty acids contained in waste oils and fats can be completely converted to methyl esters.

Lipase has been discovered that they can be used as catalyst for transesterification and esterification due to its biocompatibility, biodegradability and environmental acceptability of the biotechnical procedure. The extra cellular and the intracellular lipases are also able to catalyze the transesterification of triglycerides

effectively. On the other hand, in general lipase catalyst still unfavorable because the production cost is significantly great when compared with base-catalyzed process.

2.4.4 Non-ionic based-catalyzed processes

Organic bases has been developed and used as catalyst for organic synthesis to obtain milder reaction conditions and to simplify manipulations of the factors involved in increasing the yield of the alkyl ester. Amines were bases using in this process such as 1,2,2,6,6-pentamethylpiperidine, 2,6-di-tert-butylpyridine and 4-dimethyl-aminopyridine(DMAP). Moreover, amidines such as 1,8 diazabicyclo [5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN); guanidines such as 1,5,7 triazabicyclo[4.4.0]dec-5-ene (TBD) are frequently used in organic synthesis.

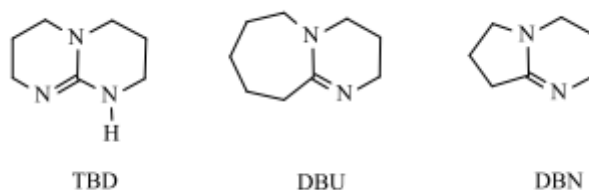


Figure 2.4 Molecular structures of some non-ionic organic bases.

2.4.5 Heterogeneously catalyzed processes

There are many heterogeneous catalysts have been used such as zeolites, clays, alumina, ion exchange resins, oxides, etc[20]. Activated calcium oxide (CaO) was used as solid-based heterogeneous catalyst for eight times without significant deactivation. Magnesium oxide, successfully used as catalyst for biodiesel development was found to be cost effective also. Guanidine, a heterogeneous basic catalyst, has the advantage of not producing soaps and thus allowing for an easy phase separation. Na/NaOH/ γ -Al₂O₃ showed almost the same catalytic activity as NaOH under the optimum reaction conditions[21]. However, because of leaching, the

catalyst could be used only nine times. The Esterfip-HTM process, a heterogeneous solid catalyst, consisted of a mixed oxide of zinc and aluminium with a spinel structure, which was developed by the Petroleum Institute of France[22]. The Esterfip-HTM process did not involve the neutralization and purification processes; therefore, the polluted water and the running costs were considerably reduced. While, glycerol with the purity of over 98% was obtained directly.

2.4.6 Noncatalytic transesterification process

A novel alcoholysis process for oil without using any catalyst is readily developing. Supercritical alcohol especially methanol is extensively used for transesterification. Due to its nature, hydrophobic with a lower dielectric constant, non-polar triglycerides can be well solvated with supercritical methanol to form a single phase oil to methanol mixture. However, liquid methanol is a polar solvent and has hydrogen bondings between OH oxygen and OH hydrogen to form methanol clusters. Thus, the oil to methyl ester conversion rate was found to increase dramatically in the supercritical state. Free fatty acids contained in crude oils and fats could also be converted efficiently to methyl esters in supercritical methanol, leading to increase of the total yield of methyl esters from used oils [23]. In addition, because the process is non-catalytic, the purification of products after the transesterification reaction is much simpler and more environmentally friendly compared with the alkali-catalyzed process in which all the catalyst and saponified products have to be removed to obtain biodiesel fuel. On the other hand, high temperature and pressure is required in this process and large amount of methanol is necessary to perform the reaction. Therefore, production process such as continuous operation, production cost and scale up has to further investigate.

2.5 Transesterification parameters

2.5.1 Moisture content and free fatty acid

To determine the viability of transesterification process, moisture

content and free fatty acid are important parameters. Vegetable oil with free fatty acid value (FFA) lower than 3%, the base catalyzed reaction is chosen to complete the reaction. If the FFA of the starting oil is high, it must be refined by saponification using NaOH solution to remove free fatty acids. The two-step esterification process is required for this oil. Initially the FFA can be converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction.

The methoxide and hydroxide of sodium or potassium should be maintained in anhydrous state because they can react with moisture and carbon dioxide in the air which diminished their effectiveness. The starting materials should be free from moisture. 0.1% of water content can be decreased the conversion of ester to a significant extent [24] and caused soap formation in base-catalyzed process.

2.5.2 Molar ratio of alcohol to oil

Molar ratio of alcohol to triglyceride is one of the most important variables affecting the yield of ester. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol. The molar ratio is associated with the type of catalyst used. Higher molar ratios result in greater ester conversion in a shorter time. When a large amount of free fatty acids was present in the oil, a molar ratio as high as 15:1 was needed under acid catalysis [25].

2.5.3 Catalyst

Alkali-catalyzed transesterification is much faster than acid-catalyzed. However, if oil contains high FFA and more water, acid-catalyzed transesterification is more suitable [25]. The acids could be sulfuric acid, or organic sulfonic acid. Sodium hydroxide was chosen to catalyze the transesterifications because it is cheaper and is used widely in large-scale processing. More recently, an immobilized lipase was employed to catalyze the methanolysis of corn oil in flowing supercritical carbon dioxide with an ester conversion of >98%.

2.5.4 Reaction time

The conversion rate of transesterification increases with reaction time. Effect of reaction time on transesterification of beef tallow with methanol was studied. During the first minute, the reaction was very slow due to the mixing and dispersion of methanol into beef tallow. However, from one to five min, the reaction proceeded very fast and the yield of methyl ester was increased from 1 to 38%. At about 15 min, the production of beef tallow slowed down and reached the maximum value. Freedman et al.[26] transesterified peanut, cotton seed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93±98%).

2.5.5 Reaction temperature

Transesterification can occur at different temperatures, depending on the oil used. For the transesterification of refined soybean oil with methanol (6:1) using 1% NaOH, three different temperatures were used [25]. After 0.1 h, ester yields were 94, 87 and 64% for 60, 45 and 32°C, respectively. After 1 h, ester formation was identical for the 60 and 45°C runs and only slightly lower for the 32°C run. Temperature clearly influenced the reaction rate and yield of esters.

2.6 Biodiesel quality

The characteristics of biodiesel are close to petroleum diesel, hence, biodiesel is needed to replace mineral diesel. Biodiesel has viscosity close to mineral diesel because the conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-thirds that of the triglycerides. These vegetable oil esters contain 10–11% oxygen by weight, which may encourage combustion than hydrocarbon-based diesel in an engine. The cetane number of biodiesel is around 50. Biodiesel has lower volumetric heating values

(about 10%) than mineral diesel but has a high cetane number and flash point. The esters have cloud point and pour points that are 15–25 °C higher than those of mineral diesel. The properties of biodiesel from different oils and diesel fuels are compared in Table 2.1.

Table 2.1 Comparison of fuel properties between diesel and biodiesel [27]

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower heating value, Btu/gal	131,295	117,093
Viscosity, at 40° C	1.3-4.1	1.9-6.0
Specific gravity kg/l at 60° F	0.85	0.88
Density, lb/gal at 15° C	7.079	7.328
Water, ppm by wt	161	0.05% max
Carbon, wt %	87	77
Hydrogen, wt %	13	12
Oxygen, by dif. wt %	0	11
Sulfur, wt %	0.05 max	0.0 - 0.0024
Boiling point (°C)	188-343	182-338
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 10
Cetane number	40-55	48-65
Stoichiometric air/fuel ratio wt./wt.	15	13.8
BOCLE Scuff, grams	3,600	>7,000

For Thailand, it has set legislative assembly characteristic and quality of biodiesel as shown in Table 2.2.

Table 2.2 Characteristic and quality of biodiesel (methyl ester of fatty acids) in Thailand [28].

Characteristic	Value	Method of standard
Methyl ester, % wt.	>96.5	EN 14103
Density at 15°C, kg/m ³	860-900	ASTM D 1298
Viscosity at 40°C, cSt	3.5-5.0	ASTM D445
Flash point, °C	>120	ASTM D 93
Carbon residue, on 10% distillation residue, % wt	<0.30	ASTM D 4530
Cetane number	>51	ASTM D 613
Sulfur, % wt.	<0.0010	ASTM D 2622
Sulfated ash, % wt.	<0.02	ASTM D 874
Water, % wt.	<0.050	ASTM D 2709
Total contaminate, % wt.	<0.0024	ASTM D 5452
Copper strip corrosion	<96.5	ASTM D 130
Oxidation stability at 110°C, hours	>10	EN 14112
Acid value, mg KOH/g	<0.50	ASTM D 664
Iodine value, g Iodine/100 g	<120	EN 14111
Linolenic acid methyl ester, % wt.	<12.0	EN 14103
Methanol, % wt.	<0.20	EN 14110
Monoglyceride, % wt.	<0.80	EN 14105
Diglyceride, % wt.	<0.20	EN 14105
Triglyceride, % wt.	<0.20	EN 14105
Free glycerin, % wt.	<0.02	EN 14105
Total glycerin, % wt.	<0.25	EN 14105
Group I metals (Na+K)	<5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg)	<5.0	EN 14538
Phosphorus, % wt.	<0.0010	ASTM D 4951

2.7 Adsorption [29]

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

2.7.1 Physisorption

Physisorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are long-range, weak attractive forces. The energy of adsorption is approximately 20 kJ/mol, insufficient to break bonds, therefore the adsorbed molecules retain their identities. The molecules remain intact, and can be freed easily (the forces are small, and short-range).

2.7.2 Chemisorption

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption. It occurs when a molecule chemically bonds to a

surface, usually through a covalent bond. The energy of this adsorption is approximately 200 kJ/mol.

The differences between physisorption and chemisorption are summarized in the Table 2.3.

Table 2.3 The differences between physisorption and chemisorption

Physisorption	Chemisorption
vander Waals' forces	chemical bond forces
Low enthalpy of adsorption (20 - 40 k.J/mole)	High enthalpy of adsorption (200 - 400 k.J/mole)
Performed at low temperature	Performed at high temperatures
Not specific	Highly specific
Multi-molecular layers are formed	monomolecular layer is formed
Reversible process	Irreversible process

2.8 Adsorption isotherm

Adsorption is usually described through isotherms functions which connect the amount of adsorbate on the adsorbent, with its pressure (gas) or concentration (liquid). Usually the amount adsorbed is only a fraction of a monolayer. Thus, to adsorb a substantial amount of material, the adsorbent must have a large specific surface area.

The six IUPAC standard adsorption isotherms are shown in Figure 2.5, they differ because the systems demonstrate different gas/solid interactions.

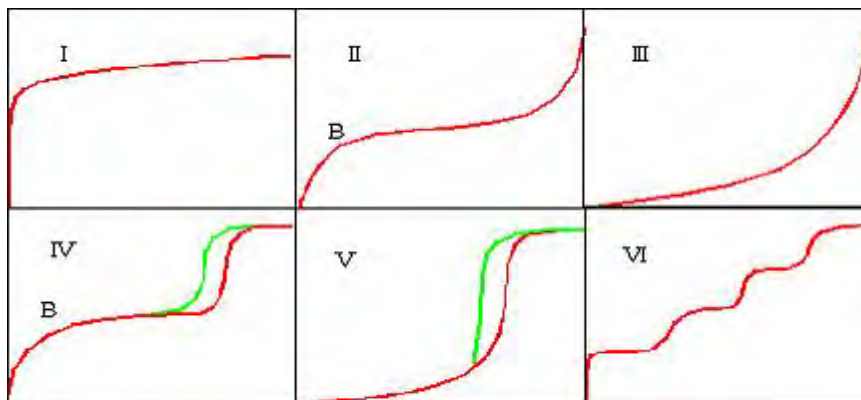


Figure 2.5 IUPAC standard adsorption isotherms.

The Type I isotherm is typical of microporous solids and chemisorption isotherms. Type II is shown by finely divided non-porous solids. Type III and V are typical of vapor adsorption (e.g. water vapor on hydrophobic materials). Type VI and V feature a hysteresis loop generated by the capillary condensation of the adsorbate in the mesopores of the solid. Finally, the rare type VI step-like isotherm is shown by nitrogen adsorbed on special carbon.

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

2.8.1 Langmuir isotherm

Langmuir isotherm was first theoretically examined in the adsorption of gases on solid surfaces. Langmuir assumed that the forces that are exerted by chemically unsaturated surface atoms (total number of binding sites) do not extend further than the diameter of one sorbed molecule and therefore sorption is restricted to a monolayer. Langmuir isotherm is based on four hypotheses:

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.

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

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 $1/(x/m)$.

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. [30], 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

2.8.2 Freundlich isotherm [31]

Freundlich's empirical equation for the description of adsorption process is based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites. The Freundlich isotherm does not predict any saturation of the sorbent by the sorbate, thus infinite surface coverage is predicted mathematically, indicating multilayer sorption of the surface.

The linearized Freundlich adsorption isotherm by taking logarithms can be written:

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

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 $\log (x/m)$.

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.

2.8.3 Brunauer-Emmett-Teller isotherm [32]

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:

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

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

2.9 Adsorbents

The adsorbents should have a large surface area. The bigger its surface area, the more molecules it can trap its surface. Generally this means that a good adsorbent will be very porous; full of many tiny little holes on its surface that effectively increase its surface area by many times. A solid with good capacity but slow kinetics is not a good choice as it takes adsorbate molecules too long a time to reach the particle interior. This means long gas residence time in a column, hence a low throughput. However, a solid with fast kinetics but low capacity is not good either as a large amount of solid is required for a given throughput. Thus, a good solid is the one that provides good adsorptive capacity as well as good kinetics.

2.9.1 Activated carbon [33]

Activated carbon also called activated charcoal or activated coal, is a general term that includes carbon material mostly derived from charcoal. It is a material with an exceptionally high surface area. One gram of activated carbon has a surface area of approximately 500 m². The three main physical carbon types are granular, powder and extruded (pellet). All three types of activated carbon can have properties tailored to the application. Activated carbon is frequently used in everyday life, in an industry, food production, medicine, pharmacy, military, etc. In pharmacy, activated charcoal is considered to be the most effective single agent available as an emergency decontaminant in the gastrointestinal tract. It is used after a person swallows or absorbs almost any toxic drug or chemical.

Activated charcoal is made by heating wood without oxygen. This removes the impurities, but leaves all the carbon in the wood mostly unburnt. About 25% of the original volume remains, and it's mostly carbon. Charcoal can then be burned itself, and very little smoke will result, because mostly it's just carbon combining with oxygen to produce CO₂ and CO (invisible gases). Activated charcoal is charcoal made from wood, sawdust, coconut shell, or bone, which has been treated with oxygen to remove all the impurities sticking to its surface inside the pores.

2.9.2 Activated clay [34]

Clay is a widely distributed, abundant mineral resource of major industrial importance for an enormous variety of uses. It acts as "chemical sponges" which hold water and dissolved plant nutrients weathered from other minerals. It has many uses today including, pottery, ceramic, lining for landfills, computer chips, cosmetics and pharmaceuticals. Clay also has the ability to attract water molecules at surface area (because the ion and water is not attracted sink inside the clay).

Smectite is a generic term that refers to a variety of related minerals also found in some clays. The smectite family of clays includes the various mineral species montmorillonite, nontronite, hectorite and saponite, all of which can be present in clay in varying amounts. The smectite minerals typically occur only as extremely small particles. Generally, smectite is believed to be composed of units made of two silica tetrahedral sheets with a central alumina octahedral sheet. Each of the tetrahedra has a tip that points to the center of the smectite unit. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer.

Clays is suitable for the activating treatment. However, not all clay materials are suitable for use in an oil bleaching process. Kaolin clay is considered to be a poor bleaching clay. kaolin clay does not perform as a bleaching clay, in contradistinction to a palygorskite-smectite clay composition. Clay minerals preferred as starting materials for making the compositions are neutral clays that already exhibit some bleaching activity. These clays have a pH value in the range of about 7 to about 9. The pH value of the clay is determined from a 5 wt% slurry of the clay in distilled water.

For acid activation of the clay mineral, the acid can be inorganic or organic having a pK_a value not greater than about 7. Mineral acids such as hydrochloric acid, phosphoric acid or sulfuric acid are preferred. Particularly preferred is sulfuric acid in a relatively high concentration.

2.9.3 Diatomite [35]

Diatomite is a chalk-like, soft, very fine grained, siliceous sedimentary rock, usually light in color (white if pure, commonly buff to gray in situ, and rarely black). It is very finely porous, very low in density (floating on water at least until saturated), and essentially chemically inert in most liquids and gases. It also has low thermal conductivity and a rather high fusion point. Analysis of oven-dried samples of crude ore from many commercial operations typically shows 80% to 90% (in some cases 95%) silica (SiO_2) plus alumina (2% to 4%, attributed mostly to clay minerals) and hematite (0.5% to 2%), with an analytical ignition loss of 4% to 6%. The melting point of diatomite ranges from $1,000^\circ\text{C}$ to $1,750^\circ\text{C}$.

In 1867, Alfred Nobel's invention of dynamite resulted in the development of the world's first significant diatomite industry, as diatomite was used as an absorbent and stabilizer for dynamite and nitroglycerine. Dynamite and nitroglycerine explosives required significant amounts of diatomite and operations began to flourish. In 1900, the first U.S. patent was issued for the use of diatomite in beer filtration, which is one of diatomite's primary applications in modern times. Diatomite continued to be used primarily for filtration (beer, cooking oils, wine), while other major uses were as absorbents, filler applications, insulation and in cement manufacturing.

2.9.4 Bentonite [36]

Bentonite is fine powder clay which can have montmorillonitic properties with a $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio of 3.77. Bentonite due to its physical and chemical characteristics (large specific area, cation exchange capacity, and adsorptive affinity for organic and inorganic ions) is highly valued for its sorptive properties. It was used as adsorbent material. Bentonite is a good adsorbent for organic species because it exhibits a variety of attractive properties such as high specific surface area, high porosity and surface activity. It is used as industrial raw material in more than 25 application areas, including the production of selective adsorbents, bleaching earth, catalyst beds, carbonless copy paper and medication. They are also used as

binders in foundries and in ceramic production since they produce muds of high plasticity with water. In particular, experience with drilling in the major oil producing countries has shown bentonite clay as the chief raw material that should be added in the preparation of drilling fluids.

Sodium bentonite has a high swelling capacity due to the much higher hydratability of the sodium ions in comparison to the calcium ions. The treatment of clays with inorganic or organic reagents increases the sorption capacity.

2.10 Literature reviews

In 2003, Kumar *et al.* [37] studied the transesterification process for producing biodiesel from vegetable oil and animal fats by using sodium hydroxide and sulfuric acid as catalysts at 70°C. The result showed that the mode of the reaction, molar ratio of the glycerides to alcohol, type and quality of catalyst, reaction time, reaction temperature and purity of oil and fats had affected the production yield. High yield of biodiesel was obtained by using 2% H₂SO₄ as acid catalyst, 10:1 ratio of methanol to oil at 70°C for 2 h and/or using 1.5% NaOH as base catalyst, 8-10:1 ratio of methanol to oil at 68-70°C for 30-40 min.

In 2003, Maskan and Bağci [38] studied the refining of used sunflower seed oil by various adsorbent treatments. Six adsorbents including CaO, MgO, Mg₂CO₃, magnesium silicate, activated charcoal and bentonite, as well as an available natural earth (e.g., pekmez earth, CaCO₃ containing special natural white soil). In this work, magnesium silicate, pekmez earth and bentonite were selected for the reduction of FFA, viscosity and color recovery, respectively. The best combination of the adsorbents was found to be 2% pekmez earth, 3% bentonite and 3% magnesium silicate for the industrial refining of used frying oils.

In 2005, Cooke *et al.* [39] had reported method of purifying a biodiesel by adsorption with at least one adsorbent material, such as magnesium silicate. They found that impurities in biodiesel such as soap, colors, odors, unreacted catalyst, metals and metallic compounds could be removed by magnesium silicate as an adsorbent. The purified biodiesel was achieved the specifications for ASTM 6751 and

EN 14214 standard and it also had potential to improved oxidative stability of biodiesel.

In 2006, Meher *et al.*[40] studied the transesterification of Karanja oil with methanol for the production of biodiesel. By using 1% KOH as catalyst, methanol to oil molar ratio 6:1, at 65 °C with rate of mixing 360 rpm for a period 3 h, 85% yield was obtained in 15 min and reaction was almost complete in two hours with 97–98% yield of methyl esters. Moreover, the reaction could be completed within 1 h by using 12:1 molar ratio of methanol to oil or higher. On the other hand, with a low rate of stirring at 180 rpm, the reaction was incomplete whereas stirring at high rpm was a time efficient process.

In 2006, Charoensinvorakul[41] studied the reducing free fatty acid in biodiesel obtained from palm oil by using different types of adsorbents. The biodiesel was synthesized by using 16:1 molar ratio of methanol to oil with 1.4%wt of sodium hydroxide at 50°C for 1.50 h. The 88-96% yield of biodiesel was obtained from these reaction conditions. Then, biodiesel with 0.184% of FFAs was further purified by adsorbents including magnesol, activated charcoal, basic alumina, molecular sieve (4Å), bentonite clay and NaOH-treated bentonite clay. The results showed that the activated charcoal and magnesol could reduced FFAs to 0.014% and 0.016%, respectively.

In 2008, Berrios and Skelton [42] had reported purification methods for biodiesel. Three different methods, the use of ion exchange resins, magnesium silicate and water washing were selected to perform in this work. Glycerol and soap content have been removed in all the processes but only water washing has purified biodiesel to the requirements of EN 14214 Standard. However, it has some disadvantages such as water supply and cost, emulsions, wastewater treatment and drying of final product. The magnesol process has had better effect on the methanol content than the ion exchange resin but none of the experiments fulfill the specification of EN 14214 standard. At least 0.75%wt of magnesol is required with a contact time of 10 min in order to decrease the glycerol and soap content. None of the processes had any significant effect on acid value, glycerides or water content.

In 2008, Mazzieri *et al.* [43] studied the refining of biodiesel by adsorption over silica gel. The result showed that glycerol has a great affinity for the silica

surface and is selectively adsorbed from biodiesel solutions. The Langmuir adsorption constant and the saturation capacity constants were found to be $2.22 \text{ cm}^3\mu\text{mol}^{-1}$ and 0.239 g.g^{-1} , respectively. During the adsorption of glycerol from biodiesel solutions and over silica gel samples, soaps do not interfere with the adsorption. However, dissolved methanol produces a decrease of the adsorption capacity by increasing the activity of glycerol in the solvent and by competition for the adsorption sites on silica. Monoglycerides also decreased the saturation capacity as a consequence of their competitive co-adsorption over silica.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1. Chemicals and materials

1. 2-Propanol: commercial grade; Merck
2. Acetic acid: analytical grade; Merck
2. Bromophenol blue: analytical grade; Carlo erba
3. Cyclohexane: analytical grade; Merck
4. EN 14105 standard and internal standard solution; Supelco
5. Ethanol: analytical grade; Merck
6. Ethyl acetate: analytical grade; Merck
7. Heptane: analytical grade; Merck
8. Methanol: analytical grade; Merck
10. N-methyl-N-(trimethylsilyl)-trifluoroacetamide: derivatization grade; Sigma-Aldrich
11. Phenolphthalein indicator: analytical grade; Merck
11. Phenol red: analytical grade; Carlo erba
12. Potassium hydroxide: analytical grade; Lab-Scan
13. Potassium dichromate: analytical grade; Lab-Scan
14. Potassium iodide: analytical grade; Lab-Scan
15. Potassium hydrogen phthalate: analytical grade; Merck
16. Refined palm oil
17. Sodium hydroxide: analytical grade; ACS
18. Sodium thiosulfate: analytical grade; Lab-Scan
19. Sulfuric acid: analytical grade; Carlo Erba
20. Toluene: analytical grade; Merck
21. Wijs solution: analytical grade; Merck

22. Activated carbon; commercial grade; N & P scientific CO., LTD.
23. Activated clay: commercial grade; Siam Taiko Marketing CO.,LTD.
24. Bentonite: commercial grade; N & P scientific CO., LTD.
25. Diatomite: commercial grade; Amphur Maeta, Lampang.

3.1.2 Equipments

1. BET Surface Area Analyzer: SA 3100 Coulter
2. Cannon Automatic Viscometer: Model CAV-3; Cannon
3. Gas Chromatography: Varian CP-3800, USA
4. Rotary evaporator: Buchi R-200, Germany
5. Water bath and shaker: Mammert W350, Germany

3.2 Procedure

3.2.1 Determination of physical and chemical properties of refined palm oil as biodiesel production

The free fatty acid, saponification value and iodine value of refined palm oil were determined according to ASTM D5555, ASTM D5558 and ASTM D5554 standards, respectively.

3.2.2 Transesterification of refined palm oil

Five hundred grams of refined palm oil was 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°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. The methyl ester layer was later brought to purification process.

In order to investigate the effect of methanol on the adsorption, methyl ester was also synthesized by using 9:1 and 12:1 molar ratio of methanol to oil.

3.2.3 Purification of crude biodiesel

3.2.3.1 Purification of crude biodiesel using various adsorbents in the presence of methanol

Four types of adsorbents including diatomite, bentonite, activated clay and activated charcoal were selected to adsorb the biodiesel impurities in this work. The size of all adsorbents was separated by passing through a screen (100 mesh).

- Effect of temperature on precipitation of soap

After transesterification was finished, 100 g of crude biodiesel on the upper phase was settled at 60, 50, 40°C and at ambient temperatures with close and open systems. Every 10 minutes, the biodiesel samples were sampling out to investigate for soap content and residual alkaline catalyst by titration method.

- Effect of contact time on soap adsorption

Fifty grams of crude biodiesel was treated with 3%wt of adsorbent at 50°C with stirring rate at 150 rpm. The contact time between adsorbents and crude biodiesel was varied in the range of 5, 10, 20 and 30 min. After the adsorbents were removed by filtration, the amount of soap content was determined by titration method.

- Effect of amount of adsorbents on soap adsorption

Fifty grams of crude biodiesel was treated with five concentrations of each adsorbents: 1, 2, 3, 4 and 5 %wt of adsorbents. The experiment was

performed at 50°C in 10 min with stirring rate at 150 rpm. Then the adsorbents were removed by filtration and the amount of soap content was determined by titration method.

3.2.3.2 Purification of crude biodiesel using various adsorbents after methanol removal

3.2.3.2.1 Methanol removal process

To represent industrial scale, methanol was first removed before the adsorption was performed. The method of methanol removal was also investigated. After glycerin layer has been separated, crude biodiesel was separated into two partitions. First partition was carried out by heating biodiesel at 80°C with stirring rate at 150 rpm for 2h while the other partition was evaporated at 50°C with rotary evaporator until there was no sign of methanol in crude biodiesel. To determine monoglycerides in crude biodiesel, the biodiesel was then washed with warm deionized water to eliminate free glycerol. The biodiesel was determined for total glycerin contents by using GC analysis according to EN14105 standard.

- Optimization of the adsorption parameters

1. Effect of amount of adsorbents on soap adsorption

After methanol removal, effect of amount of adsorbents was studied according to 3.2.2.1. In an effort to adsorb biodiesel impurities, five concentrations of each adsorbent: 0.1, 0.5, 0.8, and 1 %wt were used at 50°C with stirring rate at 150 rpm and contact time 10 min. The biodiesel was determine the soap content by titration method.

2. Effect of contact time on soap adsorption

Effect of contact time was studied according to 3.2.2.1 after methanol was removed. In 150 milliliters of flask, 50 grams of biodiesel was treated with 0.5%wt of diatomite at 50°C, with stirring rate at 150 rpm and contact time at 1, 3, 5 and 10 min. The biodiesel was subjected to determine free and total glycerin contents were determined according to EN14105 standard.

3.2.3.3 Purification of crude biodiesel with water washing

After the crude biodiesel was allowed to stand for half an hour, glycerin layer at the bottom was removed. The crude biodiesel on the upper phase was washed several times with warm deionized water (50°C) in a separatory funnel until the washed water became clear. Then, the water in purified biodiesel was then removed by evaporation under atmospheric condition. The amount of soap content was determined by titration method and free and total glycerin contents were determined according to EN14105 standard.

3.2.4 Breakthrough point and capacity of activated clay for soap adsorption

In 100 milliliters glass bottom, 30 grams of crude biodiesel was treated with 1 gram of activated clay at 50°C for 1 min. Biodiesel was poured out after crude biodiesel was treated. Then, new 30 gram of crude biodiesel was treated with used activated clay under the same conditions. This process was repeated until the effluent concentration reached 5 percent of the influent value. Exhaustion or capacity of the adsorbent was occurred when the effluent concentration reaches 95 percent of the influent concentration. All biodiesel samples were analyzed using titration method.

3.2.5 Biodiesel analysis

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

Five grams of biodiesel sample was dissolved in 100 milliliters of isopropyl alcohol with 2 milliliters of 1% phenol red as an 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:

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

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):

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

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

3.2.5.2 Determination of free and total glycerin contents (EN14105)

The free glycerol and total glycerin contents including residual mono-, di-, and triglyceride contents in biodiesel was determined by means of the chromatographic method of EN14105. N-heptane was used as a solvent. 1,2,4-Butanetriol and tricaprins 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 was added to each. Then, 1 μL of 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 Ultimet (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 $^{\circ}\text{C}$. After held for 1 min, the oven was heated at 15 $^{\circ}\text{C}/\text{min}$ to 180 $^{\circ}\text{C}$, at 7 $^{\circ}\text{C}/\text{min}$ to 230 $^{\circ}\text{C}$, and at 10 $^{\circ}\text{C}/\text{min}$ to 370 $^{\circ}\text{C}$ (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 $^{\circ}\text{C}$. The total run time was 36 min.

3.2.5.3 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
Flash point (°C)	ASTM D93
Acid number (mg KOH/g)	ASTM D974

3.2.6 Physical properties of adsorbents

The physical properties such as surface area, pore volume and average pore size of activated charcoal, bentonite, diatomite and activated clay was determined with specific surface area analyzer using BET (Brunauer-Emmett-Teller) method. It could be carried out into two steps: pretreatment and surface area analyzer.

Step1, Pretreatment; 40 milligrams of each adsorbent was 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°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.

3.2.7 Adsorption isotherm

3.2.7.1 Adsorption isotherm with surface area analyser

Activated charcoal, bentonite, diatomite and activated charcoal were determined the type of adsorption isotherm using the nitrogen adsorption isotherm at 77K. The determination method was performed the same as 3.2.6. Type of adsorption isotherm was obtained from this analysis.

3.2.7.2 Adsorption isotherm of soap

The adsorption isotherms were studied to describe how soap molecules interact with the adsorbent surface of activated clay, diatomite and bentonite. To perform the experiment, ten concentrations of adsorbents were studied in the range of 1-10 %wt. In a 100 milliliters glass bottom, 50 grams of crude biodiesel was treated with each adsorbent at optimum condition (at 50 °C, with stirring at 150 rpm and contact time at 10 min) in water bath. The adsorbents were removed by filtration and the amount of soap was analyzed according to titration method. The result obtained from the experiment were then calculated through two equations, Langmuir and Freundlich isotherms, for determination the nature of the adsorption.

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

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 $1/(x/m)$.

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

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 DISCUSSIONS

4.1 Properties of refined palm oil as biodiesel production

The properties of refined palm oil including % free fatty acid, saponification value and iodine value were investigated. The results indicated that it contained 0.62% of FFAs, saponification value 202.74 mg KOH/g of oil and iodine value 61.33 mg I₂/g of oil, respectively.

4.2 Transesterification of refined palm oil

The transesterification reaction was monitored by Thin Layer Chromatography (TLC). As can be seen in Figure 4.1, triglycerides were completely converted to methyl ester. There were trace of diglycerides and monoglycerides in crude biodiesel due to three steps of conversion of triglycerides to biodiesel. First, triglycerides were converted to diglycerides followed by the conversion of diglycerides to monoglycerides and then the monoglycerides were converted to glycerol. Each step was given one molecule of methyl ester.

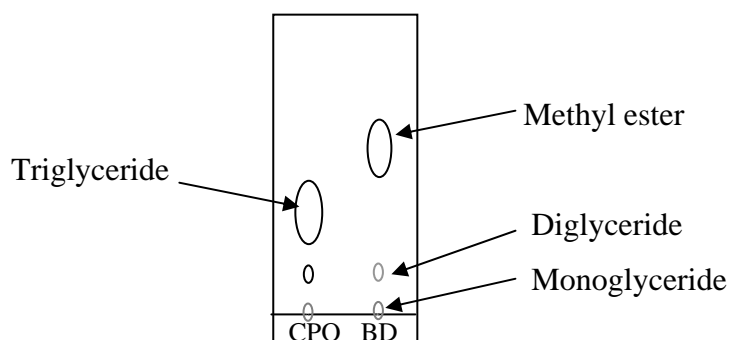


Figure 4.1 TLC of biodiesel which synthesized with base-catalyzed process when CPO: Crude palm oil, BD: Biodiesel and Mobile phase: a mixture of hexane, ethyl acetate and acetic acid (90:10:1 v/v).

4.3 Purification of crude biodiesel

4.3.1 Purification of crude biodiesel using various adsorbents in the presence of methanol

- Effect of temperature on precipitation of soap

The effect of temperature on precipitation of soap at various temperatures in close and open systems; 60°C, 50°C, 40°C and room temperature were investigated. From Figure 4.2, experiment result showed that both systems gave similar results. When the crude biodiesel was settled at 60°C, large amounts of soap and residual catalyst were observed when compared with freshly synthesized biodiesel. At 50°C, these impurities rather decreased but still remained in the biodiesel. While at the temperature 40°C and lower than that, these impurities were slightly decreased. In order to save production time and cost, the suitable temperature of the adsorption was 50°C.

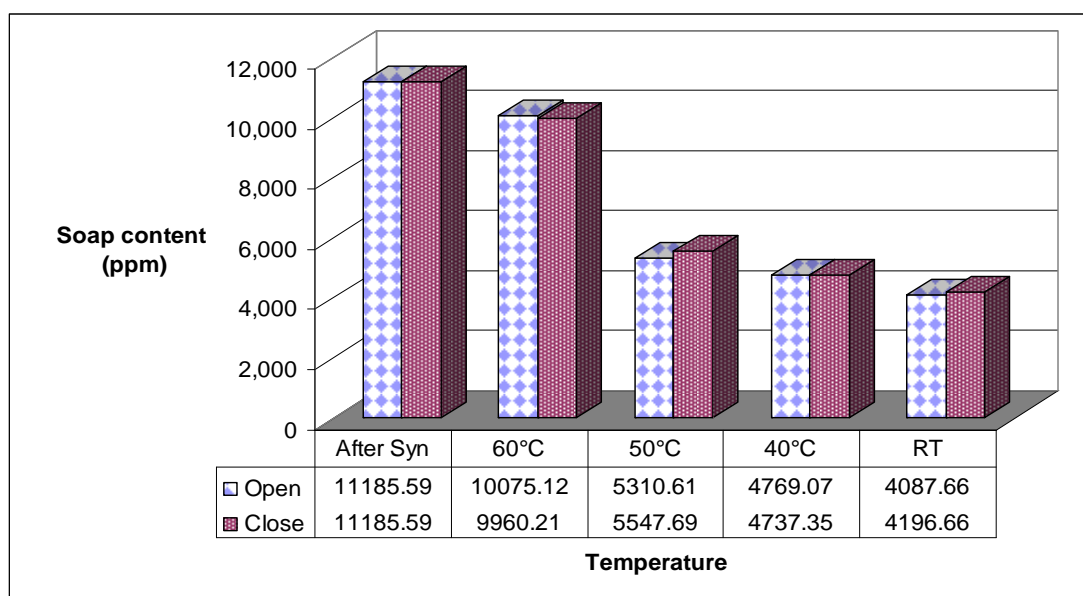


Figure 4.2 Effect of temperature on precipitation of soap.

- Effect of contact time on soap adsorption

The time-dependent behavior of the adsorption was measured by varying the equilibrium time between adsorbents and crude biodiesel in the range of 5–30 min. The experiment was carried out at 50°C with 3%wt of adsorbents and stirring rate at 150 rpm. As can be observed in Figure 4.3, at adsorbed time 5 min, soap contents were dramatically decreased more than 50% and they appeared to be reduced until 10 min of the adsorption. Afterwards, the adsorption of soap contents remained constant. Therefore, a 10 min contact time was found to be appropriate for maximum adsorption and it was used in all subsequent measurements.

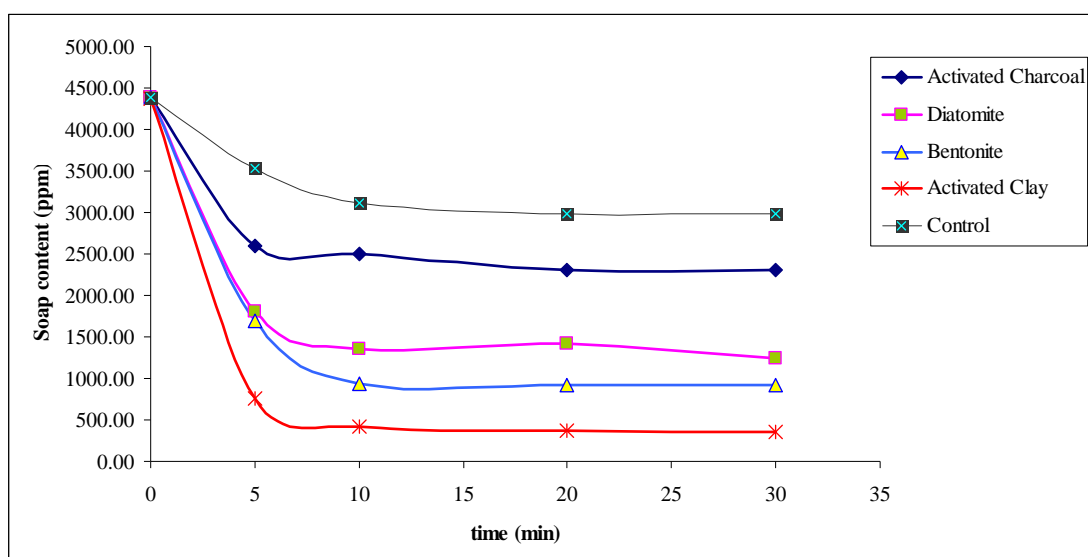


Figure 4.3 Effect of contact time on soap adsorption (3% wt of adsorbents, 50°C, stirring rate 150 rpm).

- Effect of amount of adsorbents on soap adsorption

The effect of amount of adsorbents were studied in the range of 1-5%wt of adsorbents with stirring rate 150 rpm at 50°C. In Figure 4.4, the results showed that soap adsorptions were increased with increasing the amount of

adsorbents up to 4%wt. Therefore, for all further studies 4%wt of adsorbents were used.

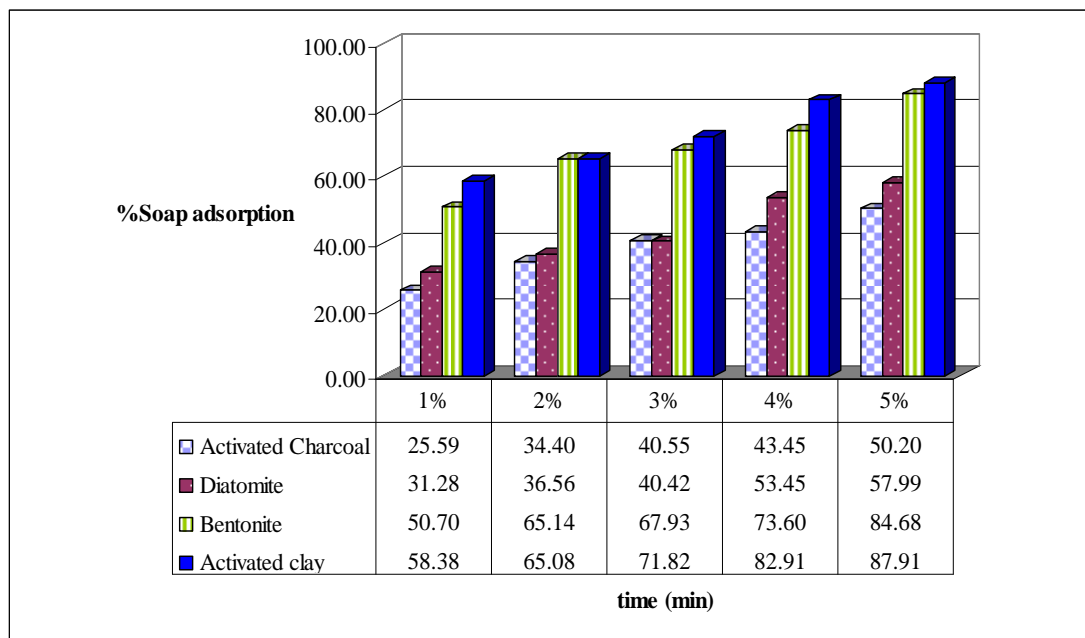


Figure 4.4 Effect of amount of adsorbents on soap adsorption (contact time 10 min, 50°C, stirring rate 150 rpm).

The optimum conditions for the purification of biodiesel in the presence of methanol by using various adsorbents were 4%wt of adsorbents, adsorption temperature 50°C with stirring rate 150 rpm for a period of 10 min.

To investigate the effect of methanol on the adsorption, biodiesel was also synthesized under the optimum conditions by using 9:1 and 12:1 molar ratio of methanol to oil. As can be observed in Figure 4.5, methanol addition reduced the efficiency of all adsorbents about 50%. The effect must be the result of both the affinity of methanol for the adsorbent surface and the increase of the affinity of glycerol for the fluid phase in the presence of methanol [43].

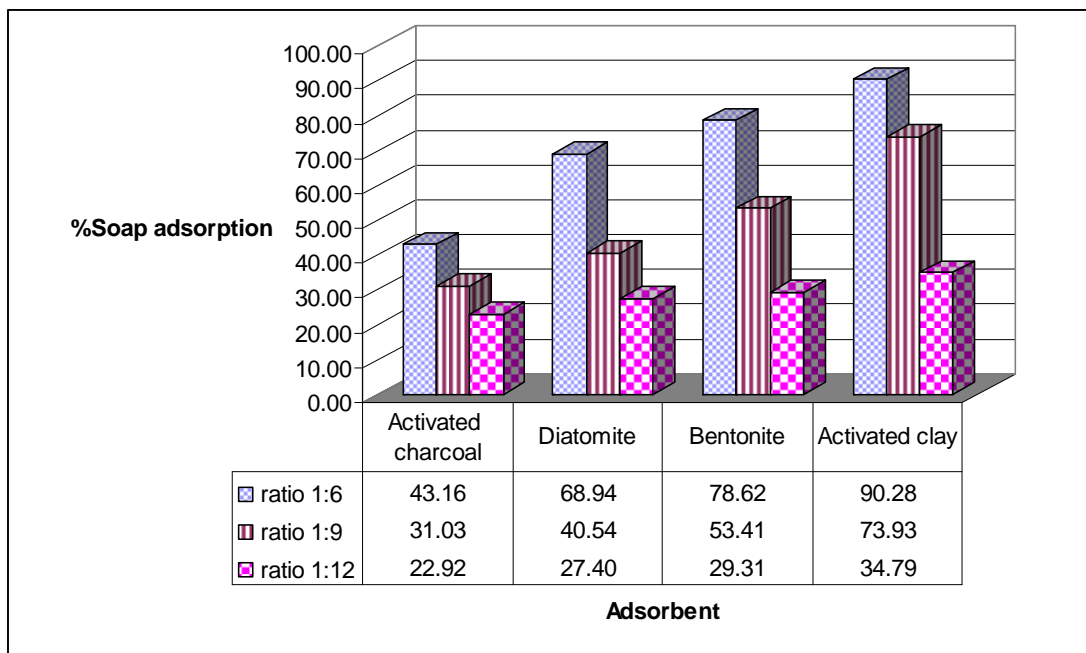


Figure 4.5 Effect of methanol on soap adsorption (4% wt of adsorbents, 50°C, contact time 10 min, stirring rate 150 rpm).

From Figure 4.5, using 4% wt of activated clay, with the optimum conditions at 50°C and stirring rate 150 rpm for 10 min, gave the best result of removing of soap content. To perform as industrial practice, methanol was first removed before the adsorption was performed [42]. The result was shown in Table 1, without methanol, sorbent could remove soap better than sorbent with the presence of methanol. Moreover, the trace of soap content by using this adsorption process was similar to the trace of soap content of the conventional water washing process.

Table 4.1 Soap contents of 4% wt of activated clay and water washing process.

Process	Soap content (ppm)
With methanol	334
Without methanol	28
Water washing	27

4.3.2 Purification of crude biodiesel using various adsorbents after the removal of methanol

4.3.2.1 Methanol removal process

The process of removing methanol was investigated before the purification was performed. After the methanol was eliminated, crude biodiesel obtained from two different processes, heating for 2 h and flash evaporating at 50°C, were then washed with warm deionized water to get rid of free glycerol in purified biodiesel. Free glycerol and total glycerin contents of purified biodiesel were determined by using GC analysis according to EN 14105 standard.

Table 4.2 Free glycerol and total glycerin contents in biodiesel with heating crude biodiesel at 80°C for 2 h compared with evaporating at 50°C.

Process	Glycerol	Monoglyceride	Diglyceride	Triglyceride	Total glycerin
Heating at 80°C for 2 h	-	0.7610	0.0418	-	0.764
Evaporating at 50°C	-	0.4317	0.0346	-	0.110

As can be seen in Table 4.2, There were no trace of free glycerol with any biodiesel samples. However, by heating biodiesel at 80°C, monoglycerides were dramatically increased when compared with biodiesel obtained from evaporation process. They can be explained with the reversibility of the transesterification reaction. If methanol is removed, back reaction is occurred giving the higher of monoglycerides instead of methyl ester molecule[10].

From Table 4.2, The percentage of monoglycerides with heating process was higher than the evaporation process for two times (0.7610 and 0.4317, respectively) and it almost reached the specification of monoglycerides in

biodiesel which was 0.8%. The evaporation process should be used to remove methanol in biodiesel. In addition, the flash evaporation could be finished in short time and the evaporating temperature was performed similar to the adsorption temperature (50°C). Therefore, concerning of monoglycerides in biodiesel, production time and energy lost, the evaporation process is more suitable for removing methanol from biodiesel.

After the methanol was removed, soap content was dramatically decreased from 4370 to 1240 ppm due to the precipitation of soap. This suggested that soap content elimination in biodiesel was influenced by the presence of methanol. Since both biodiesel and soap could be dissolved in methanol, therefore, soap was subsequently precipitated when methanol was removed. Only few amount of soap was remained in biodiesel to be further purified. Thus, the optimum conditions including contact time and the amount of adsorbents for adsorption without methanol were also investigated.

- **Optimization of the adsorption parameters**

1. Effect of amount of adsorbents on soap adsorption

The effect of amount of adsorbents were studied in the range of 0.1 - 1% wt of adsorbents with stirring rate 150 rpm at 50°C for 10 min.

In Figure 4.6, the results showed that soap adsorptions were slightly increased with increasing the amount of adsorbents up to 1% wt. By using 0.1% wt of adsorbents, %soap adsorption seem to be the good selection for the experiment, however, the soap still precipitated in biodiesel then the solution was not clear. Thereby, 1% wt of adsorbents were suitable for the adsorption.

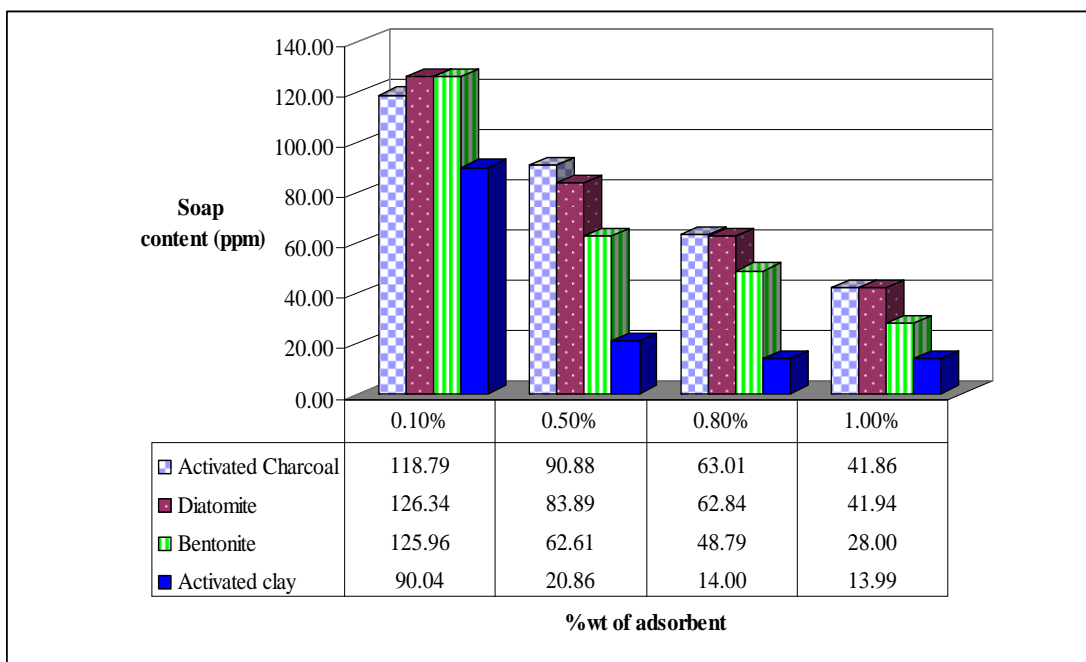


Figure 4.6 Effect of amount of adsorbents on soap adsorption (contact time 10 min, 50°C, stirring rate 150 rpm).

2. Effect of contact time on soap adsorption

The effect of contact time was carried out by varying the equilibrium time between adsorbent and crude biodiesel at 1, 3, 5 and 10 min. The experiment was performed at 50°C with 0.5% wt of diatomite and stirring rate at 150 rpm.

Table 4.3 Free glycerol and total glycerin contents in biodiesel with varying contact time in the range of 1-10 min.

Contact time	Glycerol	Monoglyceride	Diglyceride	Triglyceride	Total glycerin
1 min	0.0068	0.3125	0.0300	-	0.0908
3 min	0.0055	0.3183	0.0315	-	0.0913
5 min	0.0045	0.3462	0.0334	-	0.0976
10 min	0.0003	0.3441	0.0385	-	0.0937

As can be observed in Table 4.3, at adsorbed time 1 min, free glycerol could be decreased to 0.0068% which was lower than the specification of free glycerol (<0.2%) in biodiesel. At 3 min of the adsorption, free glycerol was slightly decreased until 10 min of the adsorption, free glycerol was reduced to 0.0003%. Hence, considering of the production time and cost, 1 min of adsorption was chosen to perform in this work.

It could be concluded that the optimum conditions for the purification of biodiesel after the removal of methanol were 1%wt of adsorbents, adsorption temperature 50°C with stirring rate 150 rpm for a period of 1 min.

Table 4.4 Product yield of biodiesel after adsorption with 1%wt of activated clay for 1 min compared with water washing process.

Process	% Product yield
Adsorbed with 1%wt of activated clay	97.65
Water washing	98.44

The percentage of purified biodiesel yield after adsorption was investigated compared with purified biodiesel obtained from water washing process. 1%wt of activated clay was chosen to perform in this section because it gave the best result of adsorbed soap content in biodiesel when compared with the other adsorbents. The result was shown in Table 4.4, by adsorption with 1%wt of activated clay, %product yield of biodiesel was 97.65% while %yield of purified biodiesel by water washing process was 98.44%. It could be described that yield of biodiesel from the adsorption process was lost when the filtration had occurred. However, the significance of product yield of biodiesel between two different purification processes was not much.

4.3.2.2 Determination of free glycerol and total glycerin contents in biodiesel according to EN 14105 standard

After the purification was completed, biodiesel was brought to determine for free glycerol and total glycerin contents to achieve the EN 14105 standard. The specification of free glycerol, monoglyceride, diglyceride, triglyceride and total glycerin in biodiesel were 0.02, 0.8, 0.2, 0.2 and 0.25%, respectively. As can be observed in Table 4.5, both purification processes could eliminate all free glycerol in biodiesel. In addition, biodiesel treated with 1% activated clay had brought the total glycerin contents down to 0.0819% which was lower than biodiesel purified with water washing process. Both purification processes had purified biodiesel to the requirement of standard.

Table 4.5 Free glycerol and total glycerin contents in biodiesel of crude biodiesel and purified biodiesel from two different processes.

	Glycerol	Monoglyceride	Diglyceride	Triglyceride	Total glycerin
Crude biodiesel	0.0113	0.3114	0.0419	-	0.0968
1% wt of activated clay	-	0.3324	0.0434	-	0.0819
Water washing	-	0.3380	0.0456	-	0.0929

4.4 Breakthrough point and capacity of activated clay for soap adsorption

Due to the efficiency of the impurities adsorption, activated clay was chosen to perform in this section. 30g of crude biodiesel was treated with 1g of activated clay at 50°C for 1 min. Crude biodiesel was poured out after treated with adsorbent. New

30g of crude biodiesel was then treated with used activated clay under the same condition.

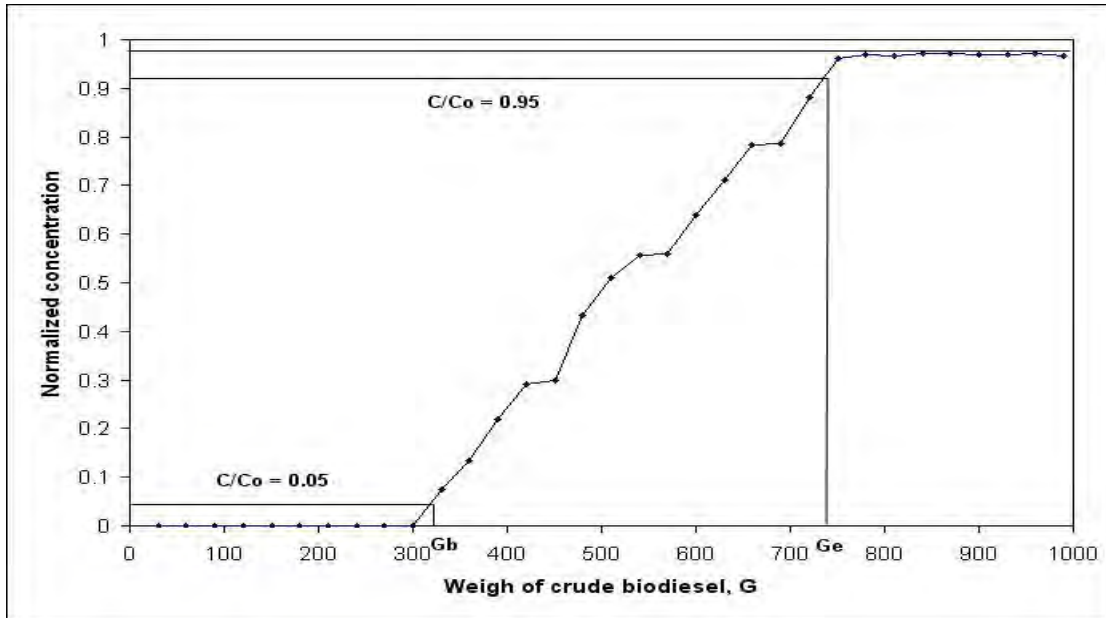


Figure 4.7 Breakthrough point and capacity of activated clay for soap adsorption.

From Figure 4.7, breakthrough has occurred when the effluent concentration achieve 5 percent of the influent value, $G_b = 325$ g. Capacity of the adsorbent was calculated when the effluent concentration achieve 95 percent of the influent concentration, $G_e = 735$ g. Therefore, breakthrough point and capacity of activated clay onto the soap adsorption were 325 g/g of crude biodiesel and 735g/g of crude biodiesel, respectively. It could be decribed that activated clay had an effective ability to adsorb soap molecule until the uptake of crude biodiesel was reached to 325 g. After that, soap molecule was gradually eluted from the surface of clay. When the uptake crude biodiesel was reached 725 g, the efficiency of adsorption was exhaustive. Then the soap content in uptake crude biodiesel was balanced to the outward biodiesel.

4.5 Properties of biodiesel

The properties of purified biodiesel such as flash point, acid value and viscosity were determined. The standard values of these properties were shown in Table 4.6.

Table 4.6 Specification for quality of biodiesel

Property	Biodiesel treated with 1%wt of activated clay	Biodiesel purified with water washing	Specification	Method
Viscosity at 40 °C (mm ² /s)	4.15	4.24	3-5 mm ² /s	ASTM D445
Flash point (°C)	>120°C	>120°C	>120 °C	ASTM D93
Acid number (mg KOH/g)	0.0673	0.0671	< 0.5 mg KOH/g	ASTM D974

The biodiesel obtained from the adsorption process had properties similar to the conventional process and it could be fulfilled the requirements of standard. As a result, conventional biodiesel purification method could be replaced by adsorption process to prevent the excessive of wastewater.

The difference of this process was adsorbed the impurities in biodiesel at high temperature (50°C) when compared with purification of biodiesel by using magnesol and silica gel which adsorbed soap and total glycerin at room temperature[42,43]. Considering of production time and energy lost, adsorption at high temperature was more suitable to purify biodiesel which was synthesized at high temperature (65-70°C). In addition, activated clay was the appropriate adsorbent for purifying biodiesel as compared to magnesol and silica gel when the competitive cost was considered. Bentonite and activated charcoal had never been used for soap and glycerin adsorption before. They were only used to reduce the color of used frying oil and FFAs in biodiesel, respectively[38,41].

4.6 Physical properties of adsorbents

Physical properties of various adsorbents such as surface area, pore volume and average pore size were investigated with specific surface area analyzer using BET (Brunauer-Emmett-Teller) method. The result was shown in Table 4.7.

Table 4.7 Physical properties of adsorbents using BET method.

Physical properties	Activated charcoal	Diatomite	Bentonite	Activated clay
BET surface area, (m ² /g)	911.38	67.75	59.37	165.16
Total pore volume (cm ³ /g)	0.3797	0.0918	0.1457	0.2896
Average Pore Diameter(Å)	16.6640	54.1870	98.1720	70.134

The surface area, pore volume and pore diameter of various adsorbents were determined from the nitrogen adsorption isotherms at 77 K. From Table 4.7, activated charcoal had the highest total pore volume when the lowest was obtained from diatomite. The surface area of activated charcoal, activated clay, diatomite and bentonite were 911.38, 165.16, 67.75, 59.37 and m²/g, respectively. From pore diameter analysis, activated charcoal was microporous with pore diameter 16.66 Å when diatomite, bentonite and activated clay were mesoporous because their pore diameters were in the range of 20-500 Å.

4.7 Adsorption isotherm

4.7.1 Determination of the adsorption isotherm with surface area analyzer

The type of adsorption isotherm of activated charcoal, bentonite, diatomite and activated charcoal were determined by using the nitrogen adsorption isotherm at 77K. The results were shown from Figures 4.8 - 4.11.

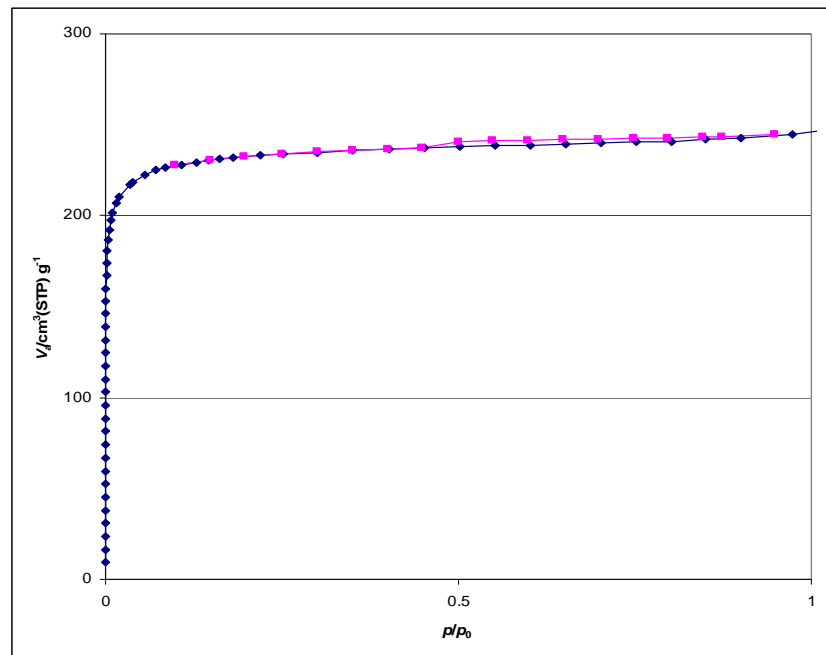


Figure 4.8 Adsorption isotherm of activated charcoal when P: Pressure, P_0 : Pressure saturated.

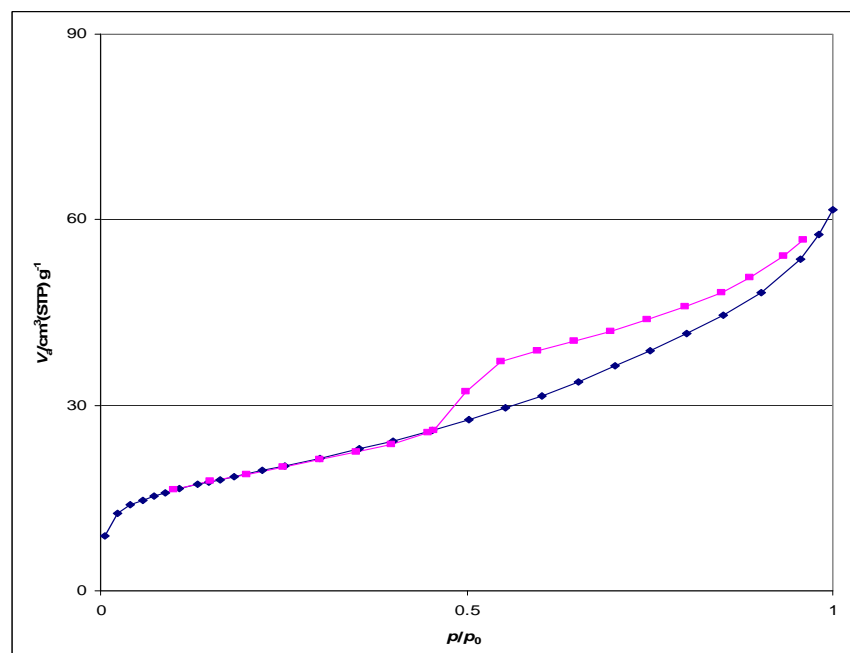


Figure 4.9 Adsorption isotherm of bentonite when P: Pressure, P_0 : Pressure saturated.

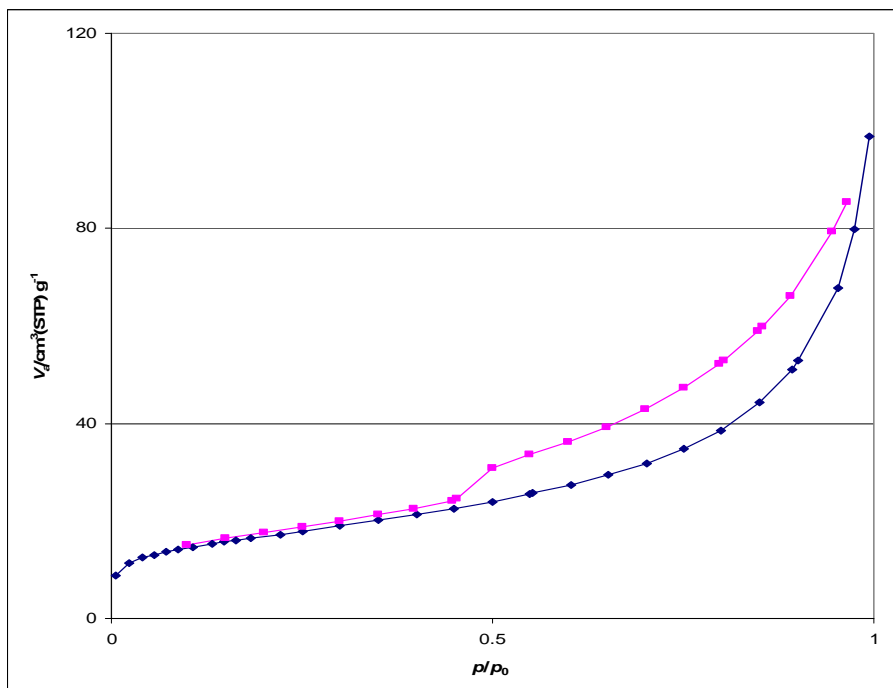


Figure 4.10 Adsorption isotherm of diatomite when P: Pressure, P_0 : Pressure saturated.

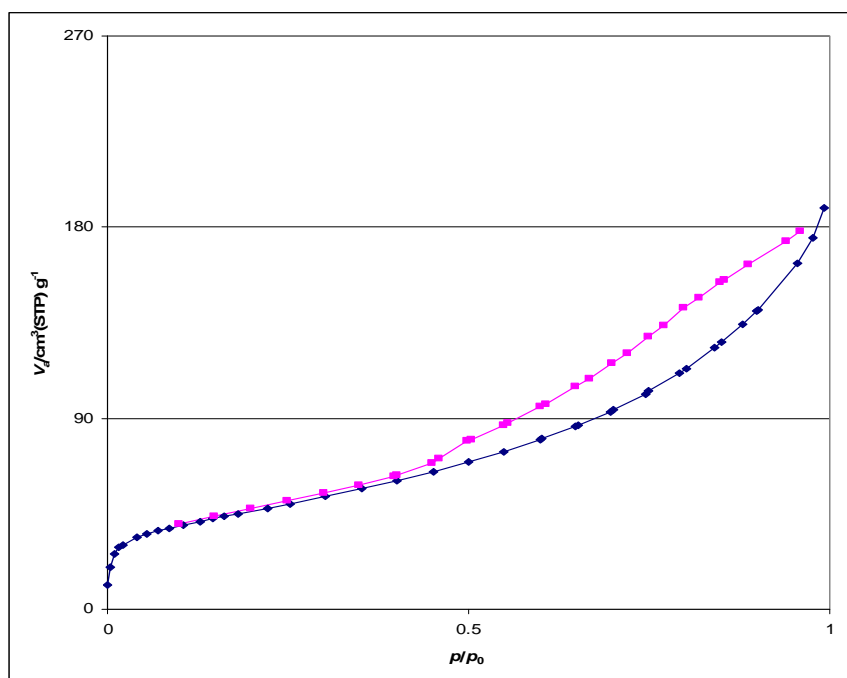


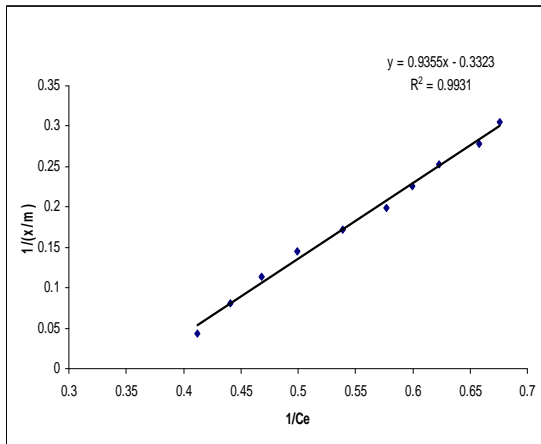
Figure 4.11 Adsorption isotherm of activated clay when P: Pressure, P_0 : Pressure saturated.

From Figure 4.8, it could be described that the adsorption isotherm of activated charcoal was Type I. When the pressure was increased, molecule of nitrogen gas would be continuously adsorbed into the surface area of activated charcoal until it stabled. It was indicated that the monolayer was completely formed. This result was led to the fact that adsorbed of nitrogen gas on activated charcoal was consisted of microporous.

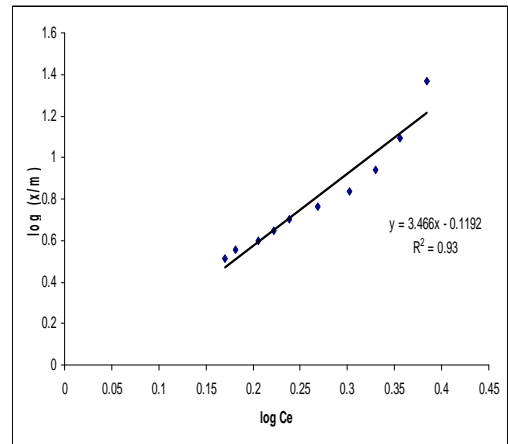
From Figures 4.9 - 4.11, the adsorption isotherm of other adsorbents including bentonite, diatomite and activated clay were Type IV. It could be explained that at lower pressure region of graph was quite similar to Type II. The monolayer was initially formed at a pressure below the saturation vapor pressure. When the pressure was increased 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 increasing 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 three adsorbents were mesoporous.

4.7.2 Adsorption isotherm of soap

To simulate the adsorption isotherm, two commonly used models, the Freundlich [44] and Langmuir [45] isotherms, were selected to explain the adsorption. Ten concentrations of diatomite, bentonite and activated clay were studied in the range of 1-10%wt of adsorbents. In a 100 milliliters glass bottom, 50 grams of crude biodiesel was treated with each adsorbent at 50 °C with stirring at 150 rpm for 10 min in water bath.

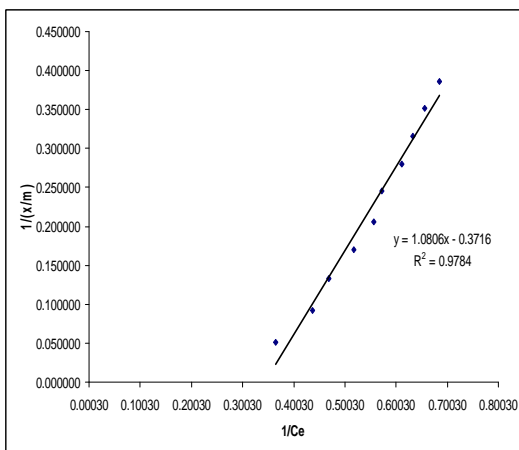


(a)

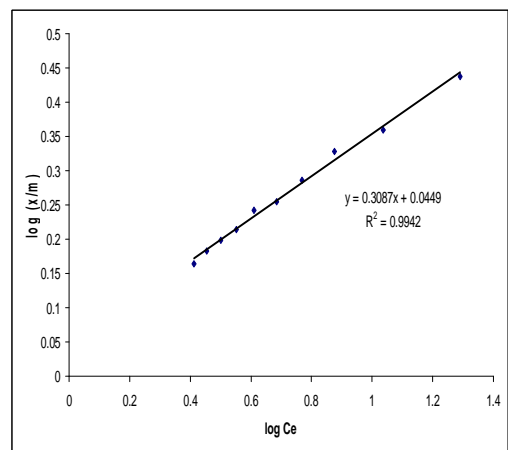


(b)

Figure 4.12 Adsorption isotherms of diatomite (a) Langmuir isotherm and (b) Freundlich isotherm.



(a)



(b)

Figure 4.13 Adsorption isotherms of bentonite (a) Langmuir isotherm and (b) Freundlich isotherm.

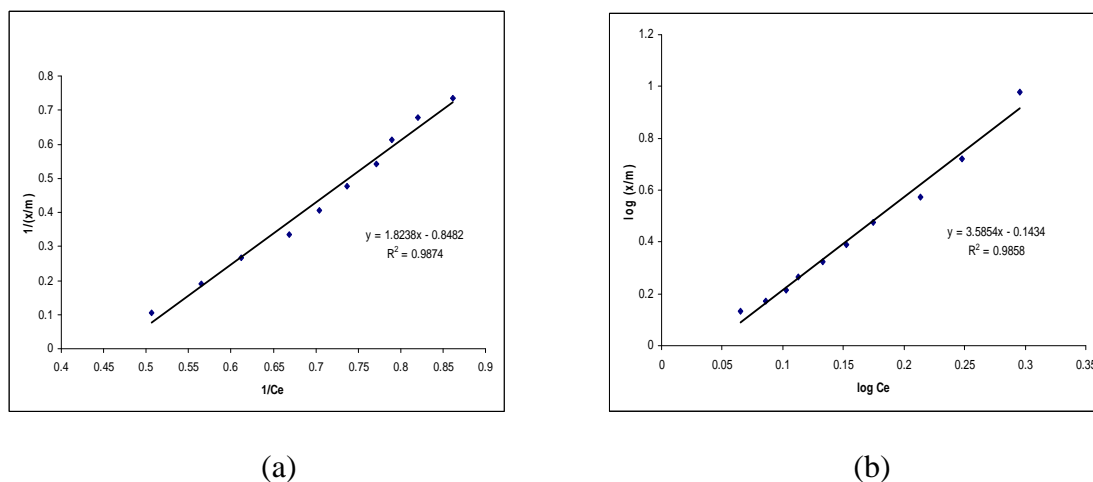


Figure 4.14 Adsorption isotherms of activated clay (a) Langmuir isotherm and (b) Freundlich isotherm.

Table 4.8 Adsorption parameters of isotherm for the adsorption of soap molecule on activated clay, bentonite and diatomite.

Adsorbent	Freundlich			Langmuir		
	K_F	n	r^2	K_L	R_L	r^2
Activated clay	1.39	0.28	0.9858	0.47	0.36	0.9874
Bentonite	1.11	3.24	0.9942	0.34	0.30	0.9784
Diatomite	0.76	0.29	0.9300	0.36	0.37	0.9931

The calculated values of Freundlich and Langmuir model's parameters were shown in Table 4.8. The n and R_L values indicated that the soap adsorption on all adsorbents were favourable for both adsorption isotherms under the experimental conditions. The experimental data of diatomite adsorption isotherm from Figure 4.12 was fit well with the Langmuir model ($r^2 = 0.9931$). This demonstrated that the formation of soap molecule on the surface of diatomite was monolayer. In contrast, from Figure 4.13, bentonite was better fit to Freundlich model because the r^2 value (0.9942) was closer to 1. This adsorption behavior indicated that the adsorption took place on a heterogeneous surface. The overall adsorptive performance was dominated as a physical adsorption process.

From Figure 4.14, the soap adsorption by activated clay was exhibited a reasonable fit to both Freundlich and Langmuir models which referred to monolayer and multilayer adsorption processes. Activated clay had much higher adsorption capacity than diatomite and bentonite because it had the highest K_F and K_L values which referred to the adsorption capacity of adsorbent.

CHAPTER V

CONCLUSION AND SUGGESTION

Purification of biodiesel by adsorption with activated clay, diatomite, bentonite and activated charcoal were performed in this work. The biodiesel was synthesized via transesterification using base-catalyzed process then crude biodiesel was purified with four adsorbents compared with water washing process. It was found that the impurities in biodiesel could be effectively eliminated by using 4%wt of adsorbents at 50°C for 10 min. Interestingly, if methanol had been removed before treatment, adsorption conditions such as contact time and amount of adsorbents could be dramatically reduced because of the precipitation of soap. The removal of methanol by heating biodiesel was not suitable because it would increase monoglycerides in biodiesel due to its reversible reaction. The impurities in biodiesel was eliminated by using 1%wt of adsorbents for 1 min after methanol was removed by flash evaporation. It was found that activated clay gave the best result in removal of impurities in biodiesel. Breakthrough point and capacity of activated clay for soap adsorption were 325 and 725 g/g of crude biodiesel, respectively. Adsorption isotherm of activated clay was fit with Langmuir and Freundlich isotherms which referred to monolayer and multilayer adsorption processes. Purified biodiesel after treated with activated clay could meet the specifications of biodiesel standard according to ASTM and EN standards. Therefore, the adsorption process using adsorbent could be used to purify biodiesel in place of water washing process which produced the large amount of wastewater.

Suggestion

1. New natural adsorbents such as kaolin, smectite, combined adsorbents, etc. which have high porosity should be studied for biodiesel purification.
2. Modified activated charcoal, diatomite, bentonite and activated clay should be studied for adsorption of mono-, di- and triglycerides in biodiesel.

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APPENDICES

APPENDIX A

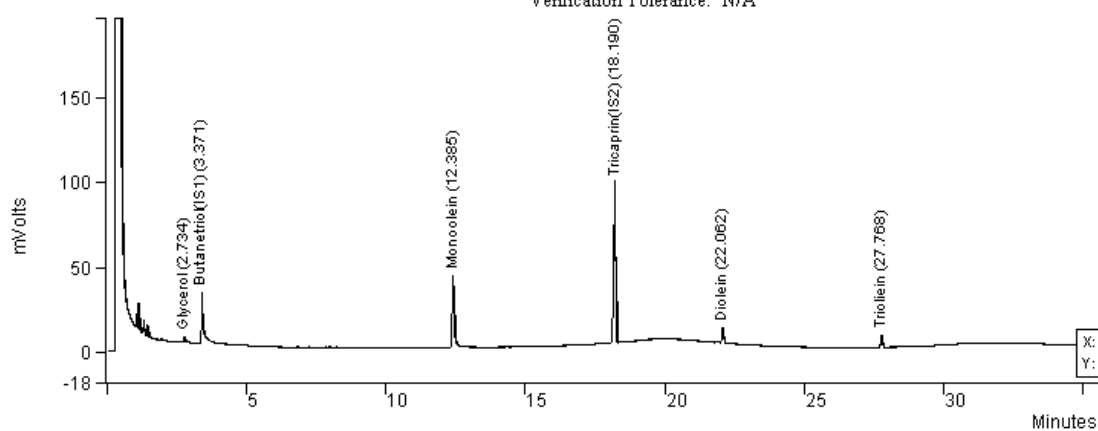
GC CHROMATOGRAM OF BIODIESEL

Appendix A

GC chromatogram

Data File: c:\star\joe\std1.1 11:30:40 am.run
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 Sample ID: std1.1
 Operator (Inj): jo
 Injection Date: 26/2/2010 11:30:40
 Injection Method: c:\star\en14105.mth
 Run Time (min): 35.775
 Workstation:
 Instrument (Inj): gc

Operator (Calc): jo
 Calc Date: 26/03/2010 17:36:25
 Times Calculated: 4
 Calculation Method: std1.1 11:30:40 am-front.mth
 Instrument (Calc): gc
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 Peak Measurement: Peak Area
 Calculation Type: Percent
 Calibration Level: N/A
 Verification Tolerance: N/A

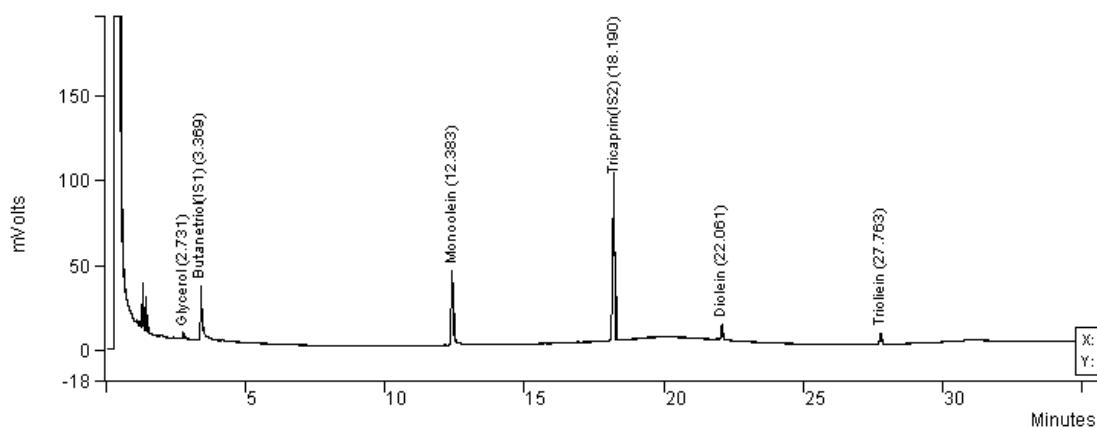


Peak No	Peak Name	Result (%)	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.2179	2.734	-0.000	10554	0.00	BB	2.6		0
2	Butanetriol(1S1)	11.9895	3.371	0.004	103900	0.00	BB	2.6		0
3	Monoolein	24.8616	12.385	-0.016	215449	0.00	BB	4.5		0
4	Tricaprin(1S2)	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
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 Injection Method: c:\star\en14105.mth
 Run Time (min): 35.775
 Workstation:
 Instrument (Inj): gc

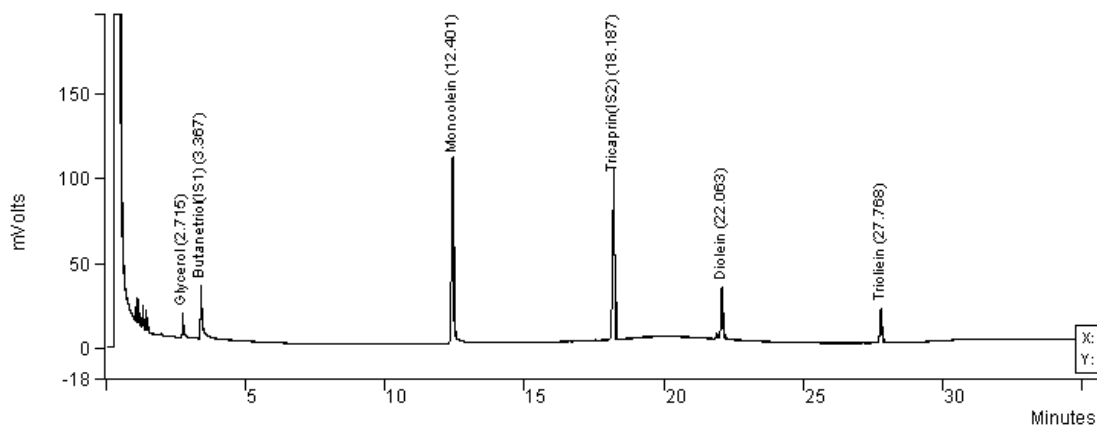
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 Times Calculated: 4
 Calculation Method: std1.1 11:30:40 am-front.mth
 Instrument (Calc): gc
 Run Mode: Analysis
 Peak Measurement: Peak Area
 Calculation Type: Percent
 Calibration Level: N/A
 Verification Tolerance: N/A



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	1.2542	2.731	-0.003	11190	0.00	BB	2.5		0
2	Butanetriol(S1)	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(S2)	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	Triolein	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).

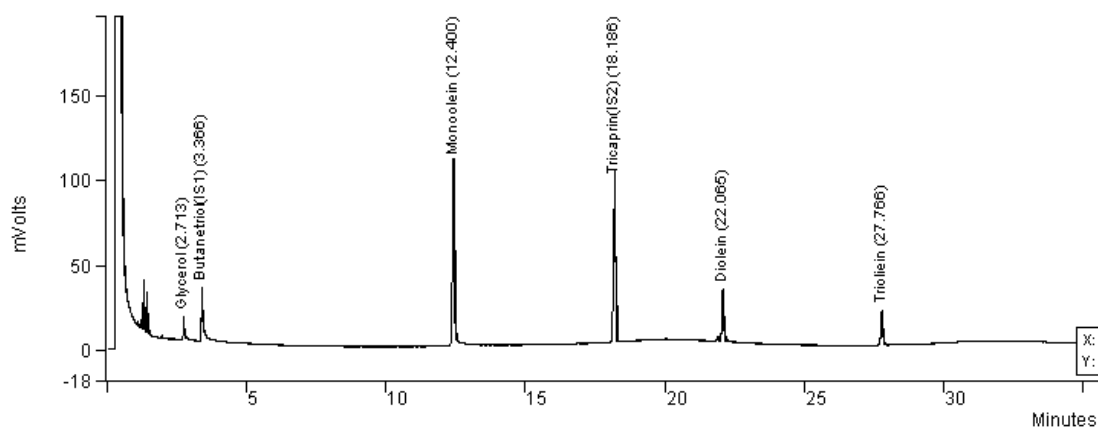
Data File: c:\star\joe\std2.1_1;12;09 pm.run Operator (Calc): jo
 Channel: Front = FID RESULTS Calc Date: 26/03/2010 17:29:48
 Sample ID: std2.1 Times Calculated: 5
 Operator (Inj): io Calculation Method: std2.1_1;12;09 pm-front.mth
 Injection Date: 26/2/2010 13:12:09 Instrument (Calc): gc
 Injection 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	2.6591	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	Triolein	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).

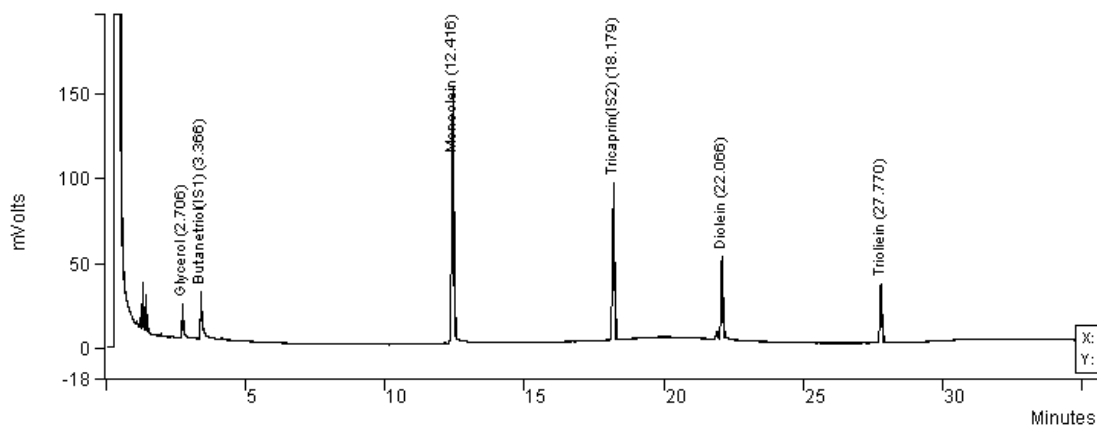
Data File: c:\star\joe\std2.2_2;02;20 pm.run Operator (Calc): jo
 Channel: Front = FID RESULTS Calc Date: 26/03/2010 17:28:04
 Sample ID: std2.2 Times Calculated: 3
 Operator (Inj): io Calculation Method: std2.1_1;12;09 pm-front.mth
 Injection Date: 26/2/2010 14:02:20 Instrument (Calc): gc
 Injection 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	Triolein	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).

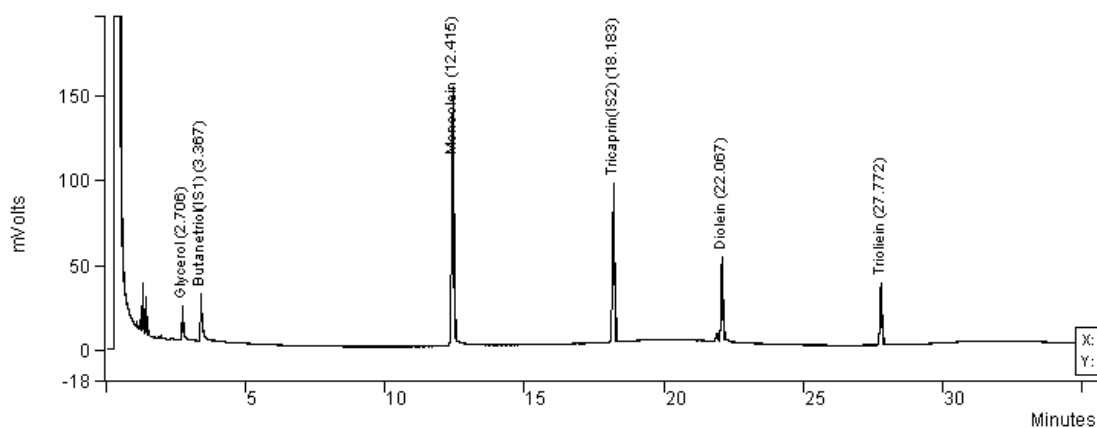
Data File: c:\star\joe\std3.1 2;52;37 pm.run Operator (Calc): jo
 Channel: Front = FID RESULTS Calc Date: 26/03/2010 17:28:05
 Sample ID: std3.1 Times Calculated: 3
 Operator (Inj): io Calculation Method: std2.1 1;12;09 pm-front.mth
 Injection Date: 26/2/2010 14:52:37 Instrument (Calc): gc
 Injection 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	3.2580	2.706	-0.009	56688	0.00	BB	2.4		0
2	Butanetriol(S1)	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(S2)	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).

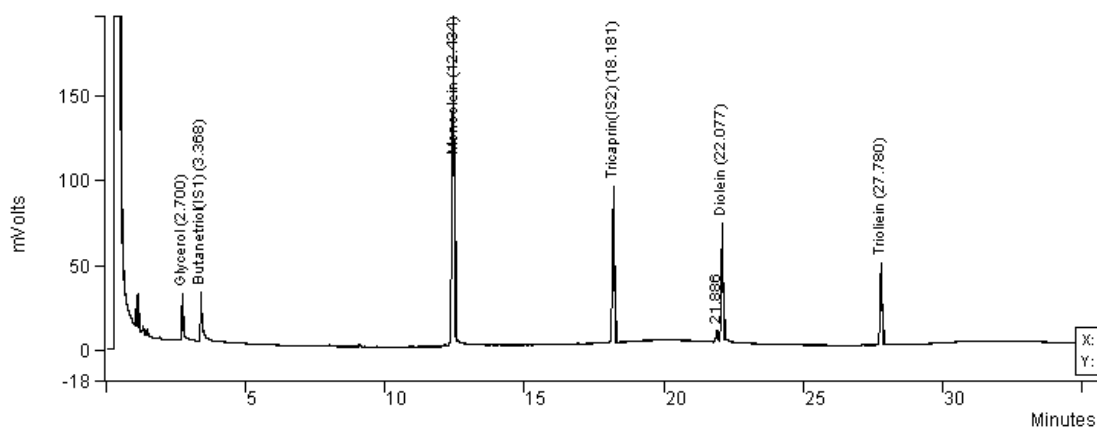
Data File: c:\star\joe\std3.2 3;42;48 pm.run Operator (Calc): jo
 Channel: Front = FID RESULTS Calc Date: 26/03/2010 17:29:48
 Sample ID: std3.2 Times Calculated: 4
 Operator (Inj): io Calculation Method: std2.1 1;12;09 pm-front.mth
 Injection Date: 26/2/2010 15:42:48 Instrument (Calc): gc
 Injection 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(S1)	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(S2)	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	Triolein	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

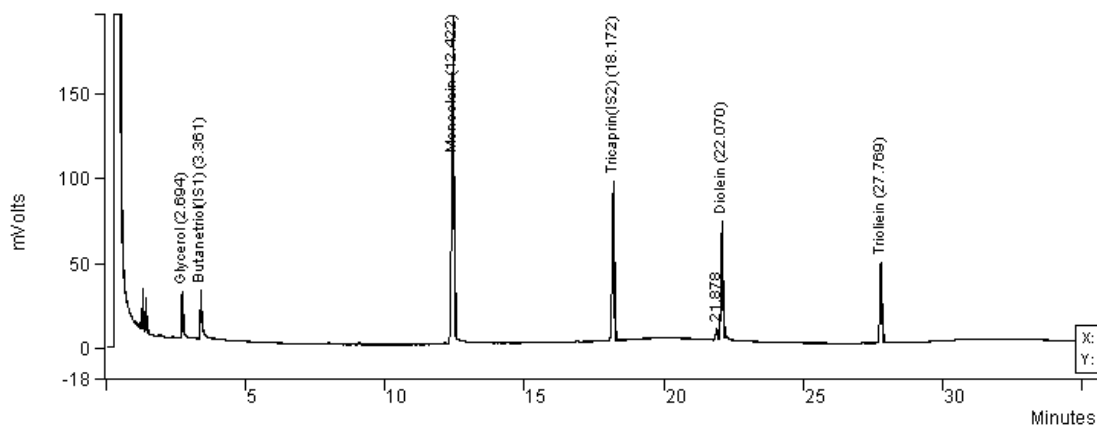


Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.5958	2.700	-0.035	79563	0.00	BB	2.5		0
2	Butanetriol (S1)	4.5792	3.368	0.001	101322	0.00	BB	2.5		0
3	Monoolein	45.8442	12.434	0.033	1014370	0.00	BB	4.9		0
4	Tricaprin (S2)	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	Diolain	13.7652	22.077	0.014	304575	0.00	VB	4.2		0
7	Triolein	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).

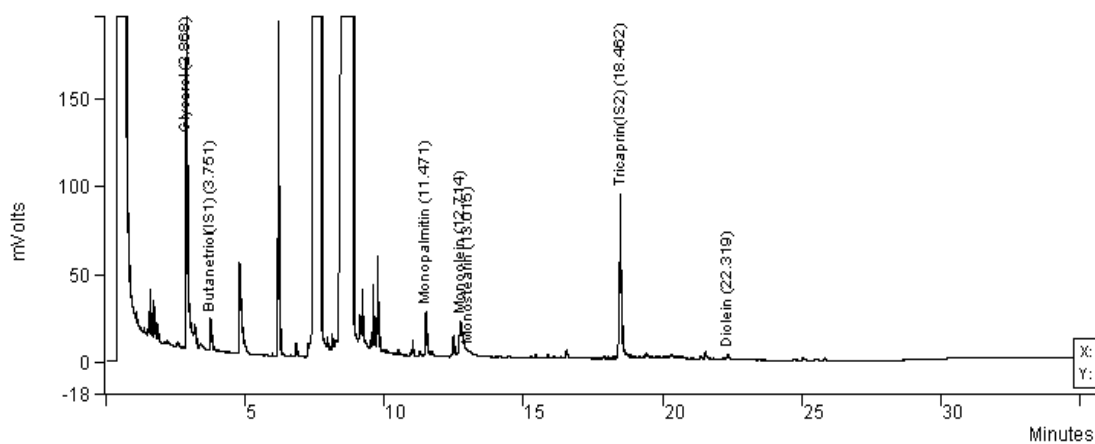
Data File: c:\star\joe\std4.2_5;29;02 pm.run
 Channel: Front = FID RESULTS
 Sample ID: std4.2
 Operator (Inj): io
 Injection Date: 26/2/2010 17:29:02
 Injection Method: c:\star\en14105.mth
 Run Time (min): 35.775
 Workstation:
 Instrument (Inj): gc

Operator (Calc): jo
 Calc Date: 26/03/2010 17:29:49
 Times Calculated: 4
 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



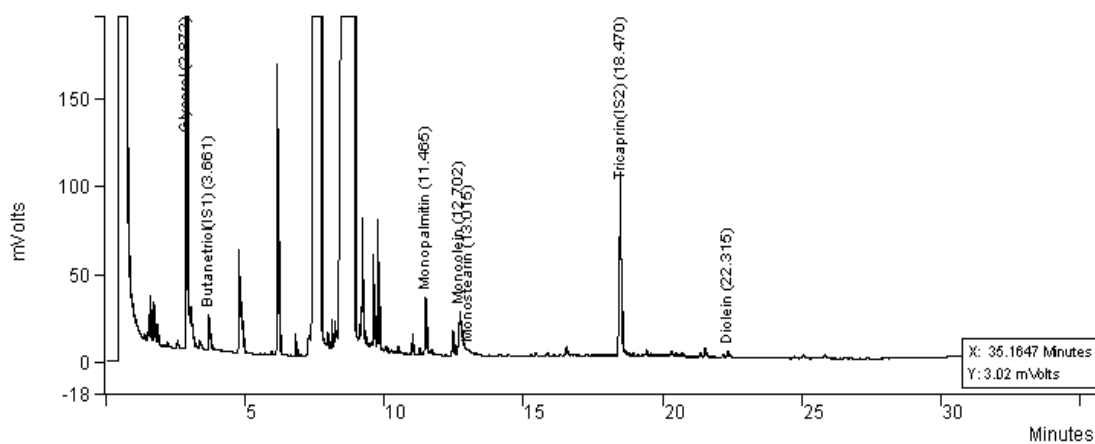
Peak No	Peak Name	Result (%)	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.6985	2.694	-0.041	81836	0.00	BB	2.5		0
2	Butanetriol (IS1)	4.6654	3.361	-0.006	103228	0.00	BB	2.5		0
3	Monoolein	45.9462	12.422	0.021	1016626	0.00	BB	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	Diolain	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).



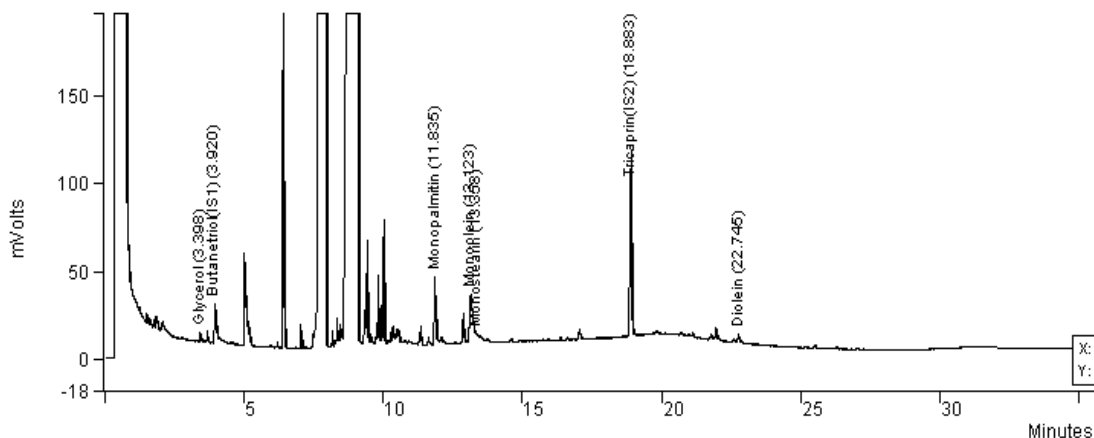
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	43.7533	2.868	-0.082	866835	0.00	BB	1.9		0
2	Butanetriol(IS1)	4.1596	3.751	-0.001	82409	0.00	GR	0.0		0
3	Monopalmitin	5.3476	11.471	-0.070	105947	0.00	BV	3.5		0
4	Monoolein	10.5532	12.714	-0.022	209078	0.00	VV	8.1		0
5	Monostearin	1.3941	13.015	-0.078	27620	0.00	VB	5.7		0
6	Tricaprin(IS2)	22.4935	18.462	-0.030	445638	0.00	VP	3.5		0
7	Diolein	0.9415	22.319	-0.005	18653	0.00	GR	0.0		0
Totals		88.6428		-0.286	1756180					

Figure A9 GC chromatogram of unwashed biodiesel (1).



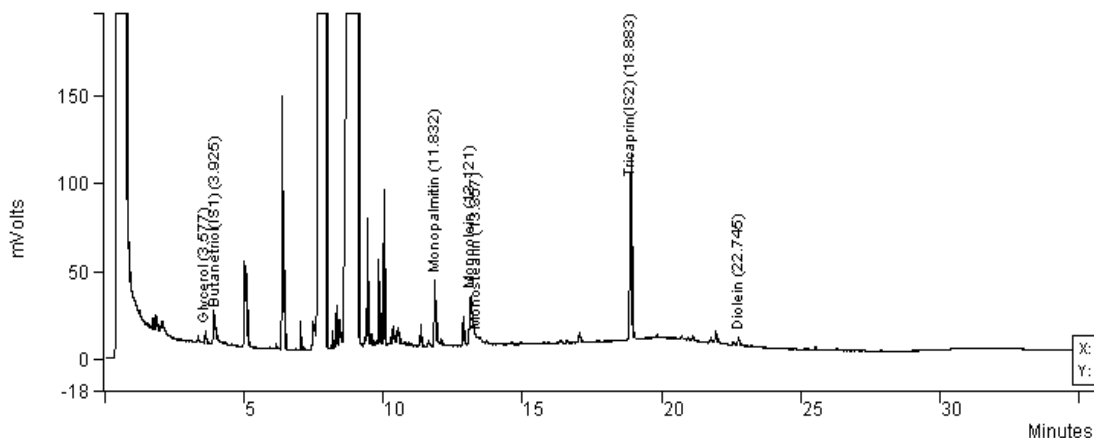
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	43.0436	2.872	0.022	1096384	0.00	GR	0.0		0
2	Butanetriol(IS1)	4.5588	3.661	0.001	106614	0.00	BB	4.6		0
3	Monopalmitin	5.4635	11.465	-0.076	136499	0.00	BB	3.2		0
4	Monoolein	9.9892	12.702	-0.034	233611	0.00	VV	7.1		0
5	Monostearin	1.3432	13.015	-0.078	32405	0.00	VB	5.6		0
6	Tricaprin(IS2)	22.5466	18.470	-0.022	527283	0.00	PP	4.4		0
7	Diolein	0.8911	22.315	-0.009	21014	0.00	GR	0.0		0
Totals		87.8360		-0.196	2153810					

Figure A10 GC chromatogram of unwashed biodiesel (2).



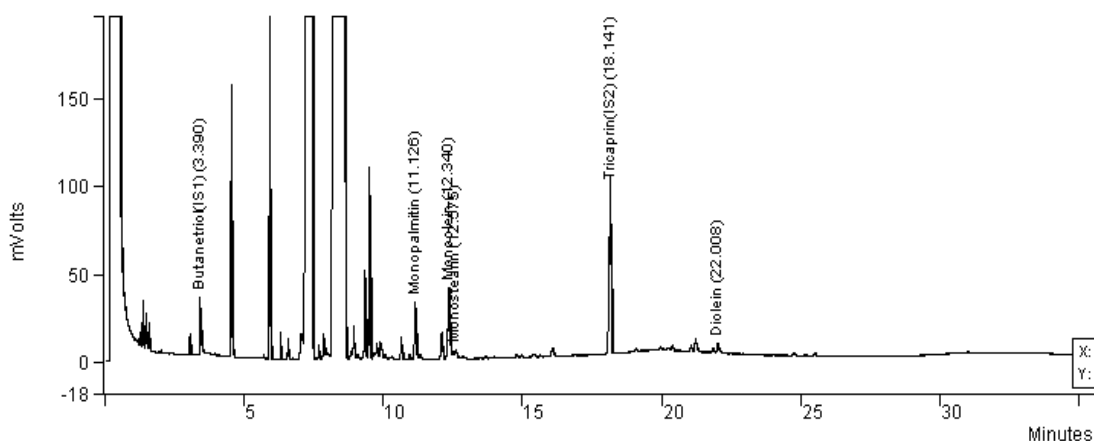
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.2777	3.398	-0.063	15278	0.00	BB	2.4		0
2	Butanetriol(IS1)	10.7500	3.920	0.000	128543	0.00	BB	4.9		0
3	Monopalmitin	11.8717	11.835	-0.094	136772	0.00	PB	3.4		0
4	Monoolein	19.1260	13.123	-0.050	200535	0.00	VV	7.2		0
5	Monostearin	1.8313	13.358	0.008	21898	0.00	VV	0.0		0
6	Tricaprin(IS2)	38.3012	18.883	-0.084	457987	0.00	GR	0.0		0
7	Diolein	1.9548	22.745	-0.062	21065	0.00	GR	0.0		0
Totals		85.1127		-0.345	982078					

Figure A11 GC chromatogram of biodiesel treated with 4% activated clay in the presence of methanol (1).



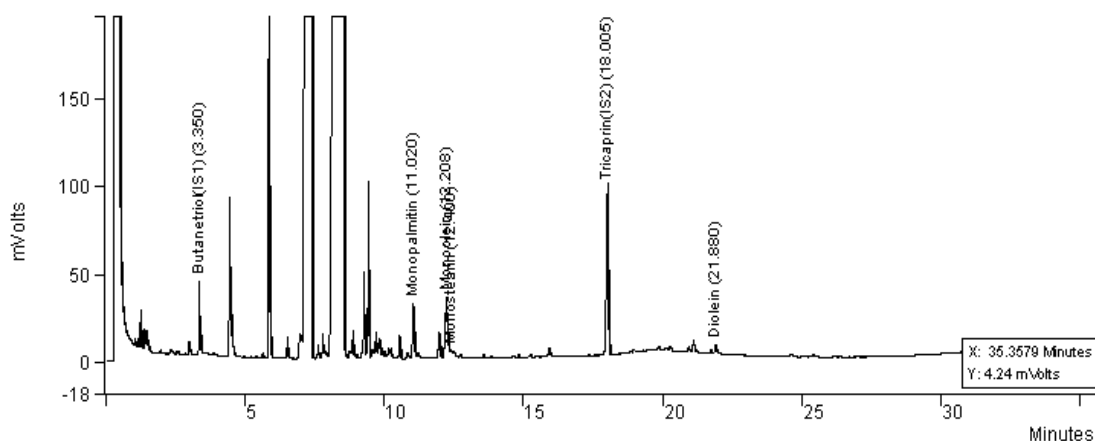
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.0122	3.577	0.115	12928	0.00	BV	1.9		0
2	Butanetriol(IS1)	8.4710	3.925	0.005	108197	0.00	GR	0.0		0
3	Monopalmitin	11.8795	11.832	-0.097	135394	0.00	PV	3.4		0
4	Monoolein	18.9855	13.121	-0.052	199326	0.00	VV	7.0		0
5	Monostearin	1.6507	13.357	0.007	21083	0.00	VV	5.6		0
6	Tricaprin(IS2)	35.6011	18.883	-0.084	454717	0.00	GR	0.0		0
7	Diolein	2.0280	22.745	-0.062	23406	0.00	GR	0.0		0
Totals		79.6280		-0.168	955051					

Figure A12 GC chromatogram of biodiesel treated with 4% activated clay in the presence of methanol (2).



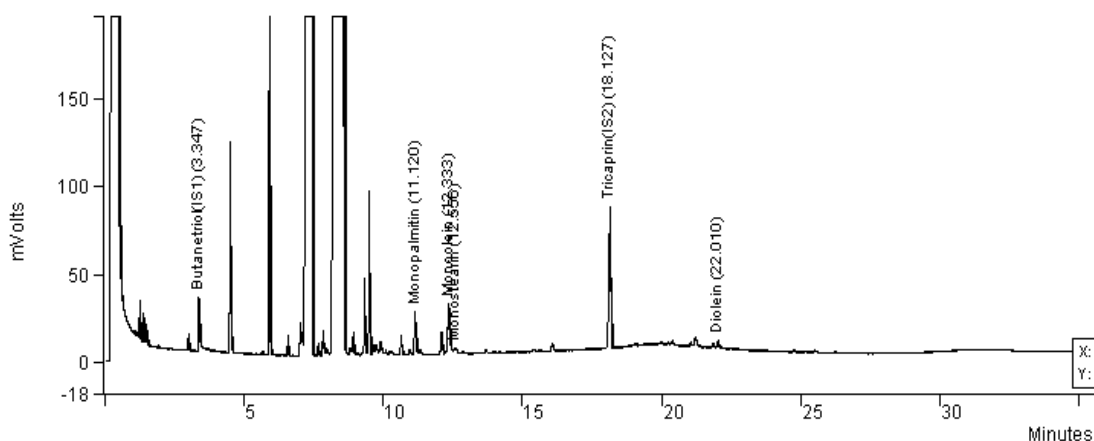
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	8.2776	3.390	-0.060	124050	0.00	BB	3.8		0
2	Monopalmitin	9.2984	11.126	-0.024	139349	0.00	BB	3.7		0
3	Monoolein	15.1436	12.340	-0.010	226946	0.00	VV	4.8		0
4	Monostearin	2.3347	12.575	-0.025	34988	0.00	VB	9.1		0
5	Tricaprin(IS2)	32.8256	18.141	0.011	491933	0.00	BB	4.6		0
6	Diolein	1.4238	22.008	0.008	21337	0.00	PB	3.8		0
Totals		69.3037		-0.100	1038603					

Figure A13 GC chromatogram of biodiesel treated with 4% activated clay after the removal of methanol (1).



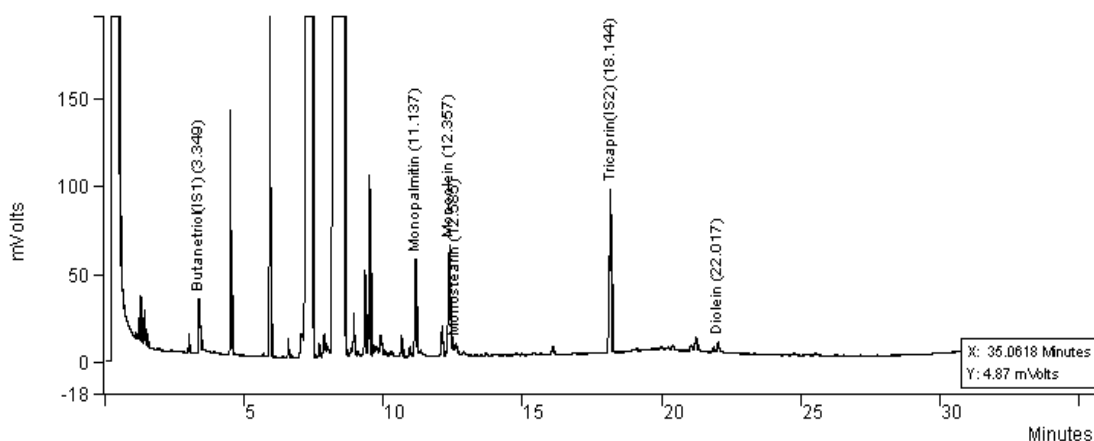
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	7.9351	3.350	-0.100	115419	0.00	GR	0.0		0
2	Monopalmitin	8.5123	11.020	-0.130	123815	0.00	BB	3.8		0
3	Monoolein	15.3168	12.208	-0.022	222790	0.00	VV	5.4		0
4	Monostearin	1.1867	12.400	-0.000	17261	0.00	VV	0.0		0
5	Tricaprin(IS2)	33.1381	18.005	-0.195	482009	0.00	PB	4.6		0
6	Diolein	1.3367	21.880	-0.020	19443	0.00	GR	0.0		0
Totals		67.4257		-0.467	980737					

Figure A14 GC chromatogram of biodiesel treated with 4% activated clay after the removal of methanol (2).



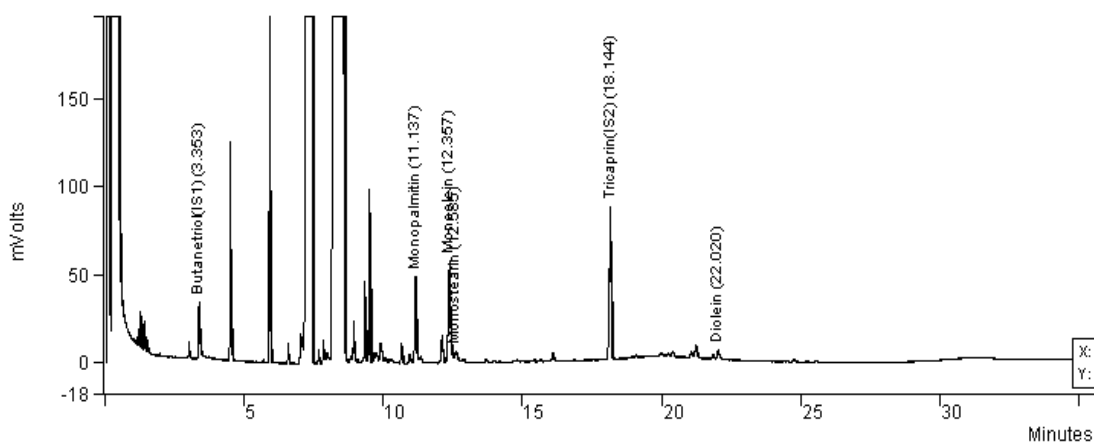
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	10.2488	3.347	-0.103	130960	0.00	VB	3.2		0
2	Monopalmitin	8.0739	11.120	-0.030	103169	0.00	BP	3.6		0
3	Monoolein	12.5001	12.333	-0.017	159728	0.00	VV	4.8		0
4	Monostearin	0.8663	12.556	0.006	11069	0.00	VV	0.0		0
5	Tricaprin(IS2)	30.7791	18.127	-0.023	393300	0.00	GR	0.0		0
6	Diolein	2.0893	22.010	0.010	18462	0.00	VP	4.0		0
Totals		64.5575		-0.157	816688					

Figure A15 GC chromatogram of water washing in the presence of methanol (1).



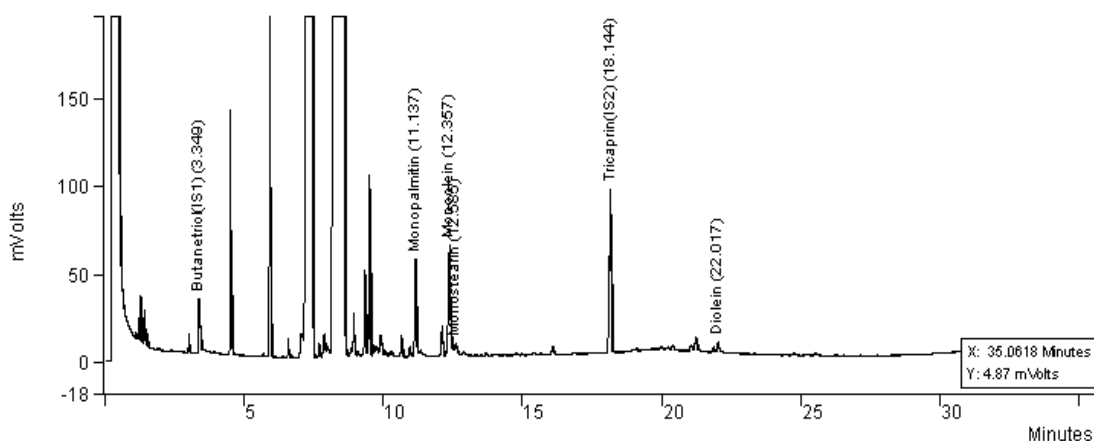
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	10.7142	3.349	-0.002	132409	0.00	VB	0.0		0
2	Monopalmitin	8.0595	11.137	-0.065	101478	0.00	BP	3.7		0
3	Monoolein	12.8154	12.357	-0.042	162775	0.00	VV	7.5		0
4	Monostearin	0.9720	12.585	-0.130	13420	0.00	VV	0.0		0
5	Tricaprin(IS2)	30.9548	18.144	-0.005	396158	0.00	GR	5.0		0
6	Diolein	2.0993	22.017	-0.030	20165	0.00	VP	4.8		0
Totals		65.5632		-0.274	826405					

Figure A16 GC chromatogram of water washing in the presence of methanol (2).



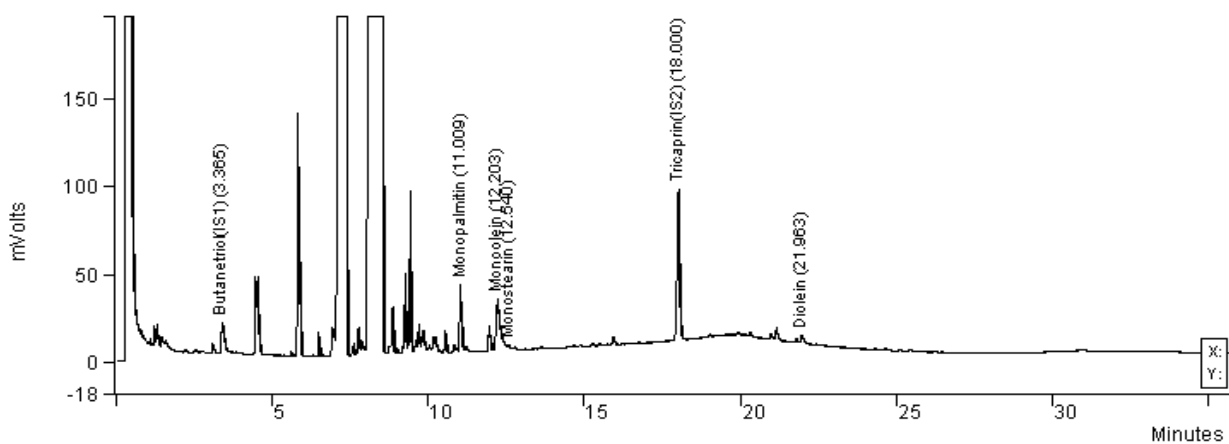
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	8.2627	3.353	0.002	104526	0.00	BB	3.2		0
2	Monopalmitin	16.0769	11.137	-0.065	203377	0.00	VB	3.6		0
3	Monoolein	24.9900	12.357	-0.042	316130	0.00	VV	4.7		0
4	Monostearin	3.5084	12.585	-0.130	44382	0.00	VP	8.0		0
5	Tricaprin(IS2)	32.3203	18.144	-0.005	408861	0.00	BP	4.4		0
6	Diolein	1.7025	22.020	-0.027	21535	0.00	PB	3.8		0
Totals		86.8608		-0.267	1098811					

Figure A17 GC chromatogram of biodiesel heating at 80°C for 2 h (1).



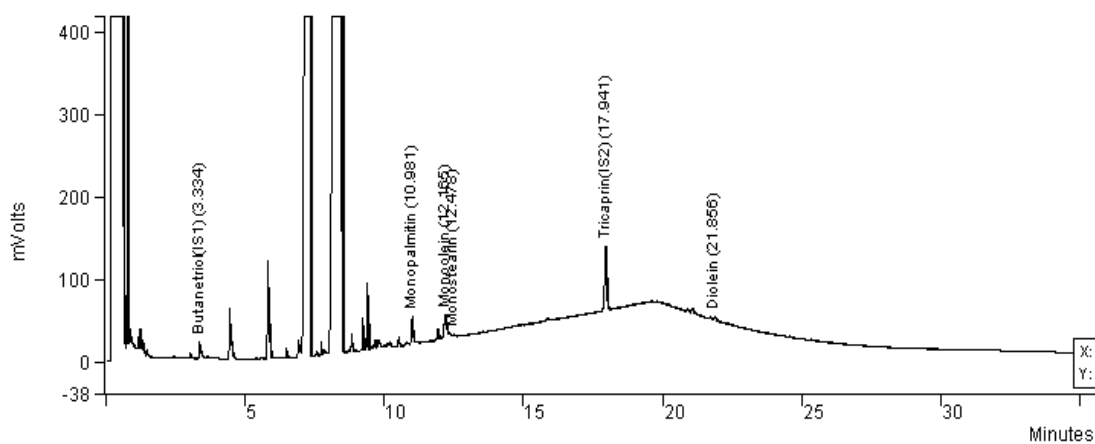
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	8.2783	3.349	-0.002	115029	0.00	BB	4.1		0
2	Monopalmitin	16.3203	11.137	-0.065	226773	0.00	PB	3.6		0
3	Monoolein	24.8622	12.357	-0.042	345466	0.00	VV	4.7		0
4	Monostearin	3.4353	12.585	-0.130	47734	0.00	VP	7.3		0
5	Tricaprin(IS2)	32.5623	18.144	-0.005	452460	0.00	BP	4.5		0
6	Diolein	1.7117	22.017	-0.030	23784	0.00	PB	3.8		0
Totals		87.1701		-0.274	1211246					

Figure A18 GC chromatogram of biodiesel heating at 80°C for 2 h (2).



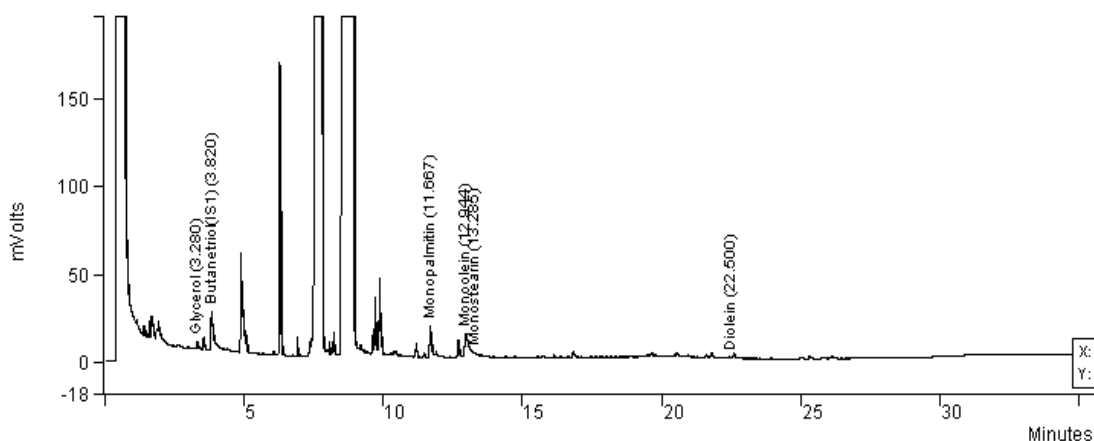
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	10.0312	3.365	0.014	116833	0.00	GR	0.0		0
2	Monopalmitin	12.8491	11.009	0.022	149653	0.00	BB	3.7		0
3	Monoolein	23.1131	12.203	0.003	202370	0.00	VV	7.5		0
4	Monostearin	1.4578	12.540	0.085	16979	0.00	VB	0.0		0
5	Tricaprin(IS2)	40.9839	18.000	0.078	477338	0.00	BB	5.0		0
6	Diolein	2.4672	21.963	0.063	23075	0.00	VB	4.8		0
Totals		90.9023		0.265	986248					

Figure A19 GC chromatogram of biodiesel evaporating at 50°C (1).



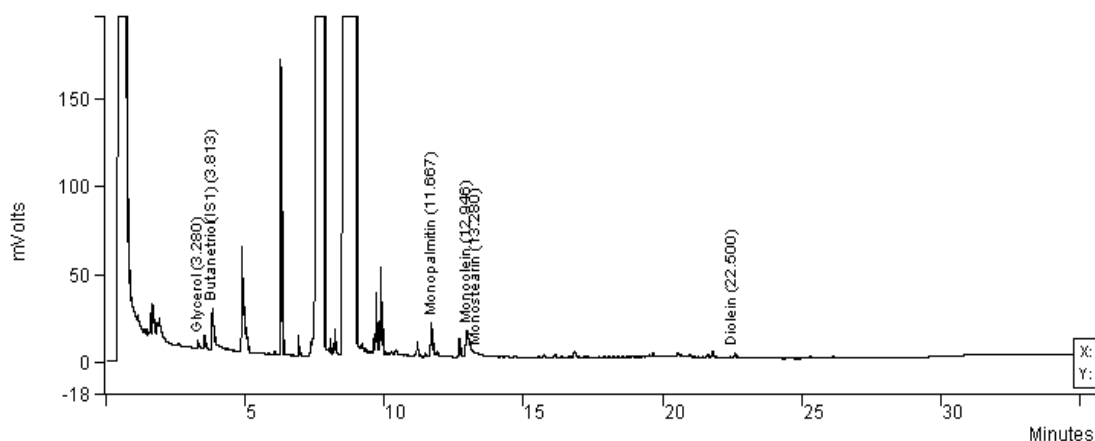
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	8.8823	3.334	-0.017	90357	0.00	BB	4.8		0
2	Monopalmitin	13.7650	10.981	-0.019	105903	0.00	VV	3.9		0
3	Monoolein	22.9250	12.165	0.015	200369	0.00	BV	6.7		0
4	Monostearin	2.1328	12.478	0.028	19871	0.00	VV	5.9		0
5	Tricaprin(IS2)	39.8766	17.941	-0.009	405651	0.00	VV	5.1		0
6	Diolein	1.6413	21.856	-0.191	16696	0.00	VB	2.1		0
Totals		89.2230		-0.193	838847					

Figure A20 GC chromatogram of biodiesel evaporating at 50°C (2).



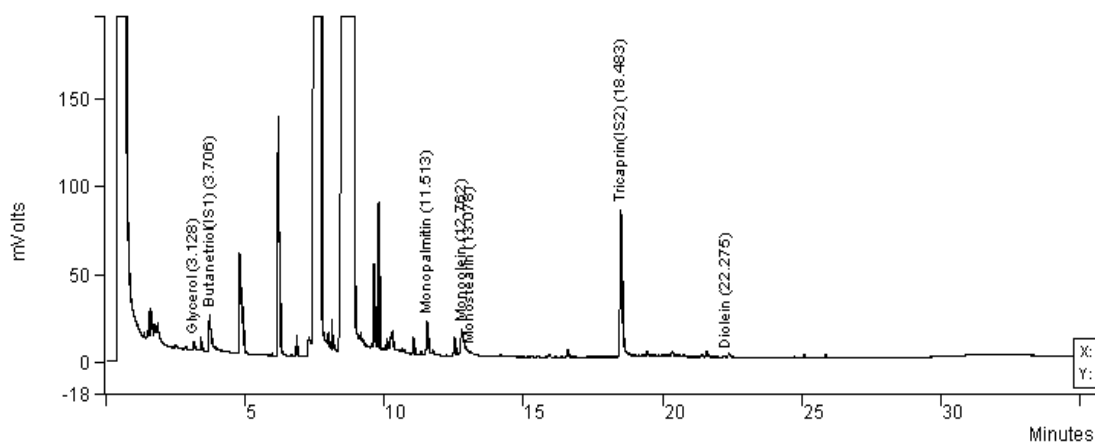
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	2.9412	3.280	0.030	16201	0.00	GR	0.0		0
2	Butanetro(IS1)	20.6705	3.820	-0.030	113856	0.00	VB	6.3		0
3	Monopalmitin	15.7373	11.667	0.017	95944	0.00	GR	0.0		0
4	Monoolein	27.5277	12.944	-0.175	170851	0.00	VV	9.1		0
5	Monostearin	3.1493	13.285	-0.065	19846	0.00	VV	5.7		0
6	Diolein	3.2315	22.500	0.000	20540	0.00	GR	0.0		0
Totals		73.2575		-0.223	437238					

Figure A21 GC chromatogram of biodiesel treated with 0.5% diatomite 1 min after the removal of methanol (1).



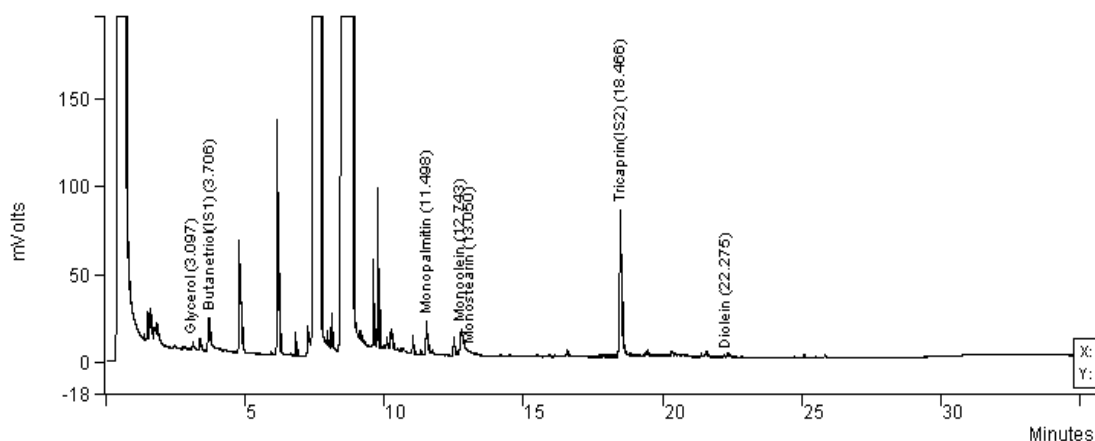
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	2.7647	3.280	0.030	15955	0.00	GR	0.0		0
2	Butanetriol(IS1)	22.2470	3.813	-0.037	128390	0.00	BV	4.6		0
3	Monopalmitin	15.7969	11.667	0.017	91165	0.00	GR	0.0		0
4	Monoolein	27.5313	12.946	-0.173	158887	0.00	VV	9.0		0
5	Monostearin	3.2925	13.280	-0.070	19001	0.00	VV	0.0		0
6	Diolein	3.1618	22.500	0.000	18247	0.00	GR	0.0		0
Totals		74.7943		-0.223	431645					

Figure A22 GC chromatogram of biodiesel treated with 0.5% diatomite 1 min after the removal of methanol (2).



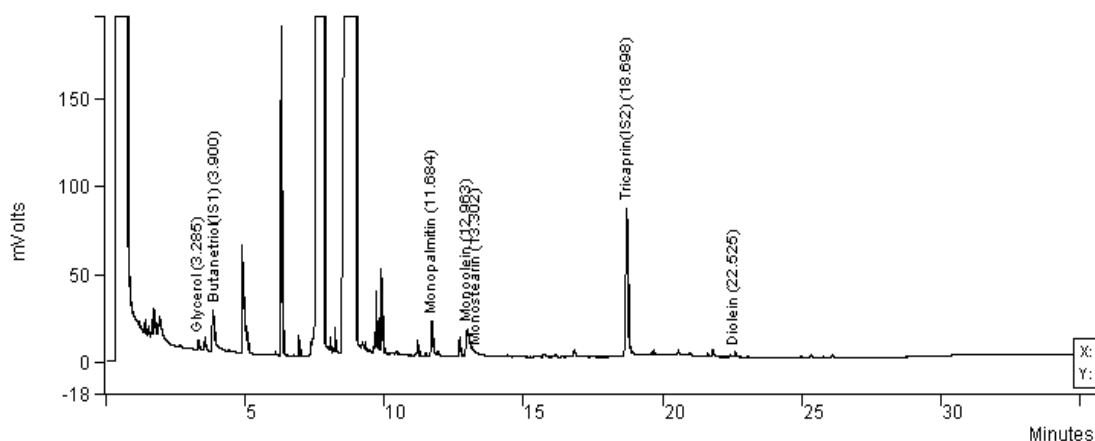
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.5242	3.128	0.051	16488	0.00	BB	3.0		0
2	Butanetriol(IS1)	12.8267	3.706	0.044	138747	0.00	GR	0.0		0
3	Monopalmitin	8.1442	11.513	-0.028	88096	0.00	VV	3.7		0
4	Monoolein	13.6598	12.762	0.026	147759	0.00	VV	7.5		0
5	Monostearin	1.9890	13.078	-0.015	21515	0.00	VB	5.1		0
6	Tricaprin(IS2)	43.6244	18.483	-0.009	471886	0.00	VP	4.4		0
7	Diolein	1.7031	22.275	-0.049	18423	0.00	GR	0.0		0
Totals		83.4714		-0.068	902914					

Figure A23 GC chromatogram of biodiesel treated with 0.5% diatomite 3 min after the removal of methanol (1).



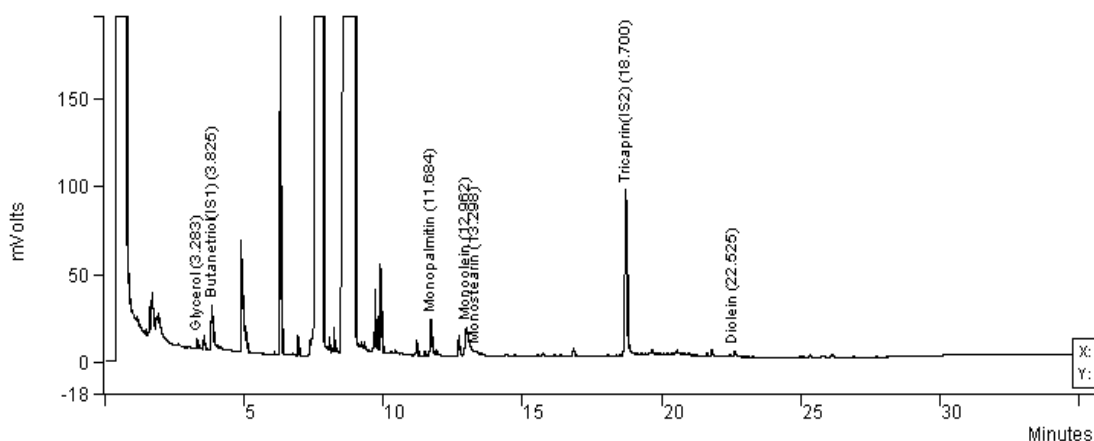
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.2424	3.097	0.020	14012	0.00	BV	3.1		0
2	Butanetriol(IS1)	11.2124	3.706	-0.044	126452	0.00	GR	0.0		0
3	Monopalmitin	7.3957	11.498	-0.043	83408	0.00	BB	3.7		0
4	Monoolein	12.9107	12.743	0.007	145605	0.00	VV	7.8		0
5	Monostearin	1.8410	13.050	-0.043	20763	0.00	VV	33.0		0
6	Tricaprin(IS2)	40.7509	18.466	-0.026	459585	0.00	VP	4.2		0
7	Diolein	1.7833	22.275	-0.049	20112	0.00	GR	0.0		0
Totals		77.1364		-0.178	869937					

Figure A24 GC chromatogram of biodiesel treated with 0.5% diatomite 3 min the removal of methanol (2).



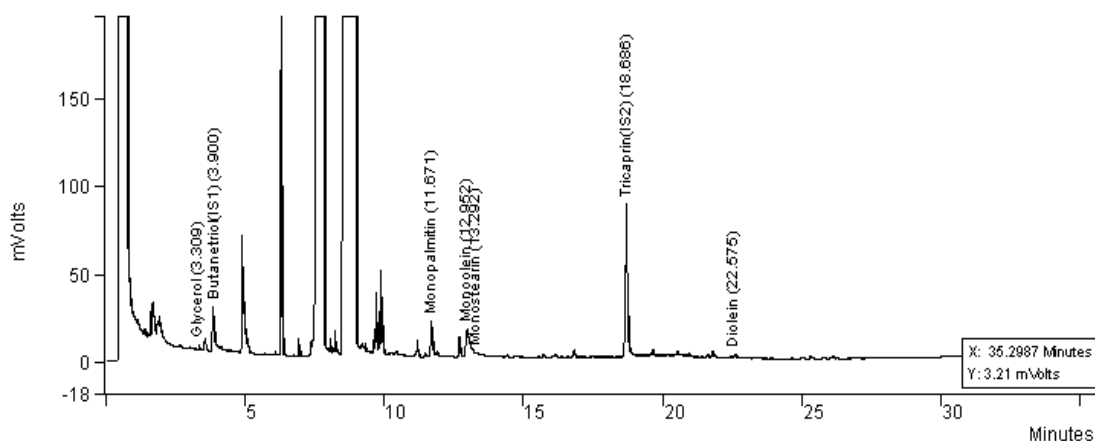
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.9188	3.285	-0.115	13476	0.00	BV	2.5		0
2	Butanetriol(IS1)	13.6413	3.900	0.045	141011	0.00	GR	0.0		0
3	Monopalmitin	9.2816	11.684	-0.005	95944	0.00	BV	4.0		0
4	Monoolein	16.5280	12.963	-0.026	170851	0.00	VV	9.0		0
5	Monostearin	1.9198	13.302	0.109	19846	0.00	VV	6.0		0
6	Tricaprin(IS2)	43.5775	18.698	-0.035	450464	0.00	BB	4.7		0
7	Diolein	2.1261	22.525	-0.071	20064	0.00	GR	0.0		0
Totals		88.9931		-0.098	911655					

Figure A25 GC chromatogram of biodiesel treated with 0.5% diatomite 5 min after the removal of methanol (1).



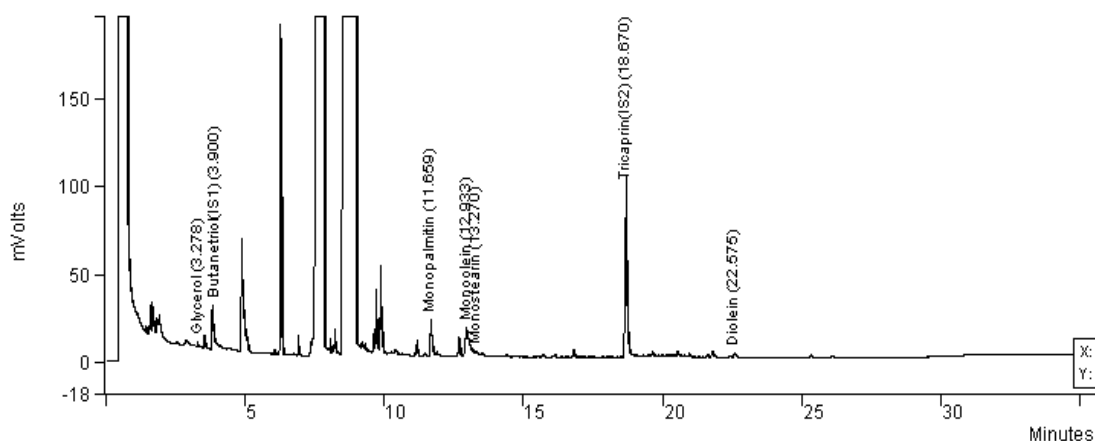
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.7962	3.283	-0.017	12805	0.00	BV	2.5		0
2	Butanetriol(IS1)	11.5060	3.825	0.025	125844	0.00	BV	4.2		0
3	Monopalmitin	9.0448	11.684	-0.005	98926	0.00	BV	4.0		0
4	Monoolein	15.9591	12.962	-0.027	174550	0.00	VV	8.8		0
5	Monostearin	1.8683	13.298	0.105	20434	0.00	VV	5.6		0
6	Tricaprin(IS2)	42.5033	18.700	-0.033	464871	0.00	VB	4.2		0
7	Diolein	1.7854	22.525	-0.071	19528	0.00	GR	0.0		0
Totals		84.4631		-0.023	916958					

Figure A26 GC chromatogram of biodiesel treated with 0.5% diatomite 5 min after the removal of methanol (2).



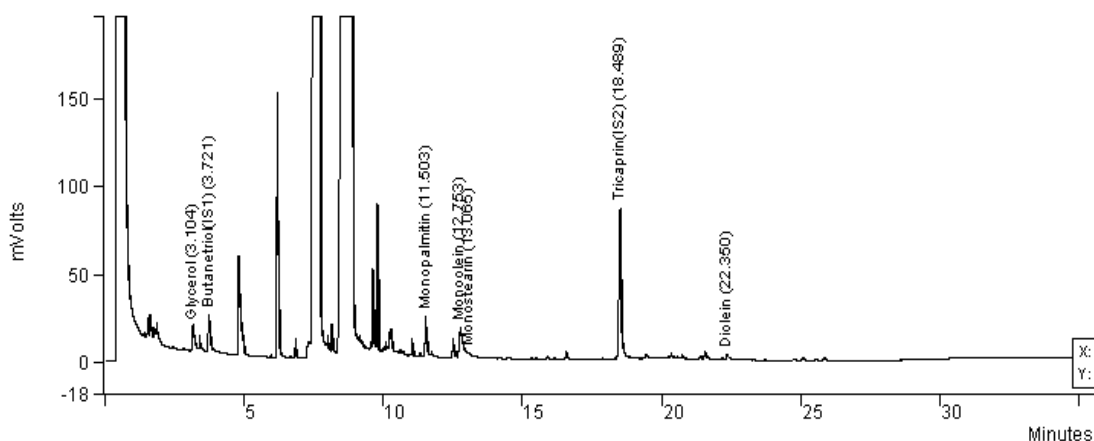
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	0.4376	3.309	-0.000	4469	0.00	BV	1.3		0
2	Butanetriol(IS1)	14.1268	3.900	0.045	144265	0.00	GR	0.0		0
3	Monopalmitin	9.4232	11.671	-0.018	96231	0.00	BV	4.1		0
4	Monoolein	16.7495	12.952	-0.037	171049	0.00	VV	9.1		0
5	Monostearin	1.9257	13.292	0.099	19666	0.00	VV	6.3		0
6	Tricaprin(IS2)	42.7649	18.686	-0.047	436722	0.00	PP	4.2		0
7	Diolein	2.1080	22.575	-0.021	21527	0.00	GR	0.0		0
Totals		87.5357		0.021	893929					

Figure A27 GC chromatogram of biodiesel treated with 0.5% diatomite 10 min after the removal of methanol (1).



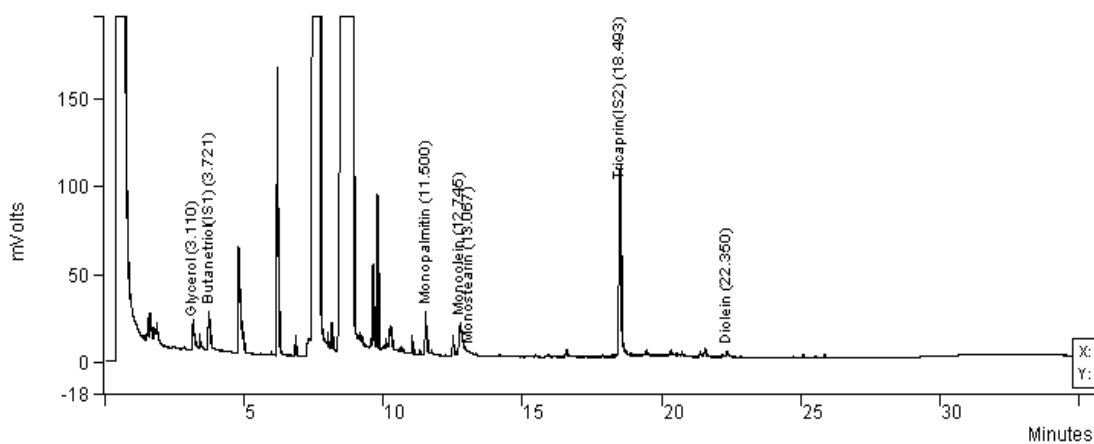
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	0.5189	3.278	-0.032	5604	0.00	PP	1.1		0
2	Butanetriol(IS1)	12.5151	3.900	0.045	135156	0.00	GR	0.0		0
3	Monopalmitin	9.0089	11.659	-0.030	97291	0.00	BV	4.0		0
4	Monoolein	16.0894	12.933	-0.056	173756	0.00	VV	8.8		0
5	Monostearin	1.9256	13.270	0.077	20796	0.00	VV	5.9		0
6	Tricaprin(IS2)	44.7804	18.670	-0.063	483602	0.00	BB	3.5		0
7	Diolein	2.1712	22.575	-0.021	23448	0.00	GR	0.0		0
Totals		87.0095		-0.080	939653					

Figure A28 GC chromatogram of biodiesel treated with 0.5% diatomite 10 min after the removal of methanol (2).



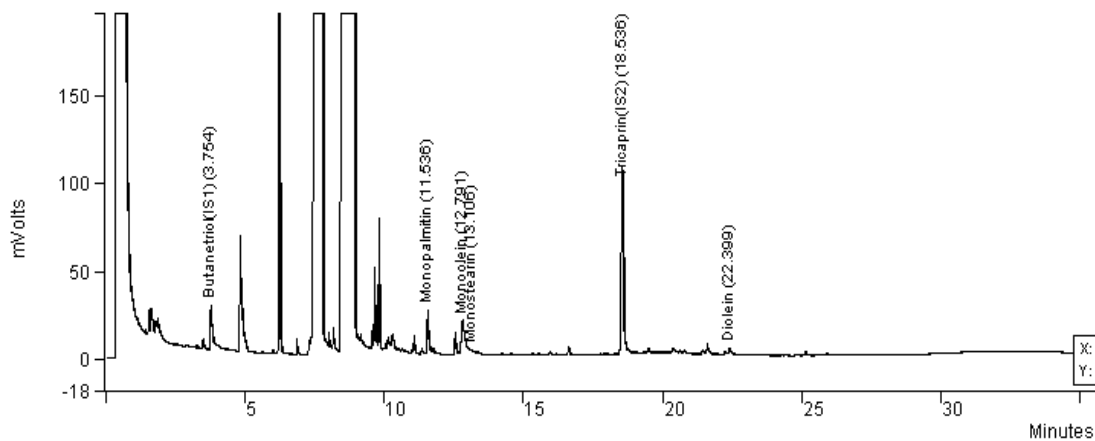
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.9908	3.104	0.027	24098	0.00	PV	2.6		0
2	Butanetriol(IS1)	10.0012	3.721	-0.029	121061	0.00	GR	0.0		0
3	Monopalmitin	8.1155	11.503	-0.038	98235	0.00	VV	3.5		0
4	Monoolein	14.2132	12.753	0.017	172045	0.00	VV	7.8		0
5	Monostearin	1.9655	13.065	-0.028	23791	0.00	VB	6.2		0
6	Tricaprin(IS2)	40.5999	18.489	-0.003	491448	0.00	PP	4.6		0
7	Diolein	2.2722	22.350	0.026	25410	0.00	GR	0.0		0
Totals		79.1583		-0.028	956088					

Figure A29 GC chromatogram of unwashed biodiesel after the removal of methanol (1).



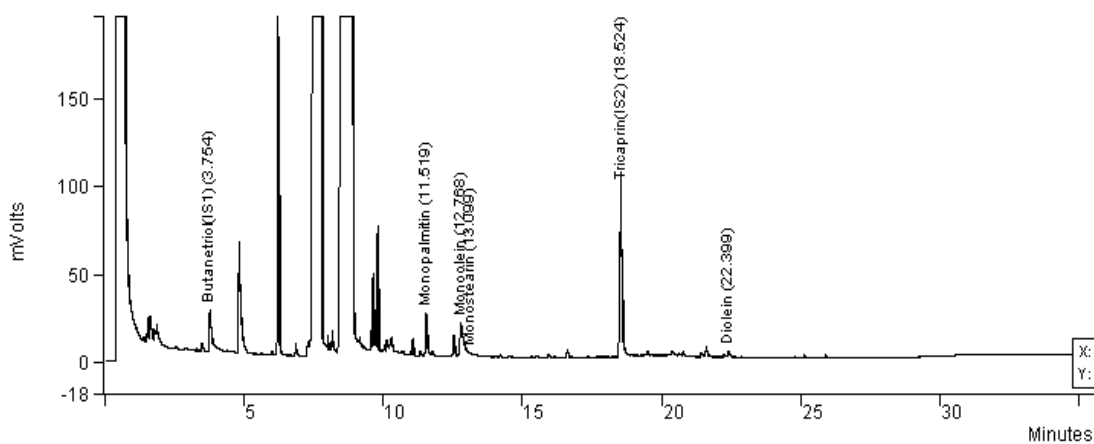
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.9196	3.110	0.033	24496	0.00	BV	2.8		0
2	Butanetriol(IS1)	9.2460	3.721	-0.029	117988	0.00	GR	0.0		0
3	Monopalmitin	7.3550	11.500	-0.041	93858	0.00	BB	3.4		0
4	Monoolein	14.0810	12.745	0.009	179688	0.00	VV	7.4		0
5	Monostearin	1.7696	13.067	-0.026	22560	0.00	VB	5.4		0
6	Tricaprin(IS2)	41.8112	18.493	0.001	533554	0.00	VP	3.7		0
7	Diolein	2.2860	22.350	0.026	28965	0.00	GR	0.0		0
Totals		78.4667		-0.027	1001109					

Figure A30 GC chromatogram of unwashed biodiesel after the removal of methanol (2).



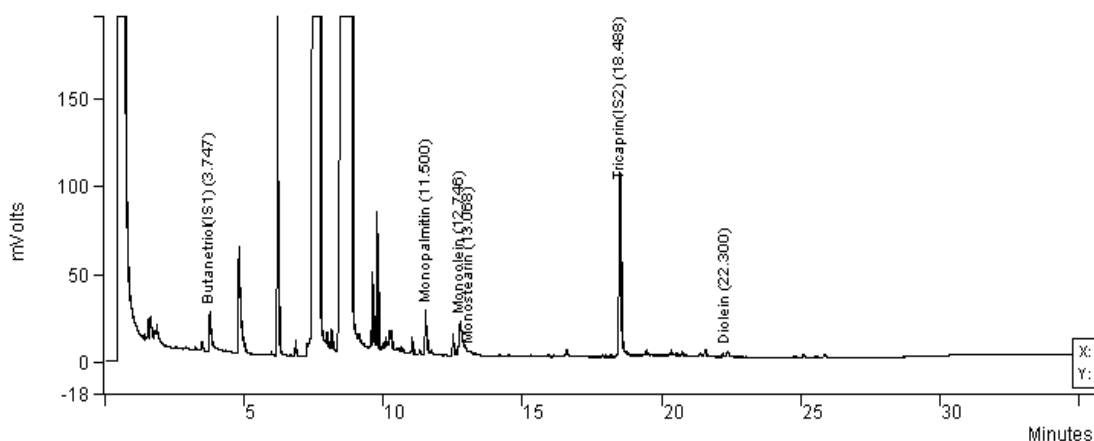
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	11.0546	3.754	-0.046	135064	0.00	GR	0.0		0
2	Monopalmitin	8.4265	11.536	-0.005	102953	0.00	BV	3.6		0
3	Monoolein	15.6759	12.791	0.055	191526	0.00	VV	7.8		0
4	Monostearin	1.7135	13.106	0.012	20935	0.00	VV	16.3		0
5	Tricaprin(IS2)	46.8735	18.536	0.044	572694	0.00	PP	4.6		0
6	Diolein	2.8517	22.399	-0.001	34841	0.00	GR	0.0		0
Totals		86.5957		0.059	1058013					

Figure A31 GC chromatogram of biodiesel treated with 1% activated clay after the removal of methanol (1).



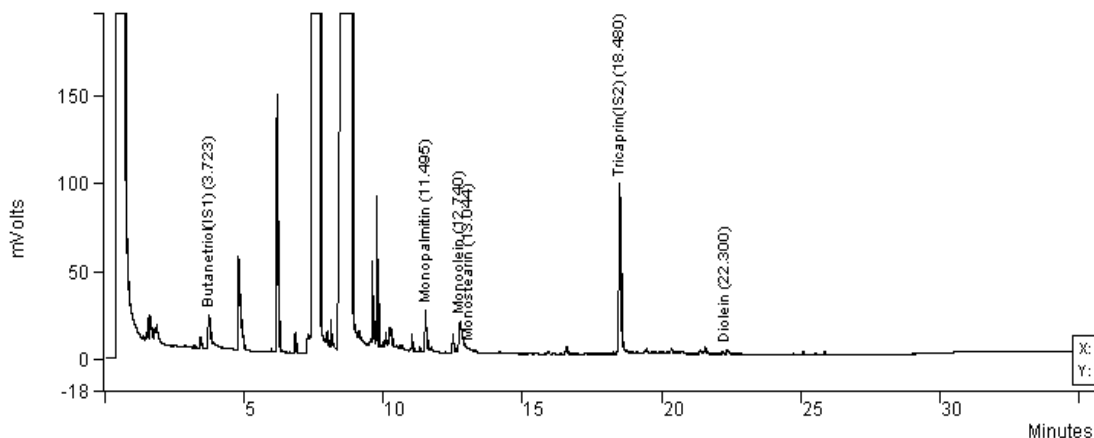
Peak NO	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	10.5093	3.754	-0.046	127542	0.00	GR	0.0		0
2	Monopalmitin	8.2422	11.519	-0.022	100028	0.00	BV	3.5		0
3	Monoolein	15.3725	12.768	0.032	186561	0.00	VV	8.0		0
4	Monostearin	1.5449	13.099	0.006	18750	0.00	VV	19.3		0
5	Tricaprin(IS2)	46.2199	18.524	0.032	560928	0.00	VP	4.6		0
6	Diolein	2.2236	22.399	-0.001	26986	0.00	GR	0.0		0
Totals		84.1124		0.001	1020795					

Figure A32 GC chromatogram of biodiesel treated with 1% activated clay after the removal of methanol (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)	9.1235	3.747	-0.003	105730	0.00	VB	5.7		0
2	Monopalmitin	8.4333	11.500	-0.041	97732	0.00	BB	3.5		0
3	Monoolein	16.0513	12.746	0.010	186015	0.00	VV	7.4		0
4	Monostearin	2.2691	13.068	-0.025	26297	0.00	VB	5.5		0
5	Tricaprin(IS2)	43.6348	18.488	-0.004	505675	0.00	VP	3.6		0
6	Diolein	2.4879	22.300	-0.024	28832	0.00	GR	0.0		0
Totals		81.9999		-0.087	950281					

Figure A33 GC chromatogram of water washing biodiesel after the removal of methanol (1).



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)	7.3551	3.723	-0.027	83226	0.00	VV	6.2		0
2	Monopalmitin	8.8605	11.495	-0.046	100261	0.00	VV	3.6		0
3	Monoolein	15.4609	12.740	0.004	174947	0.00	VV	7.6		0
4	Monostearin	1.8286	13.044	-0.049	20692	0.00	VV	12.6		0
5	Tricaprin(IS2)	41.2797	18.480	-0.012	467097	0.00	VP	3.6		0
6	Diolein	2.3503	22.300	-0.024	26598	0.00	GR	0.0		0
Totals		77.1351		0.0154	872821					

Figure A34 GC chromatogram of water washing biodiesel after the removal of methanol (2).

APPENDIX B

CALCULATIONS

Appendix B

CALCULATIONS

1. Calculation of soap content

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

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

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 adsorbents in the presence of methanol at various contact time.

Contact time	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before purified	1	5.00	7.40	4369.97	4384.73
	2	5.00	7.45	4399.49	
Activated Charcoal					
5 min	1	5.00	4.35	2568.83	2595.74
	2	5.01	4.45	2622.64	
10 min	1	5.02	4.20	2470.37	2492.27
	2	5.05	4.30	2514.16	
20 min	1	5.01	3.95	2327.96	2306.39
	2	5.04	3.90	2284.81	
30 min	1	5.00	3.95	2332.62	2303.09
	2	5.00	3.85	2273.56	

Contact time	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Activated Clay					
5 min	1	5.03	1.25	733.77	764.70
	2	5.01	1.35	795.63	
10 min	1	5.00	0.75	442.90	424.88
	2	5.08	0.70	406.87	
20 min	1	5.02	0.65	382.32	368.32
	2	5.00	0.60	354.32	
30 min	1	5.00	0.65	383.85	353.35
	2	5.03	0.55	322.86	
Bentonite					
5 min	1	5.00	2.85	1683.03	1697.79
	2	5.00	2.90	1712.55	
10 min	1	5.05	1.65	964.74	937.30
	2	5.03	1.55	909.87	
20 min	1	5.02	1.65	970.50	922.90
	2	5.06	1.50	875.30	
30 min	1	5.01	1.60	942.97	911.75
	2	5.03	1.50	880.52	
Diatomite					
5 min	1	4.98	3.00	1778.72	1813.91
	2	5.03	3.15	1849.09	
10 min	1	5.08	2.35	1365.91	1362.07
	2	5.00	2.30	1358.23	
20 min	1	5.00	2.35	1387.76	1414.40
	2	5.02	2.45	1441.05	
30 min	1	5.00	2.15	1269.65	1246.33
	2	5.07	2.10	1223.00	

Table B2 Soap content of biodiesel treated with adsorbents in the presence of methanol at various amount of adsorbents.

% wt adsorbent	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	
Activated Charcoal					
1 %	1	5.00	5.25	2902.74	2891.79
	2	5.00	5.20	2880.84	
2 %	1	5.03	4.65	2560.77	2549.53
	2	5.02	4.60	2538.28	
3 %	1	5.00	4.15	2299.13	2310.58
	2	5.07	4.25	2322.03	
4 %	1	5.02	4.00	2207.20	2197.77
	2	5.00	3.95	2188.33	
5 %	1	5.01	3.55	1962.80	1935.16
	2	5.01	3.45	1907.51	
Activated Clay					
1 %	1	5.01	3.00	1658.71	1617.24
	2	5.01	2.85	1575.77	
2 %	1	5.00	2.40	1329.62	1357.32
	2	5.00	2.50	1385.02	
3 %	1	5.00	2.05	1135.72	1095.22
	2	4.99	1.90	1054.72	
4%	1	5.03	1.25	688.38	664.02
	2	4.98	1.15	639.67	
5%	1	5.01	0.9	497.61	469.97
	2	5.01	0.80	442.32	

% wt adsorbent	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Bentonite					
1 %	1	5.03	3.45	1899.93	1915.94
	2	5.09	3.55	1931.95	
2 %	1	5.01	2.50	1382.26	1354.61
	2	5.01	2.40	1326.97	
3 %	1	5.00	2.20	1218.82	1246.52
	2	5.00	2.30	1274.22	
4 %	1	4.98	1.90	1056.84	1026.03
	2	5.01	1.80	995.22	
5 %	1	5.00	1.00	554.01	595.56
	2	5.00	1.15	637.11	
Diatomite					
1 %	1	5.02	4.80	2648.64	2670.87
	2	5.04	4.90	2693.09	
2 %	1	5.00	4.50	2493.04	2465.34
	2	5.00	4.40	2437.64	
3 %	1	5.01	4.25	2349.83	2315.19
	2	4.98	4.10	2280.56	
4%	1	5.03	3.35	1844.86	1808.84
	2	5.00	3.20	1772.83	
5%	1	5.00	3.00	1662.02	1632.72
	2	5.01	2.90	1603.42	

Table B3 Soap content of biodiesel treated with 4% wt of activated clay at various methanol to oil ratio.

Ratio	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
RATIO 6:1					
Before purification	1	5.00	7.40	4369.97	4384.73
	2	5.00	7.45	4399.49	
6:1	1	5.00	0.75	442.90	424.88
	2	5.08	0.70	406.87	
RATIO 9:1					
Before purification	1	5.01	13.35	7705.69	7742.32
	2	5.00	13.45	7778.94	
9:1	1	5.03	3.50	2012.19	2018.12
	2	5.00	3.50	2024.26	
RATIO 12:1					
Before purification	1	5.03	19.30	11095.77	11085.68
	2	5.00	19.15	11075.59	
12:1	1	5.00	12.55	7258.42	7229.50
	2	5.00	12.45	7200.58	

Table B4 Soap content of biodiesel treated with adsorbents after methanol removal at various amount of adsorbents.

% wt adsorbent	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before purification	1	10.00	4.30	1204.21	1204.21
	2	10.00	4.30	1204.21	
Activated Charcoal					
0.1 %	1	10.01	0.45	125.90	118.79
	2	10.03	0.40	111.68	
0.5 %	1	10.02	0.35	97.82	90.88
	2	10.01	0.30	83.93	
0.8 %	1	10.00	0.20	56.01	63.01
	2	10.00	0.25	70.01	
1 %	1	10.02	0.15	41.92	41.86
	2	10.05	0.15	41.80	
Activated Clay					
0.1 %	1	10.13	0.30	82.94	90.04
	2	10.09	0.35	97.14	
0.5 %	1	10.10	0.05	13.86	20.86
	2	10.05	0.10	27.87	
0.8 %	1	10.01	0.05	13.99	14.00
	2	10.00	0.05	14.00	
1%	1	10.00	0.05	14.00	13.99
	2	10.02	0.05	13.97	

% wt adsorbent	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Bentonite					
0.1 %	1	10.01	0.45	125.90	125.96
	2	10.00	0.45	126.02	
0.5 %	1	10.09	0.25	69.39	62.61
	2	10.03	0.20	55.84	
0.8 %	1	10.07	0.20	55.62	48.79
	2	10.01	0.15	41.97	
1 %	1	10.00	0.10	28.00	28.00
	2	10.00	0.10	28.00	
Diatomite					
0.1 %	1	11.00	0.50	127.29	126.34
	2	10.05	0.45	125.39	
0.5 %	1	10.02	0.30	83.85	83.89
	2	10.01	0.30	83.93	
0.8 %	1	10.05	0.25	69.66	62.84
	2	10.00	0.20	56.01	
1%	1	10.00	0.15	42.01	41.94
	2	10.03	0.15	41.88	

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

2.1 Free Glycerol

Table B5 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 B6 Calculation of glycerol calibration function (continued).

X	Y	X^2	Y^2	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
$\Sigma X = 3.576$	$\Sigma Y = 2.750$	$\Sigma X^2 = 2.113$	$\Sigma Y^2 = 1.297$	$\Sigma XY = 1.654$

$$(\Sigma X)^2 = 12.787 \quad (\Sigma Y)^2 = 7.563 \quad N = \text{number of measure} = 8$$

From obtained data can calculate:

$$a_g = \frac{(N \times \Sigma XY) - (\Sigma X \times \Sigma Y)}{(N \times \Sigma X^2) - (\Sigma X)^2} = \frac{(8 \times 1.654) - (3.576 \times 2.750)}{(8 \times 2.113) - 12.787} = 0.8264$$

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

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 B7 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 B8 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
$\Sigma X = 11.007$	$\Sigma Y = 7.625$	$\Sigma X^2 = 18.707$	$\Sigma Y^2 = 9.023$	$\Sigma XY = 12.992$

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

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

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

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

2.3 Diglyceride

Table B9 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 B10 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
$\Sigma X = 3.019$	$\Sigma Y = 2.750$	$\Sigma X^2 = 1.529$	$\Sigma Y^2 = 1.297$	$\Sigma XY = 1.408$

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

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

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

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

2.4 Triglyceride

Table B11 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 B12 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
$\Sigma X = 2.296$	$\Sigma Y = 2.250$	$\Sigma X^2 = 0.889$	$\Sigma Y^2 = 0.859$	$\Sigma XY = 0.874$

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

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

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

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

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:

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

Where:	G	= percentage (m/m) of free glycerol
	A_g	= peak area of the glycerol
	A_{ei1}	= peak area of internal standard No. 1
	M_{ei1}	= 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:

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

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

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

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 B13 The percentage of free glycerol of biodiesel.

Samples		Peak area (Sample)	Peak area (IS1)	Weight of sample (mg)	%Free	Average	SD
Unwashed biodiesel	1	866835	82409	100.3	0.6913	0.6835	0.0110
	2	1096384	106614	100.3	0.6758		
4% activated clay	1	15278	128543	100.1	0.0058	0.0058	0.0000
	2	12928	108197	100.1	0.0058		
4% activated clay demeth	1	-	124050	100.2	-	-	-
	2	-	115419	100.2	-		
Water Washing	1	-	130960	99.9	-	-	-
	2	-	132409	99.9	-		
Heat 80°C 2 h	1	-	104526	100.1	-	-	-
	2	-	115029	100.1	-		
Evaporated at 50°C	1	-	116833	100.2	-	-	-
	2	-	90357	100.2	-		
0.5% diatomite 1 min	1	16201	113856	100.0	0.0074	0.0068	0.0008
	2	15955	128390	100.0	0.0062		
0.5% diatomite 3 min	1	16488	138747	100.6	0.0058	0.0055	0.0004
	2	14012	126452	100.6	0.0052		
0.5% diatomite 5 min	1	13476	141011	99.9	0.0043	0.0045	0.0003
	2	12805	125844	99.9	0.0047		

Samples		Peak area (Sample)	Peak area (IS1)	Weight of sample (mg)	%Free	Average	SD
0.5% diatomite 10 min	1	4469	144265	100.0	0.0000	0.0003	0.0005
	2	5604	135156	100.0	0.0007		
Before adsorption demeth	1	24098	121061	100.7	0.0110	0.0113	0.0004
	2	24496	117988	100.7	0.0116		
1%wt activated clay demeth	1	-	135064	100.3	-	-	-
	2	-	127542	100.3	-		
Water washing demeth	1	-	105730	100.5	-	-	-
	2	-	83226	100.5	-		

Table B14 The percentage of monoglyceride of biodiesel.

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Mono	Average	SD
Unwashed biodiesel	1	342645	445638	100.3	0.4203	0.4187	0.0022
	2	402515	527283	100.3	0.4172		
4% activated clay	1	359205	457987	100.1	0.4297	0.4292	0.0052
	2	355803	454717	100.1	0.4287		
4% activated clay demeth	1	401283	491933	100.2	0.4469	0.4299	0.0241
	2	363866	482009	100.2	0.4128		
Water Washing	1	273966	393300	99.9	0.3789	0.3813	0.0028
	2	277673	396158	99.9	0.3837		
Heat 80°C 2 h	1	563889	408861	100.1	0.7636	0.7610	0.0035
	2	619973	452460	100.1	0.7585		
Evaporated at 50°C	1	326143	405651	100.2	0.4404	0.4317	0.0123
	2	369002	477338	100.2	0.4230		
0.5% diatomite 1 min	1	255656	455980	100.0	0.3046	0.3125	0.0113
	2	269053	456702	100.0	0.3205		

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Mono	Average	SD
0.5% diatomite 3 min	1	275050	471886	100.6	0.3151	0.3183	0.0045
	2	273086	459585	100.6	0.3215		
0.5% diatomite 5 min	1	286641	450464	99.9	0.3474	0.3462	0.0016
	2	293910	464871	99.9	0.3451		
0.5% diatomite 10 min	1	286946	435722	100.0	0.3595	0.3441	0.0219
	2	291843	483602	100.0	0.3286		
Before adsorption demeth	1	294071	491448	100.7	0.3235	0.3114	0.0171
	2	296106	533554	100.7	0.2993		
1% wt activated clay demeth	1	315415	572694	100.3	0.3311	0.3324	0.0018
	2	305339	560928	100.3	0.3337		
Water washing demeth	1	310044	505675	100.5	0.3324	0.3380	0.0080
	2	295900	467097	100.5	0.3437		

Table B15 The percentage of diglyceride of biodiesel.

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Di	Average	SD
Unwashed biodiesel	1	18653	445638	100.3	0.0321	0.0311	0.0013
	2	21014	527283	100.3	0.0302		
4% activated clay	1	21065	457987	100.1	0.0358	0.0383	0.0035
	2	23406	454717	100.1	0.0408		
4% activated clay demeth	1	21337	491933	100.2	0.0334	0.0320	0.0019
	2	19443	482009	100.2	0.0307		
Water Washing	1	18462	393300	99.9	0.0331	0.0367	0.0058
	2	20165	396158	99.9	0.0403		
Heat 80°C 2 h	1	21535	408861	100.1	0.0418	0.0418	0.0001
	2	23784	452460	100.1	0.0417		

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Di	Average	SD
Evaporated at 50°C	1	16696	405651	100.2	0.0314	0.0346	0.0046
	2	23075	477338	100.2	0.0379		
0.5% diatomite 1 min	1	17799	455980	100.0	0.0295	0.0300	0.0006
	2	18247	456702	100.0	0.0304		
0.5% diatomite 3 min	1	18423	471886	100.6	0.0294	0.0315	0.0030
	2	20112	459585	100.6	0.0336		
0.5% diatomite 5 min	1	20064	450464	99.9	0.0346	0.0334	0.0016
	2	19528	464871	99.9	0.0323		
0.5% diatomite 10 min	1	21527	435722	100.0	0.0388	0.0385	0.0005
	2	23448	483602	100.0	0.0381		
Before adsorption demeth	1	25410	491448	100.7	0.0407	0.0419	0.0016
	2	28965	533554	100.7	0.0430		
1%wt activated clay demeth	1	34841	572694	100.3	0.0491	0.0434	0.0081
	2	26986	560928	100.3	0.0376		
Water washing demeth	1	28832	505675	100.5	0.0456	0.0456	0.0000
	2	26598	467097	100.5	0.0455		

Table B16 The percentage of triglyceride of biodiesel.

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Tri	Average	SD
Unwashed biodiesel	1	-	445638	100.3	-	-	-
	2	-	527283	100.3	-		
4% activated clay	1	-	457987	100.1	-	-	-
	2	-	454717	100.1	-		
4% activated clay demeth	1	-	491933	100.2	-	-	-
	2	-	482009	100.2	-		

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Di	Average	SD
Water Washing	1	-	393300	99.9	-	-	-
	2	-	396158	99.9	-		
Heat 80°C 2 h	1	-	408861	100.1	-	-	-
	2	-	452460	100.1	-		
Evaporated at 50°C	1	-	405651	100.2	-	-	-
	2	-	477338	100.2	-		
0.5% diatomite 1 min	1	-	455980	100.0	-	-	-
	2	-	456702	100.0	-		
0.5% diatomite 3 min	1	-	471886	100.6	-	-	-
	2	-	459585	100.6	-		
0.5% diatomite 5 min	1	-	450464	99.9	-	-	-
	2	-	464871	99.9	-		
0.5% diatomite 10 min	1	-	435722	100.0	-	-	-
	2	-	483602	100.0	-		
Before adsorption demeth	1	-	491448	100.7	-	-	-
	2	-	533554	100.7	-		
1%wt activated Clay demeth	1	-	572694	100.3	-	-	-
	2	-	560928	100.3	-		
Water washing demeth	1	-	505675	100.5	-	-	-
	2	-	467097	100.5	-		

Table B17 The percentage of total glycerin of biodiesel.

Samples		Free glycerol	Mono	Di	Tri	Total glycerin	Average	SD
Unwashed biodiesel	1	0.6913	0.4203	0.0320	-	0.8031	0.7948	0.0117
	2	0.6758	0.4172	0.0302	-	0.7866		
4% activated clay								
4% activated clay	1	0.0058	0.4297	0.0358	-	0.1206	0.1209	0.0004
	2	0.0058	0.4298	0.0408	-	0.1211		
4% activated clay Demeth								
4% activated clay Demeth	1	-	0.4469	0.0334	-	0.1188	0.1143	0.0064
	2	-	0.4128	0.0307	-	0.1097		
Water Washing								
Water Washing	1	-	0.3789	0.0331	-	0.1015	0.1026	0.0006
	2	-	0.3837	0.0413	-	0.1037		
Heat 80°C 2 h								
Heat 80°C 2 h	1	-	0.7636	0.0418	-	0.2008	0.2002	0.0009
	2	-	0.7585	0.0417	-	0.1995		
Evaporated 50°C								
Evaporated 50°C	1	-	0.4404	0.0314	-	0.1169	0.1151	0.0025
	2	-	0.4230	0.0379	-	0.1134		
0.5% diatomite 1 min								
0.5% diatomite 1 min	1	0.0074	0.3046	0.0295	-	0.0893	0.0908	0.0021
	2	0.0062	0.3205	0.0304	-	0.0923		
0.5% diatomite 3 min								
0.5% diatomite 3 min	1	0.0058	0.3151	0.0294	-	0.0904	0.0913	0.0012
	2	0.0052	0.3215	0.0336	-	0.0921		
0.5% diatomite 5 min								
0.5% diatomite 5 min	1	0.0043	0.3474	0.0346	-	0.0979	0.0976	0.0004
	2	0.0047	0.3451	0.0323	-	0.0974		
0.5% diatomite 10 min								
0.5% diatomite 10 min	1	0.0000	0.3595	0.0388	-	0.0973	0.0937	0.0052
	2	0.0007	0.3286	0.0381	-	0.0900		
Before adsorption demeth								
Before adsorption demeth	1	0.0110	0.3235	0.0407	-	0.0995	0.0968	0.0037
	2	0.0116	0.2993	0.0430	-	0.0942		

Samples		Free glycerol	Mono	Di	Tri	Total glycerin	Average	SD
1% activated clay demeth	1	-	0.2981	0.0491	-	0.0832	0.0819	0.0018
	2	-	0.2945	0.0376	-	0.0806		
WaterWashing demeth	1	-	0.3324	0.0456	-	0.0914	0.0929	0.0020
	2	-	0.3437	0.0455	-	0.0943		

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:

$$\% \text{ free fatty acids} = (\text{ml of alkali} \times N \times 28.2) / \text{weight of sample}$$

$$N = \text{normality of alkaline solution}$$

$$\text{ml of alkali} = \text{ml of sodium hydroxide solution}$$

Table B18 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	1.0600	0.10	0.2354	0.62
	1.0679	0.10	0.2354	

5. Determination of the Saponification value (ASTM D5558)

Reagent

1. Phenolphthalein
2. Alcoholic KOH solution
3. 0.5 N HCl

To the 250 ml of Erlenmeyer flask, oil sample (1 g), alcoholic potassium hydroxide (25 ml) and 1 ml of 1% phenolphthalein were added. The mixture was subject to titrate with 0.5 N of hydrochloric acid until the pink color has disappeared. Prepare a blank determination and carried out same with the sample. The ml of acid solution used was recorded.

The saponification value was calculated as follows:

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

$$A = \text{titration of blank}$$

$$B = \text{titration of sample}$$

$$N = \text{normality of hydrochloric acid solution}$$

$$\text{Alcoholic KOH} = 40 \text{ g of potassium hydroxide} \\ \text{dissolved in 1 L of ethanol}$$

Table B19 Saponification value of crude oil.

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	SN
Refined palm oil	1.0100	25.45	32.75	201.72 ^a
	1.0132	25.50	32.75	

$$a = 0.4975 \text{ N}$$

6. Determination of the Iodine value (ASTM D5554)

Reagent

1. KOH solution
2. Wijs solution
3. CCl₄
4. 0.1 N Na₂S₂O₃
5. Starch

To the 500 ml of Glass-Stopper flask, oil sample (0.1 g), carbon tetra chloride (20 ml) and Wijs solution (25 ml) were added. Store the flasks in a dark place for 30 min. From storage, removed the flasks and add 20 ml of KI solution followed by 100 ml of distilled water. The mixture was subject to titrate with 0.1 N of sodium thiosulfate until the yellow color has almost disappeared, add 2 ml of starch indicator solution, and continued the titration until the blue color has just disappeared. Prepare a blank determination and carried out same with the sample. The ml of sodium thiosulfate used was recorded.

The iodine value was calculated as follows:

$$\text{Iodine value} = (B - S) \times N \times 12.69 / \text{weight of sample}$$

B = titration of blank

S = titration of sample

N = normality of Na₂S₂O₃ solution

Table B20 Iodine value of crude oil.

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	IV
Refined palm oil	0.1135	41.60	46.90	61.33 ^a
	0.1045	42.00	46.90	

$a = 0.1035 \text{ N}$

7. 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 occurred. 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:

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

$$A = \text{titration of sample}$$

$$B = \text{titration of blank}$$

$$N = \text{normality of alcoholic KOH solution}$$

$$\text{Alcoholic KOH} = 0.6 \text{ g of potassium hydroxide}$$

dissolved in 100 ml of isopropyl alcohol

Table B21 Acid value of biodiesel.

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	AV
1% wt of activated clay	2.0016	0.075	0.05	0.0673 ^a
	2.0025	0.075	0.05	
Water washing	2.0094	0.075	0.05	0.0671 ^a
	2.0053	0.075	0.05	

$$a = 0.0961 \text{ N}$$

8. 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:

$$\text{viscosity} = Ct$$

$$C = \text{Constant of viscometer tube (mm}^2/\text{s}^2)$$

$$\text{time} = \text{measured flow times for } t1 \text{ and } t2, \\ \text{respectively(s)}$$

Table B22 Viscosity of biodiesel.

Sample	Time 1 (s)	Time 2 (s)	Constants of tube	Viscosiy (cSt)
1% wt activated clay	289.41	289.77	0.01434 ^a	4.15
Water washing	295.78	295.15	0.01434 ^a	4.24

VITA

Miss Budsaya Sriwichan was born on March 12, 1984 in Bangkok, Thailand. She graduated at Satreesamutprakan School in 2002. She received the Bachelor Degree of Science in chemistry, Chulalongkorn University in 2007. She continued her Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkom University in 2007 and completed the program in 2010.

Conference

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