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PURIFICATION OF BIODIESEL BY ADSORPTION WITH ACTIVATED LOW SILICA BENTONITE

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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งานวิจัยนี้ใช้เบนโทไนต์กัมมันต์ที่มีซิลิกาต่ำเป็นดูดซับในการทำไบโอดีเซลให้บริสุทธิ์โดยทำการศึกษาผลของความเข้มข้นของกรดซัลฟูริก เวลาที่ใช้ในการกระตุ้น ขนาดอนุภาค และปริมาณตัวดูดซับของเบนโทไนต์กัมมันต์ที่กระตุ้นด้วยกรด จากการทดลองพบว่าเบนโทไนต์กัมมันต์ที่มีซิลิกาต่ำจะมีประสิทธิภาพดีที่สุดในการทำไบโอดีเซลให้บริสุทธิ์เมื่อกระตุ้นด้วยกรดซัลฟูริกที่เข้มข้น 0.25 โมลาร์ในน้ำที่ปราศจากไอออน ที่อุณหภูมิ 100 องศาเซลเซียส เป็นเวลา 1 ชั่วโมง ใช้ปริมาณเบนโทไนต์กัมมันต์ที่มีซิลิกาต่ำร้อยละ 5 โดยน้ำหนักตัวอย่างไบโอดีเซลขนาดอนุภาค 60-80 เมช ซึ่งให้ร้อยละการดูดซับสบู่เป็น 57.22 และสอดคล้องกับไอโซเทอมการดูดซับแบบฟรุนดลิดช์ วิเคราะห์หาพื้นที่ผิว องค์ประกอบทางเคมี และโครงสร้างโดยใช้เทคนิค BET XRF และ FTIR ตามลำดับ พื้นที่ผิวสามารถเพิ่มขึ้นจาก 25.398 เป็น 48.928 ตารางเมตรต่อกรัมโดยการกระตุ้นด้วยกรด การแลกเปลี่ยนไอออนของอลูมิเนียม เหล็ก และ แมกนีเซียม (Al^{3+}, Fe^{3+}และ Mg^{2+}) กับ ไฮโดรเจนไอออน (H^{+}) เป็นผลให้เกิดการเปลี่ยนแปลงองค์ประกอบในชั้นของออกตะฮีดรอลวิเคราะห์โดยใช้เทคนิค XRF นอกจากนี้ค่าความเข้มของพีค IR ของ Al-Al-OH แบนด์ที่ 915 ซม$^{-1}$จะลดลงหลังจากกระตุ้นด้วยกรด ดังนั้นเบนโทไนต์กัมมันต์ที่มีซิลิกาต่ำซึ่งกระตุ้นด้วยกรดสามารถเป็นตัวดูดซับที่มีประสิทธิภาพเพื่อใช้ในกระบวนการทำไบโอดีเซลให้บริสุทธิ์

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต…………………………….…….
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URAILUCK LEERUANG: PURIFICATION OF BIODIESEL BY ADSORPTION WITH ACTIVATED LOW SILICA BENTONITE ADSORBENT. ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 113 pp.

A natural low silica bentonite (LSB) was used as adsorbent for purifying biodiesel. The concentrations of sulfuric acid, activating time, particle size and amount of adsorbent parameters to activate LSB were studied. The most efficient of LSB for purifying crude biodiesel was obtained by activating LSB with 0.25 M H_2SO_4 in DI water at 100 ^{0}C for 1 hour. By using 5% of activated LSB with 60-80 mesh size, 57.22% of soap could be removed and the adsorption isotherm was fit with Freundlich isotherm. The surface area, chemical composition and structure were characterized by BET, XRF and FTIR techniques, respectively. The specific surface area could be improved from 25.398 to 48.928 $m^2\ g^{-1}$ by acid treatment. An exchange of Al^{3+}, Fe^{3+} and Mg^{2+} with H^+ ions leading to a modification of composition in the octahedral sheets was exhibited by XRF. Moreover, intensity of Al–Al–OH band at 915 cm^{-1} was decreased after acid activation. Acid activated LSB was showed to be an efficacious adsorbent for purifying biodiesel.

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

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LIST OF ABBREVIATIONS

Å = Angstrom

Al^{3+} = Aluminium ion

µl = Microliter

µm = Micrometer

ASTM = American Standard Test Method

B100 = Pure biodiesel

BET = Brunauer-Emmett-Teller

BXX = XX% biodiesel, (100-XX) % petroleum diesel

°C = Degree Celsius

Ca^{2+} = Calcium ion

CO = Carbon monoxide

CO_2 = Carbon dioxide

EN = European Standards

Fig = Figure

FFA = Free fatty acid

FT-IR = Fourier Transform InfraRed

g = Gram

h = Hour

H_2SO_4 = Sulfuric acid

HC = Hydrocarbon

K = Potassium

K^+ = Potassium ion

K_L = Langmuir constant

K_F = Freundlich constant

KOH = Potassium hydroxide

LSB = Low silica bentonite

Mg = Magnesium

m = Meter

min = Minute

mg = Miligram

Mg^{2+} = Magnesium ion

ml = Milliliter

mm = Millimeter

Na^{+} = Sodium ion

No. = Number

P = Pressure

ppm = parts per million

rpm = Revolution per minute

TLC = Thin Layer Chromatography

XRF = X-Ray Fluorescence

v/v = Volume by volume

% wt = Percent by weight

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CHAPTER I

INTRODUCTION

Thailand's economy has slowed slightly over the past year but the biodiesel industry in Thailand has poised for rapid growth. 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. Global's diesel consumption is currently at 50 million litres/day and the government is expected to have an installed biodiesel production capacity of 8.5 million litres/day by 2012 so that B10 (10% biodiesel in diesel) can meet the national diesel requirements. A key element of the Government's strategic plan for biodiesel is plantation development for the vegetable oil crops to be used as feedstock [1]. 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 [2].

Biodiesel, a renewable fuel, is produced from vegetable oils and animal fats by a process called transesterification. It is the chemical conversion process of vegetable oil or animal fats to biodiesel as the main product and glycerin as the by product [3]. The glycerin phase is much dense than crude biodiesel phase and can be separated from crude biodiesel [4].

The impurities left in the crude biodiesel after the reaction are dangerous to any combustion system and must be removed. The longest standing method for purification is water washing method. This method works very well, however, wastewater it becomes difficult and costly to treat and dispose. Dry wash with adsorbent is an alternative method to biodiesel purification. The adsorbent has highly developed structure of pores on the surface of which is sites with easily trapped and released ions [5].

Bentonite is an absorbent which is mainly composed of montmorillonite. It is 2:1 type aluminium phyllosilicate, the unit layer structure of which consists of one octahedral sheet between two tetrahedral sheets. The octahedral sheet results in a net negative charge on the clay surfaces [6]. The charge imbalance is offset by exchangeable cations of H^+, Na^+ or Ca^{2+} on the layer surfaces. In aqueous solutions, water molecules are intercalated into the interlamellar space of bentonite, leading to an expansion of the minerals. The chemical nature and pore structure of bentonite generally determine their adsorption ability [7].

Adsorption properties of bentonite are a function of the content of montmorillonite and the number of interlayer cations. In order to remove impurities and various exchangeable cations, bentonite was modified such as acid treatments can often replace exchangeable cations with H^+ ions, followed by dissolution of the tetrahedral and octahedral sheets. Octahedral cations of Al^{3+}, Fe^{2+}, Fe^{3+}, and Mg^{2+} can be depleted by acid treating the clay minerals [8]. The ion exchange capacity of clay minerals is attributed to structural defects, broken bonds. Also, acid treatment of bentonite has been shown to create enhanced mesoporosity depending on acid concentrations and treatment time which is important structural changes and partial decomposition of montmorillonite [9].

1.1 Objectives of the research

The objective of this research is to purify biodiesel impurities by using low silica bentonite as adsorbent.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Biodiesel

Biodiesel, an alternative fuel substitute for conventional diesel, is produced from renewable resources such as plant oils (soybean oil, cotton seed oil, canola oil, etc.), used cooking oils or animal fats (beef tallow, pork lard,etc.). This biodiesel is biodegradable and nontoxic. The process to produce biodiesel is to convert oils and fats into long-chain mono alkyl esters [10]. The physical and chemical properties of biodiesel are similar to diesel fuel. 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 of engine [11].

2.1.1 Biodiesel advantage

Biodiesel has many environmentally beneficial properties compared with petroleum-based diesel because it is derived from a renewable domestic resource. Biodiesel's advantages are as follows [12].

- Renewable

Biodiesel is renewable, energy efficient, and can be used in most diesel engines with no or only minor modifications. It is made from either agricultural or recycled resources. Biodiesel is biodegradable and can help reduce dependency on fossil fuel.

- Reduces Air Pollution

Biodiesel is environmental friendly because of lower HC emissions, smoke and soot reductions, lower CO emissions, reduction of greenhouse gases. Vegetable oil burns cleanly and thus helps solve another thorny issue - air pollution from conventional fossil fuels. Like biodiesel, vegetable oil use reduces carbon dioxide emissions. The fuel itself is often called carbon neutral but that's not entirely true. Sure, the amount produced during combustion equals the amount the plants take up during photosynthesis, but remember, it takes energy to make this fuel (gasoline to power a tractor, for instance). The consumption of energy, in turn, produces carbon dioxide. Even so, the fuel is light years ahead of conventional fossil fuels in the greenhouse gas production department.

- Better ignition and combustion

Biodiesel can be used directly in compression ignition engines with no substantial modifications of the engine. B20 can be used without engine modifications. Biodiesel has better ignition and combustion characteristics (due to a higher Cetane Index), which allows the engine to run more smoothly with less of the "knocking" sounds typical of diesel engines [13].

- Reduces exhaust emissions

Biodiesel substantially reduces exhaust emissions (unburned hydrocarbons, carbon monoxide and particulate matter). It contains naturally occurring oxygen, which enables the fuel to burn more completely and all but eliminate the black smoke normally associated with diesel engines. There may be a slight increase in NOx emissions but this is dependant on the engine type and its operating environment.

- Improves lubricity & reduces engine wear

Biodiesel has very good intrinsic lubrication properties. Even blends as low as B1 can improve the lubricity in highly de-sulphurised mineral diesel. In engines approved for operation with B100 Biodiesel, the engine wear is significantly reduced.

- Safer, biodegradable and non toxic

Biodiesel has a higher flashpoint than mineral diesel. It is also readily biodegradable and non toxic, which makes it a safer and more environmentally friendly fuel to handle, particularly in sensitive areas.

- Sulphur free

Biodiesel is naturally free of sulphur and so produces no sulphur dioxide, considered to be one of the main precursors to acid rain.

- Carbon dioxide neutral

Biodiesel is made from renewable resources, which means it reduces the contribution of carbon dioxide (one of the main greenhouse gases) to the atmosphere. Biodiesel does not produce greenhouse effects, because the balance between the amount of CO_2 emissions and the amount of CO_2 absorbed by the plants producing vegetable oil is equal [14].

2.1.2 Biodiesel disadvantage

The central problem in using vegetable oil as diesel fuel is that vegetable oil is much more viscous (thicker) than conventional diesel fuel (petro-diesel). Vegetable oil also has very different chemical properties and combustion characteristics to those of conventional diesel fuel. If the fuel is too thick it will not atomize properly when the fuel injectors spray it into the combustion chamber and it will not combust properly. The injectors get coked up, leading to poor performance, higher exhaust emissions and reduced engine life [15].

2.1.3 Biodiesel production

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 dilution, micro-emulsification, pyrolysis and transesterification [16].

2.1.3.1 Dilution (Blending)

Crude vegetable oils can be blended directly or diluted with the diesel fuel to improve viscosity. Dilution reduces the viscosity, engine performance problems such as injector coking, and more carbon deposits. However, dilution is not suitable for long term use in a direct injection engine. Pure biodiesel or 100% biodiesel is referred to as B100. A biodiesel blend is pure biodiesel blended with petrodiesel. Biodiesel blends are referred to as BXX. The XX indicates the amount of biodiesel in the blend (i.e., a B90 blend is 90% biodiesel and 10% petrodiesel).

2.1.3.2 Micro-emulsification

Micro-emulsion is another approach to reduce the viscosity of vegetable oils. Emulsion is a dispersion of oil in water or water in oil and this dispersion is also known as macro-emulsion. On the other hand, micro-emulsion is a thermodynamically stable dispersion of oil in water and water in oil. Both used surfactant as the principal agent to enable water and oil to mix. Micro-emulsion is not used for synthesis of biodiesel. It is just a technique to reduce the viscosity of oil.

2.1.3.3 Pyrolysis (Thermal cracking)

Pyrolysis is a method of conversion of one substance into another through heating or heating with the aid of the catalyst in the absence of air or oxygen. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The material used for pyrolysis can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The liquid fuel produced from this process has almost identical chemical components to conventional diesel fuel.

2.1.3.4 Transesterification

Transesterification, also called alcoholysis, is a chemical reaction of an oil or fat with an alcohol in the presence of a catalyst to form esters and glycerol. It involves a sequence of three consecutive reversible reactions where triglycerides are converted to diglycerides and then diglycerides are converted to monoglycerides followed by the conversion of monoglycerides to glycerol. In each step an ester is produced and thus three ester molecules are produced from one molecule of triglycerides. Among the alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are used most frequently. However methanol is preferred because of its low cost. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. It also gives glycerol as a byproduct which has a commercial value. Transesterification is the most viable process adopted known so far for the lowering of viscosity and for the production of biodiesel. Thus biodiesel is the alkyl ester of fatty acids, made by the transesterification of oils or fats, from plants or animals, with short chain alcohols such as methanol and ethanol in the presence of catalyst and glycerin is consequently a by-product from biodiesel production [13].

2.1.4 Biodiesel transesterification

The Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerine. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalysed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production, either base can be used for the methyl ester. The Fig. 2.1 shows the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion [4].

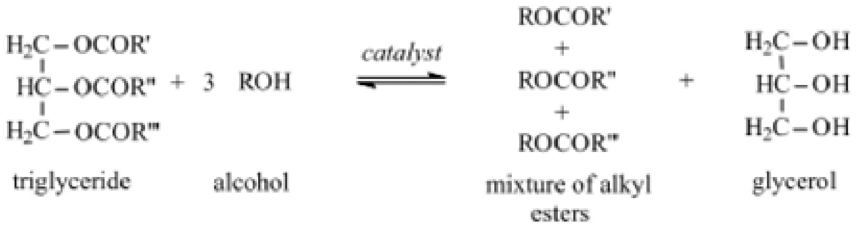


Figure 2.1 Equation for transesterification of vegetable oil.

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 [17]. 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.

2.1.5 Biodiesel Purification

The biodiesel produced has impurities that settle out into the glycerol layer, including unfiltered particulates, methanol and glycerin. Some sources encourage using unwashed biodiesel because washing biodiesel is a time-consuming process. However, some alcohol, catalyst and soap remain suspended throughout the biodiesel after the transesterification is complete. Two generally accepted methods to purify biodiesel are wet and dry washing [18].

2.1.5.1 Wet washing

The longest standing method for purification is the wet or water wash method is widely used to remove excess contaminants and leftover production chemicals from biodiesel. It is a process where a certain percentage of water is added to the crude biodiesel and the water is let to settle. As the water passes through the fuel, it attaches to impurities. (An air wash or bubble wash is sometimes paired with this process to accelerate the water passing through the fuel.) The fuel's impurities are removed as the water settles to the bottom of the tank. Once settled, the contaminated water is drained off. This process is repeated until the water removed is clear in color. This purification method works very well. However, the inclusion of additional water to the process offers many drawbacks, including increased cost and production time to treat and dispose of the highly contaminated water [19].

2.1.5.2 Dry washing

The dry wash process offers advantages over the wet wash system and is quickly becoming the method of choice among biodiesel producers for several reasons.

- The dry wash process decreases production time. With biodiesel becoming increasingly attractive to end users because of its environmental and cost-saving advantages, producers are looking at streamlining production to cope with growing demand. Dry washed biodiesel can be ready for use in a few hours and is significantly quicker to produce than wet-washed fuel.

- The dry wash process can also lower costs. In addition to the ever-increasing cost of water and the significant expense of water removal equipment, disposal of effluent water is often the single largest cost during production. Environmental agencies are vigorously pursuing illegal disposal of effluent waste. Hefty fines and imminent closure await those found breaking the law.

- Less space is required to conduct the dry wash process. Settling is the key to effective water removal. Numerous large wash tanks and additional water settling tanks are usually required in the wet wash process. Plant space can be used more effectively with dry washing.

- The dry wash process creates high-quality fuel. Since water isn't added in the dry wash process, it's possible to achieve less than 500 parts per million (ppm) water content in accordance with ASTM D 6751. In wet washing, the fuel's water content is usually more than 1,000 ppm, making it expensive, difficult and time-consuming to effectively remove.
- Another advantage to the dry wash process can be reused. Adsorbent used in the dry wash process has commercial use as compost and an animal feed additive. It also holds fuel source potential [20].

2.2 Adsorption

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 [21].

The molecules of gases or liquids or the solutes in solutions get adhered to the surface of the solids. In adsorption process two substances are involved. One is the solid or the liquid on which adsorption occurs and it is called adsorbent. The second is the adsorbate, which is the gas or liquid or the solute from a solution which gets adsorbed on the surface.

- Adsorbent : The substance on whose surface the adsorption occurs is known as adsorbent.

- Adsorbate : The substance whose molecules get adsorbed on the surface of the adsorbent (i.e. solid or liquid) is known as adsorbate [22].

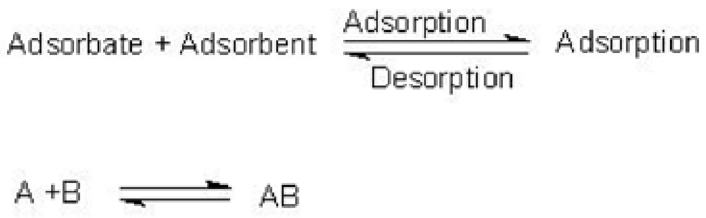


Figure 2.2 Adsorption process.

Adsorption is the binding of molecules or particles to a surface must be distinguished from absorption, the filling of pores in a solid. The binding to the surface is usually weak and reversible. The most common industrial adsorbents are activated carbon, silica gel, and alumina and activated bentonite because they present enormous surface areas per unit weight [23].

Adsorption process can distinguish between 2 types depending on which of these 2 force types plays the bigger role in the process. Adsorption processes can be classified as either physical adsorption (van der Waals adsorption) or chemisorption (activated adsorption) depending the nature of forces existing between adsorbate molecules and adsorbent.

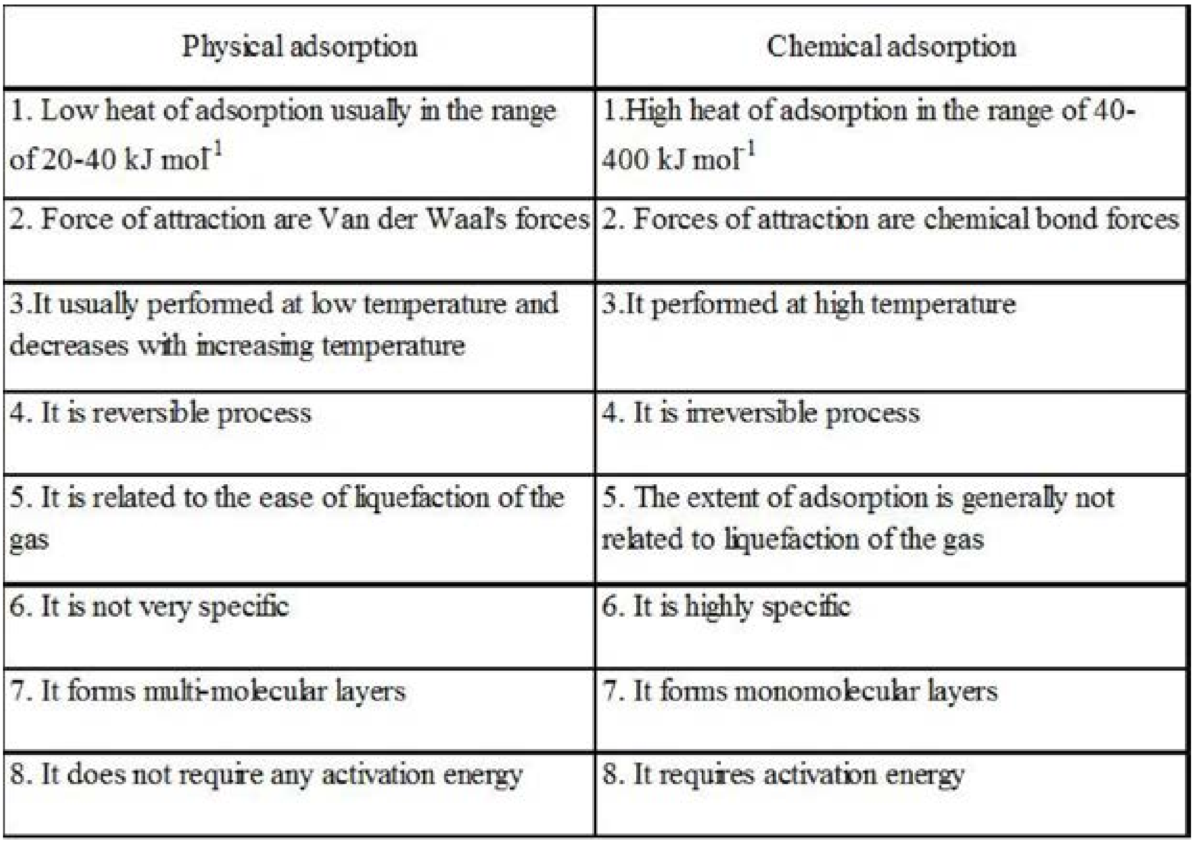
2.2.1 Physical adsorption (physisorption)

Physical adsorption is a type of adsorption in which the force of attraction existing between adsorbate and adsorbent are Vander Waal's forces. It is also known as Vander Waal's adsorption. In physical adsorption the force of attraction between the adsorbate and adsorbent are very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure. The energy of adsorption is approximately 20-40 kJ mol^{-1}. Physical adsorption occurs quickly and may be mono-molecular (unimolecular) layer or monolayer, or 2, 3 or more layers thick (multi-molecular). As physical adsorption takes place, it begins as a monolayer. It can then become multi-layer, and then, if the pores are close to the size of the molecules, more adsorption occurs until the pores are filled with adsorbate. Accordingly, the maximum capacity of a porous adsorbent can be more related to the pore volume than to the surface area [24].

2.2.2 Chemical adsorption (chemisorption):

Chemical adsorption is a type of adsorption in which force of attraction existing between adsorbate and adsorbent are almost same strength as chemical bonds, the adsorption is called chemical adsorption. It is also known as Langmuir adsorption. In chemisorption the force of attraction is very strong, therefore adsorption cannot be easily reversed. The energy of this adsorption is approximately 40-400 kJ mol^{-1}. The monolayer capacity is defined, for chemisorption, as the amount of adsorbate which is needed to occupy all adsorption sites as determined by the structure of the adsorbent and by the chemical nature of the adsorptive [25].

Table 2.1 Compare between physical adsorption and chemical adsorption



Physical adsorption	Chemical adsorption
1. Low heat of adsorption usually in the range of 20-40 kJ mol^{-1}	1.High heat of adsorption in the range of 40-400 kJ mol^{-1}
2. Force of attraction are Van der Waal's forces	2. Forces of attraction are chemical bond forces
3.It usually performed at low temperature and decreases with increasing temperature	3.It performed at high temperature
4. It is reversible process	4. It is irreversible process
5. It is related to the ease of liquefaction of the gas	5. The extent of adsorption is generally not related to liquefaction of the gas
6. It is not very specific	6. It is highly specific
7. It forms multi-molecular layers	7. It forms monomolecular layers
8. It does not require any activation energy	8. It requires activation energy

2.3 Adsorbent

The material upon whose surface the adsorption takes place is called an adsorbent. Activated charcoal, silica gel, magnesium silicate and activated bentonite is used as an adsorbent.

- Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm.

- They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption.

- The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapors.

- Activated bentonite is used for adsorption of organic substances and non-polar adsorbates and it is also usually used for waste gas (and waste water) treatment. It is the most widely used adsorbent since most of its chemical (e.g. surface groups) and physical properties (e.g. pore size distribution and surface area) can be tuned according to what is needed. Its usefulness also derives from its large micropore (and sometimes mesopore) volume and the resulting high surface area [26].

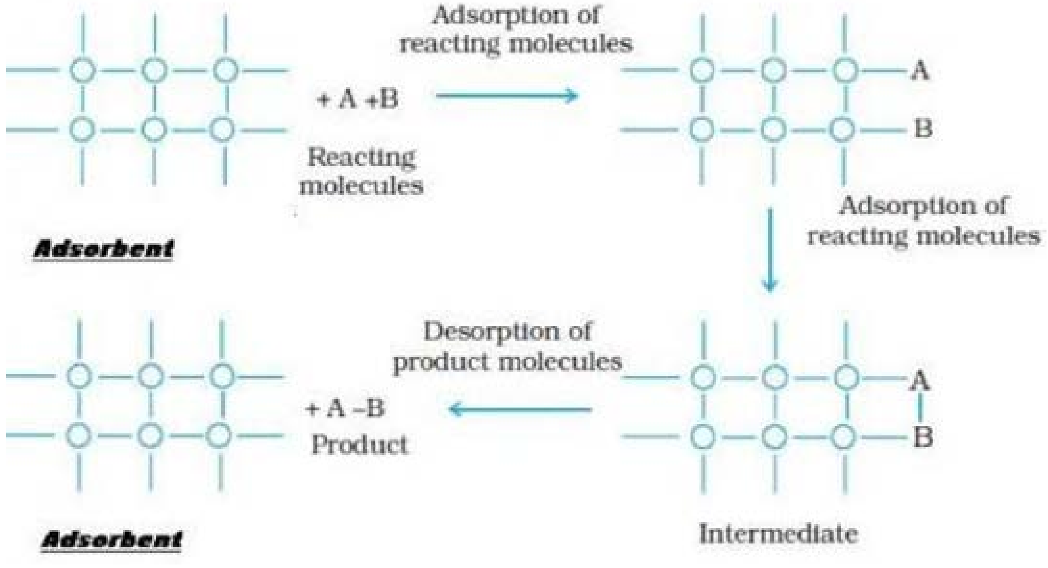


Figure 2.3 Mechanism of adsorption using adsorbent.

2.4 Bentonite

Bentonite is a type of impure clay. There are different types of bentonite, but it consists mostly of montmorillonite. The unique properties of bentonite are ideal for a variety of applications. Bentonite can absorb 7 to 10 times its own weight in water, making it extremely useful as an absorbent. The Bentonite clay is inexpensive and is available in powdered form. It is highly absorbent, and is able to hold several hundred times its weight in water [27].

2.4.1 Structure of bentonite

Chemical structure of bentonite complicated, non-stoichiometric structure $2[(Al_{1.67}Mg_{0.33})(Si_{3.5}Al_{0.5})O_{10}(OH)_2]$. It is 3 layer clay with 1 aluminum oxide sheet surrounded by 2 silicon oxide sheets. The internal aluminum sheet and external silicon oxide sheets share oxygen atoms. The net negative charge must then be counterbalanced a layer of cations is therefore present between the platelets. Typically these are Mg^{2+}, Ca^{2+} and/or Na^+ [28].

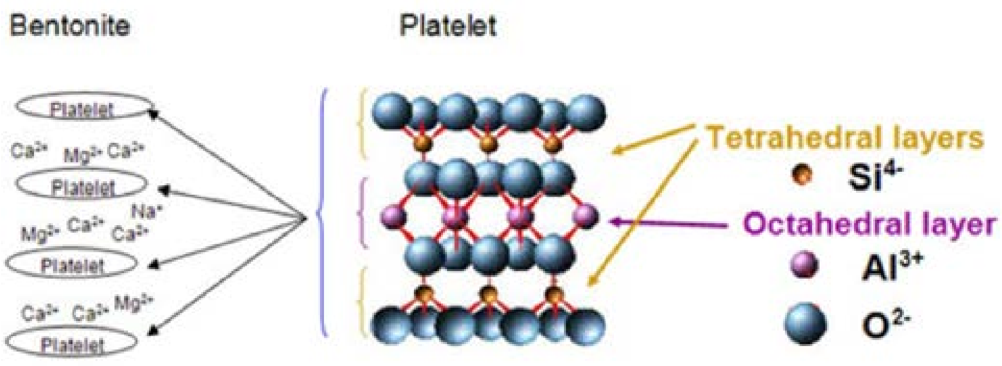


Figure 2.4 Structure of bentonite.

2.4.2 Composition of bentonite

2.4.2.1 Montmorillonite

The major composition in bentonite is montmorillonite, making up roughly 90 percent of most types. Montmorillonite consists of phyllosilicate minerals that combine to form soft clay. Montmorillonite is a member of the smectite family, and its water composition is highly variable. It is a 1 to 2 on the hardness scale and comes in white, yellow.

2.4.2.2 Silica

Silica, or quartz, is the second most prominent component. It makes up less than 5 percent of bentonite. Silica is also the second most common mineral found in the earth's crust. Silica is a semi-precious material used for jewelry and ornamentation and ranges from clear to black in color.

2.4.2.3 Calcium Carbonate

Calcium carbonate is found in calcium bentonite and can compose up to 20 percent of the clay. Calcium carbonate is found in rocks all over the world and is a common substance in the shells of organisms. Calcium carbonate is used as a medicinal supplement and is the primary constituent of limestone. The calcium carbonate makes calcium bentonite a useful absorber of ions, as well as of fats and oils.

2.4.2.4 Sodium

The presence of sodium makes sodium bentonite an ideal absorber of liquids. Sodium is extremely common in rock forms, and its presence in bentonite allows it to expand up to 15 times larger than its dry size. In high concentrations, sodium bentonite forms a gel-like substance, making it ideal for applications such as cement [29].

2.4.3 Properties of bentonite

The properties of bentonite creates viscosity at low concentrations in water, forms low permeability filter cakes, has very high surface area per unit mass, absorbs very large amounts of water, holds onto water very strongly, swells in contact with water/creates swelling pressure, water does not flow through a confined layer of bentonite, forms stable colloid in water; does not settle over reasonable time, has very high aspect ratio (l/w), platelets impermeable to gases, has high ion-exchange capacity, undergoes specific selectivity reaction with K^+ ion, oxide/hydroxide surfaces interact with many adsorbents. Available in large quantities can derivative with cationic molecules [30].

2.4.4 Type of bentonite

2.4.4.1 Sodium Bentonite

Because of its high absorbency and clumping tendency, sodium bentonite is useful as a sealant. Its swelling capacity gives sodium bentonite the ability to bond with soil and create and impenetrable barrier. Sodium bentonite is also used for mud drilling, clumping cat litter, and as a bonding agent for feeds, medicines and cosmetics. Currently, sodium bentonite is being investigated as an absorbing agent to remove E-Coli bacteria from food.

2.4.4.2 Calcium Bentonite

Calcium bentonite is referred to as "living clay" because of the belief found in many cultures that it is useful as a medicine. The practice of geophagy or "earth eating" is centered on the belief that some clays such as calcium bentonite is able to be safely ingested for the absorption and removal of toxins from the gastrointestinal tract. Both external and internal uses of clay as a medicine were recorded in a medical treatise on clay therapy. The modern alternative healthcare industry uses calcium bentonite extensively for internal and external toxin removal that is believed to be based on ion exchange [31].

2.4.5 Applications of bentonite

The bentonite is finding increasing use in the manufacture and industrial.

- Use as grouting material

Bentonite has great water binding ability and consequently very low permeability to water. It has been found, that the permeability of the soil is reduced considerably when substituted by sodium bentonite. Hence, this material is often employed in construction engineering to make a porous medium water-tight. It can be used alone or with some other grouting material.

- Use in drilling muds

Drilling muds consist of water to which sodium bentonite and pulverized are added. Such muds are prepared mainly for deep drilling, like oil-well drilling. Bentonite imparts two properties. It gives the fluid a viscosity several times that of water and thixotrophy. It seals the wall of the holes, thus preventing water loss. The quantity of bentonite used is variable depending upon the depth of the hole to be drilled. Generally one ton of bentonite is used to prepare about 100 barrels of mud.

- Use as decolourizer

Decolourizing bentonites are those which carry Ca and / or Mg as an exchangeable ion. They are used in the decolourization of animal and vegetable facts (like ground-nut, castor-oili) and petroleum oil, lubricants, paraffins and other waxes. These are decolourized in two ways (By the percolation method and by the contact method).

- Use as foundry sands

Bentonite is utilized in foundry to bind the sand grains into desired shapes. Bentonite helps in retaining the mechanical shape of the mould by making the particles of sands adhere and also making the surface impermeable. Strength and fusion point are the two important properties desired for selecting bentonite. Generally, the swelling type of bentonite is used though other types of bentonites have also been used.

- Use in cosmetic and pharmaceutical preparations

Bentonite gels are used as a carrier for a number of cosmetic preparations, tooth-pastes, creams for skin and other similar products. For the preparation of cosmetic creams, bentonite is generally used as a paste formed with water and glycerin. Bentonite when intimately mixed with water in the proportion of one to four gives a pasty mass with the consistency of heavy grease and in this form it is used for the preparation of medicinal ointments. Bentonite in the natural state is non-poisonous and harmless; thus it finds use in tooth-paste and even in the preparation of lipstick [32].

2.5 Adsorption isotherm

Adsorption process is generally determined through graphs known as adsorption isotherm. That is the amount of adsorbate on the adsorbent as a function if its pressure (gas) or concentration (liquid) at constant temperature .The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Basic adsorption isotherm can predict that after saturation pressure Ps, adsorption does not occur anymore, that is there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, adsorption is independent of pressure.

2.5.1 Adsorption/desorption Isotherm

Surface area and pore size distribution were measured by the use of nitrogen adsorption/desorption isotherms at liquid nitrogen temperature and relative pressures (P/Po) ranging from 0.05-1.0. Six different types of adsorption isotherm and their characteristics are described in Fig.2.5 - 2.10. The large uptake of nitrogen at low P/Po indicates filling of the micropores (< 20 Angstrom) in the catalyst. The linear portion of the curve represents multilayer adsorption of nitrogen on the surface and the concave upward portion of the curve represents filling of mesopores (20 - 500 Angstrom) and macropores (>500 Angstrom). An entire isotherm is needed for one to calculate the pore size distribution of the catalyst. However, for a surface area evaluation, data in the relative pressure range of 0.05-0.30 are generally used. [33]

The six IUPAC standard adsorption isotherms are shown in 2.5.1.1 - 2.5.1.6, they differ because the systems demonstrate different gas/solid interactions.

2.5.1.1 Type I Adsorption Isotherm

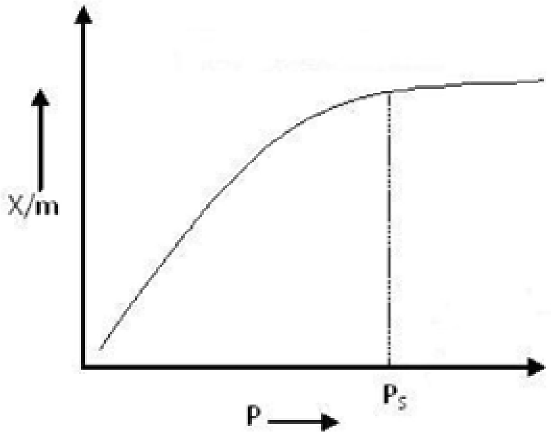


Figure 2.5 Type I Adsorption Isotherm.

Type I Adsorption Isotherm graph was depicted monolayer adsorption and given by microporous solids having relatively small external. This graph can be easily explained using Langmuir Adsorption Isotherm. If BET equation, when P/P0 << 1 and c >> 1, then it leads to monolayer formation. (e.g.activated carbons, molecular sieve zeolites and certain porous oxides).

2.5.1.2 Type II Adsorption Isotherm

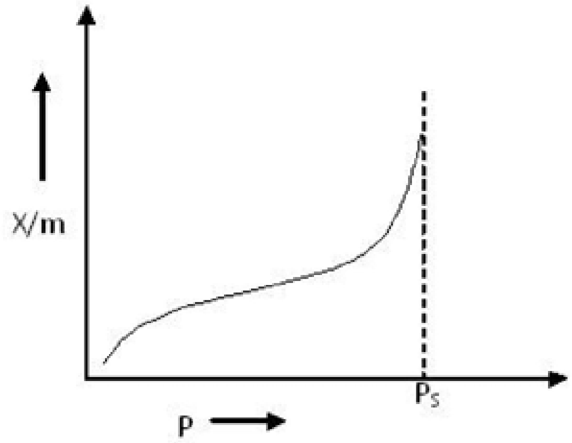


Figure 2.6 Type II Adsorption Isotherm.

Type II Adsorption Isotherm was displayed large deviation from Langmuir model of adsorption. The isotherm represents unrestricted monolayer-multilayer adsorption. The beginning of the almost linear middle section of the isotherm is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption about to begin.

2.5.1.3 Type III Adsorption Isotherm

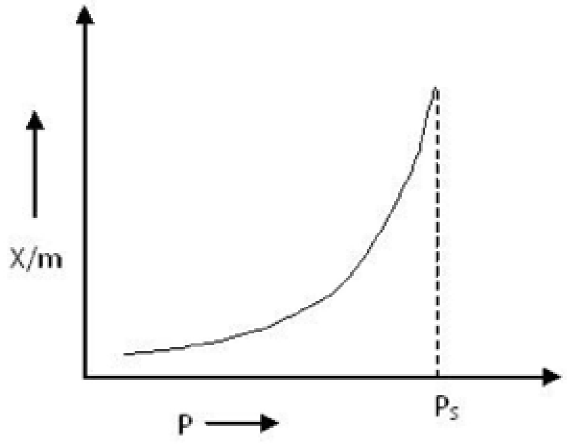


Figure 2.7 Type III Adsorption Isotherm.

Type III Adsorption Isotherm also was shown large deviation from Langmuir model. In BET equation value if C <<< 1 Type III Adsorption Isotherm obtained. This isotherm explains the formation of multilayer. There is no flattish portion in the curve which indicates that monolayer formation is missing. Examples of Type III Adsorption Isotherm are Bromine (Br_2) at 790°C on silica gel or Iodine (I_2) at 790°C on silica gel.

2.5.1.4 Type IV Adsorption Isotherm

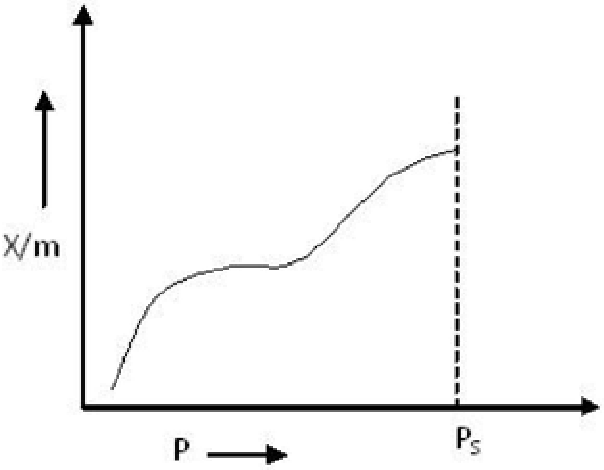


Figure 2.8 Type IV Adsorption Isotherm.

Type IV Adsorption Isotherm was described at lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer. The intermediate flat region in the isotherm corresponds to monolayer formation. The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure (P_S) of the gas. Examples of Type IV Adsorption Isotherm are of adsorption of Benzene on Iron Oxide (Fe_2O_3) at 500°C and adsorption of Benzene on silica gel at 500°C.

2.5.1.5 Type V Adsorption Isotherm

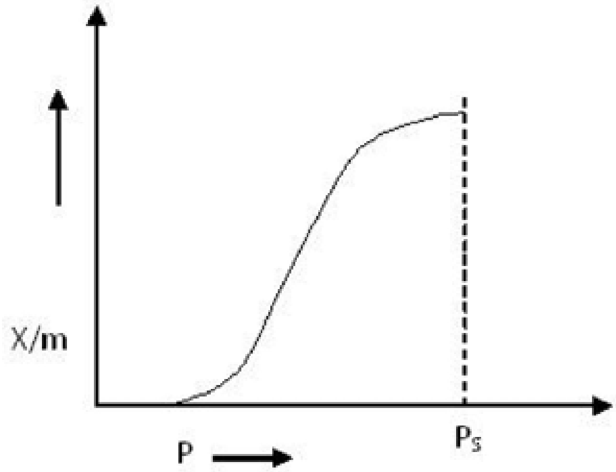


Figure 2.9 Type V Adsorption Isotherm.

Explanation of Type V graph is uncommon. It is similar to Type IV and related to the Type III isotherm in that the adsorbent-adsorbate interaction is weak, but is obtained with certain porous adsorbents. Example of Type V Adsorption Isotherm is adsorption of water (vapors) at 1000°C on charcoal. Type IV and V shows phenomenon of capillary condensation of gas.

2.5.1.6 Type VI Adsorption Isotherm

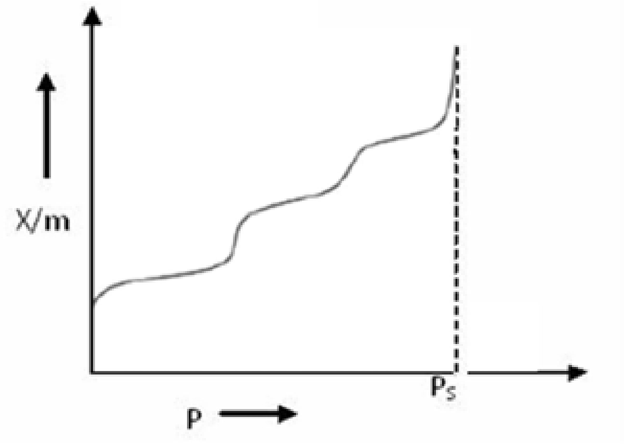


Figure 2.10 Type VI Adsorption Isotherm.

The Type VI isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorption on a uniform non-porous surface. The step-height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers. The best examples of Type VI isotherms are those obtained with argon or krypton on graphitized carbon blacks at liquid nitrogen temperature [26].

2.5.2 Adsorption isotherm of soap

The theory of adsorption of Langmuir and Freundlich isotherms was put forward to explain the phenomena of adsorption. The determination was given below.

2.5.2.1 Langmuir isotherm

Langmuir isotherm for gases adsorbed to solids. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. It is based on four assumptions.

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
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.

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

Where,

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

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

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

K_L = Langmuir constant (l/mg)

The Langmuir constants, K_L and n can be determined from the linear plot of 1/Ce versus 1/(x/m) [34].

2.5.2.2 Freundlich isotherm

Freundlich isothermal expressed variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. The 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. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm.

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Where ,

x/m = adsorption per gram of adsorbent which is obtained be dividing the amount of adsorbate (x) by the weight of the adsorbent (m).

P = Pressure

k and n = are constants whose values depend upon adsorbent and gas at particular temperature.

Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure. This relation is called as the Freundlich adsorption isotherm. As see the following diagram. The value of x/m is increasing with increase in p but as n>1 it does not increase suddenly. This curve is also called the Freundlich isotherm curve.

Taking the logarithms of a first equation.

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

Hence, if a graph of log(x/m) is plotted against logCe, it will be a straight line in the following diagram.

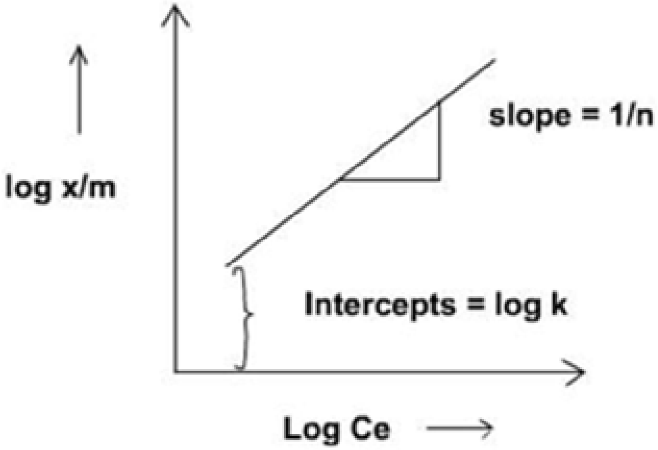


Figure 2.11 Freundlich isotherm.

From this the value of slope equal to 1/n and the value of intercept equal to log K_F can be obtained. Over and above, it the graph of log (x/m) against log Ce comes out to be a straight line, it can be assured that the Freundlich adsorption isotherm is satisfied for this system. 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 [26].

2.6 Characterization

2.6.1 BET (Brunauer-Emmett-Teller)

A different equation is more likely to describe adsorption where the adsorbate exceeds a monolayer. Its assumptions are adsorbed molecules stay put, enthalpy of adsorption is the same for any layer, energy of adsorption is the same for layers other than the first and a new layer can start before another is finished. The Brunauer-Emmett-Teller (BET) equation is as follow.

$$q = \frac{q_m K_b C}{[C_s - C]\{1 + [K_b - 1][C/C_s]\}}$$

Where,

C_s = concentration at which all layers are filled

K_b = a coefficient

For evaluation of the specific surface area, pore volume and average pore size distribution from a single adsorption isotherm, nitrogen (at 77 ^{0}K) is the recommended adsorptive [35].

2.6.2 XRF (X-Ray Fluorescence)

X-ray fluorescence (XRF) method is widely used to measure the elemental composition of materials and quantitative multi-element technique that provides excellent accuracy. It is non-destructive and reliable, requires no, or very little, sample preparation and is suitable for solid, liquid and powdered samples. It can be used for a wide range of elements, from sodium (11) to uranium (92), and provides detection limits at the sub-ppm level. It can also measure concentrations of up to 100% easily and simultaneously. This technique is being used for monitoring, process control, quality assurance, compliance and research [36].

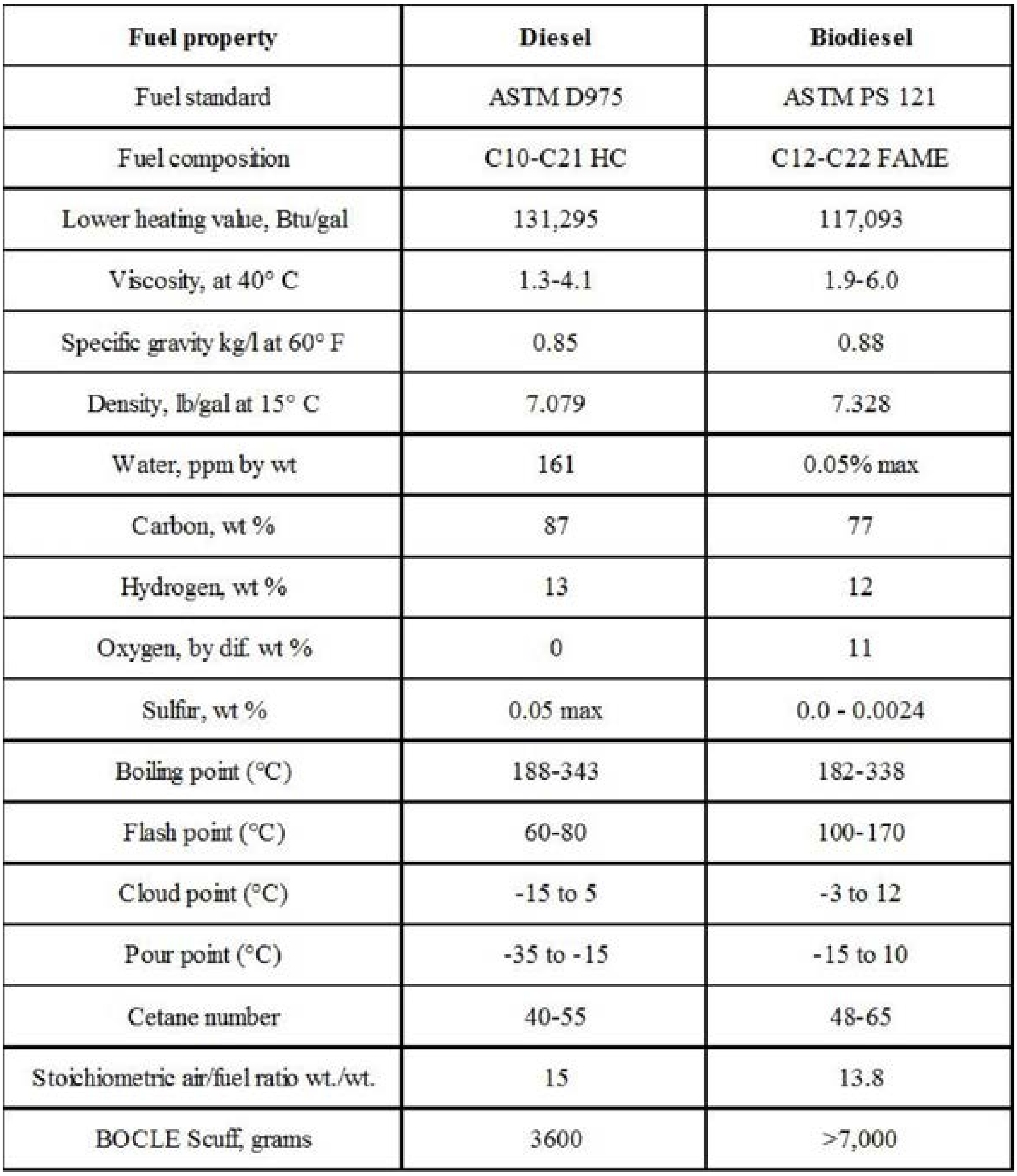
2.6.3 FT-IR (Fourier Transform InfraRed)

FTIR is most useful for identifying chemicals that are either organic or inorganic. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to IR spectrum [37].

2.7 Properties of diesel and biodiesel

The different physical and chemical properties between diesel and biodiesel were summarized in Table 2.2.

Table 2.2 Comparison of fuel properties between diesel and biodiesel [38]

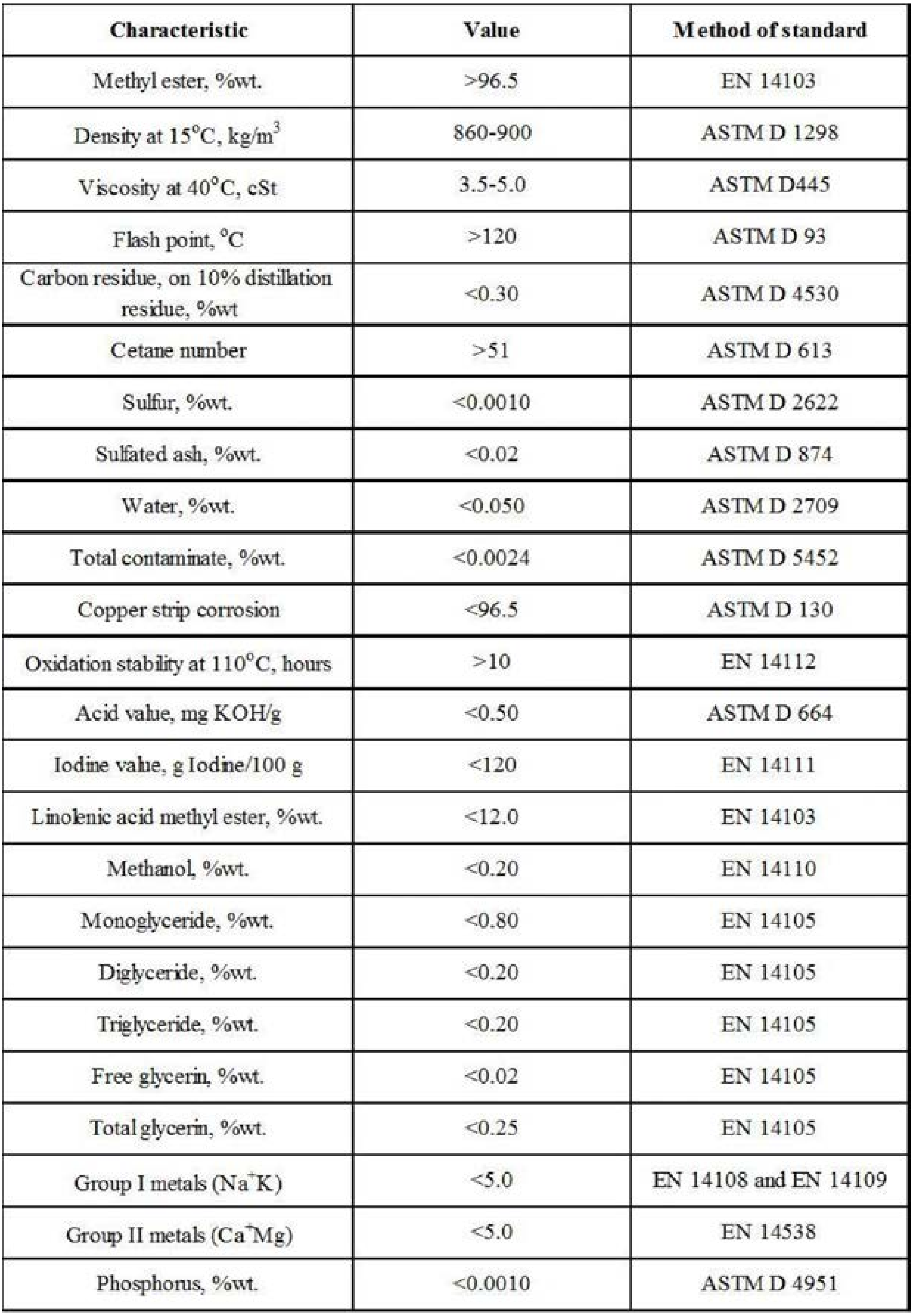


Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower heating value, Btu/gal	131,295	117,093
Viscosity, at 40° C	1.3-4.1	1.9-6.0
Specific gravity kg/l at 60° F	0.85	0.88
Density, lb/gal at 15° C	7.079	7.328
Water, ppm by wt	161	0.05% max
Carbon, 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	3600	>7,000

2.8 Characteristic and quality of biodiesel

The physical and chemical properties of biodiesel used in Thailand needed for safe and satisfactory diesel engine operation and must meet the properties specified in Table 2.3

Table 2.3 Characteristic and quality of biodiesel in Thailand [39].



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

2.9 Literature reviews

In 2003, Maskan and Bağci [40] studied the refining of used sunflower seed oil by various adsorbent treatments. There are six adsorbents including CaO, MgO, Mg_2CO_3, magnesium silicate, activated charcoal and bentonite. In this work, magnesium silicate and bentonite were selected for the reduction of Free Fatty Acid, viscosity and color recovery. The best combination of the adsorbents was found to be 3% bentonite and 3% magnesium silicate for the industrial refining of used sunflower seed oils.

In 2004, Safa Özcan and Adnan Özcan [41] studied adsorption of acid dyes from aqueous solutions onto acid-activated bentonite. The adsorption of two dyes, namely, Acid Red 57 (AR57) and Acid Blue 294 (AB294) onto acid-activated bentonite in aqueous solution was studied with respect to the temperature. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. The Freundlich model agrees very well with experimental that data confirmed the nature of physical adsorption of AR57 and AB294 onto acid-activated bentonite. Bentonite has proven for the removal of contaminants from wastewater. The capacity of acid-activated bentonite to adsorb AR57 and AB294 dyes used in the textile industry were (416.3 mg g^{-1} for AR57 and 119.1 mg g^{-1} for AB294) at 20 ◦C. It could be successfully applied to clean the wastewaters of the dyeing industry.

In 2007, Sun, X., Li, C., Wu, Z., Xu, X., Ren, L., and Zhao, H., [42] studied adsorption of protein from model wine solution by bentonites under different pH values, contact time and concentrations of ethanol. The results showed that ethanol molecules could broaden the protein molecules' channel to the interlayer of bentonite, and the maximum protein adsorption amount occurred under an ethanol concentration of 12% (by volume) and a pH value of 3.56. The increased single point Brunauer-Emmitt-Teller (BET) surface area (S_{BET}) from 31.5 to 71.1 m^2/g and adsorption pore volume (V_{Ads}) from 5.25 to 7.32 ml/g suggested a larger amount of active adsorption sites of the bentonite surface and a wider protein channel from the surface to the inner adsorption sites of bentonite. At the same time, higher temperature was found favorable to eliminate more proteins and it took about 20 to 40 min to reach the maximum adsorption.

In 2008, Berrios M. and Skelton R.L [43] had reported the purification methods for biodiesel. Two different methods, the use of 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. 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 soap content water washing. 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 and water content.

In 2011, M. M. Kashani Motlagh , A. A. Youzbashi and Z. Amiri Rigi, [44] studied natural bentonite from Khorasan, Iran. It was submitted to acid activation with sulphuric acid. Sample 5g were leached with 100 ml H_2SO_4 solutions of various concentrations (2–7N) at 80±2 ^{0}C for 2 hours. Chemical analysis, infrared spectroscopy and specific surface area measurements were performed in order to evaluate important structural modifications occurring as a result of acid attack. Bentonite samples were tested in order to verify their capacity to bleach soybean oil, and their performances were compared to commercial bleaching clay. The bleaching ability of the natural clay was poor when compared with that of the industrial adsorbent. Acid activation of the bentonite sample with 7N sulphuric acid yielded an adsorbent material which was highly efficient in the bleaching of the oil functioned better than the commercial clay product under the same conditions. Partial destruction of montmorillonite increased the specific surface area from 23 to 171 m^2 g^{-1}. Leaching of the bentonite with 7N sulfuric acid yielded a sample which was more efficient in bleaching than the commercial bleaching clay.

In 2011, Pálková H, Jankovič L, Zimowska M and Madejová J [45] studied alterations of the surface and morphology of tetraalkyl-ammonium modified montmorillonites upon acid treatment. The effect of short alkyl chain cations on the modification of the structure, surface and textural properties of organo-montmorillonites upon their acid treatment was investigated. Samples prepared from tetramethylammonium (Me4N+–), tetraethylammonium (Et4N+–), tetrapropylammonium (Pr4N+–) and tetrabutylammonium (Bu4N+–) salts were treated with 6 M HCl at 80 ^{0}C for 2–8 h. Acid treatment of organo-montmorillonites caused gradually release of Al and Mg from the octahedral sheets and destroy their layered structure. Pore size analysis showed the generation of pore network upon organo-montmorillonites dissolution. For longer period of acid treatment, pore volume is increased and pore size distribution curves were shifted to pores with diameter above 25 ^{0}A. The surface area of acid-treated samples is increased due to the destruction of the montmorillonite layers and formation of the SiO_2 rich reaction product. The highest value 475 m^2/g was observed for Me4N–SAz.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1. Chemicals and materials

1. Acetic acid: analytical grade; Merck
2. Bromophenol blue : analytical grade; Carlo erba
3. Ethanol: analytical grade; Merck
4. Ethyl acetate: analytical grade; Merck
5. Hydrochloric acid: analytical grade; Merck
6. Isopropyl alcohol: commercial grade; Merck
7. Methanol: analytical grade; Merck
8. Methylene blue
9. Phenolphthalein indicator: analytical grade; Merck
10. Phenol red: analytical grade; Carlo erba
11. p-Naphtholbenzein: Analytical grade; Carlo erba
12. Potassium hydroxide: analytical grade; Lab-Scan
13. Potassium iodide: analytical grade; Lab-Scan
14. Refined palm oil
15. Sodium hydroxide: analytical grade; ACS
16. Sulfuric acid: analytical grade; Carlo Erba
17. Toluene: analytical grade; Merck
18. Bentonite: commercial grade; N & P scientific CO., LTD.

3.1.2 Equipments

1. BET Surface Area Analyzer: SA 3100 Coulter
2. Fourier-Transform Infrared Spectrophotometer: Model Impact 410; Nicolet
3. X-Ray Fluorescence (XRF): Model EDX 720

3.2 Procedure

3.2.1 Preparation of crude biodiesel by transesterification of refined palm oil

Biodiesel was synthesized by transesterification. The refined palm oil in this study was bought from local market. Five hundred grams of refined palm oil were added into round bottom flask equipped with a reflux condenser. The reaction was made at 65 °C. The solution of sodium hydroxide (5.0 g) in methanol (144.82 ml, the stoichiometry of reaction required 6 mol of methanol and 1 mol of refined palm oil) was slowly added into the reaction and then the mixture was heated to 65^oC for 1.50 h. After the reaction, the glycerol was separated by separatory funnel. After removing the glycerol phase, acid activated LSB was used as adsorbent for purifying crude biodiesel [46].

3.2.2 Preparation of LSB

3.2.2.1 Preparation of raw LSB

The raw LSB from the deposit of Lopburi Thailand was provided by Thai Nippon chemical industry Co.,Ltd. The raw LSB was dried at 110 ^0C for 24 h in oven and then was ground to pass through a sieve with a mesh size of 60-80 mesh, 80-100 mesh, 100-120 mesh and 120-200 mesh.

3.2.2.2 Preparation of activated LSB.

To activate this LSB, 50 g raw LSB was slowly added to 200 ml of 0.10 - 1.00 M H_2SO_4 in deionized water (DI water), ethanol and isopropanol 500 ml of round bottom flask equipped with condenser. The reaction was heated to 100, 78 and 82.5 ^{0}C for 1, 2, 6 and 12h, respectively. The activated LSB slurry was washed thoroughly several times with distilled water until the pH reached 6 - 7. The activated LSB was dried in oven at 110 ^{0}C for 24 h and pulverized to pass through a sieve with a mesh size of 60-80, 80-100, 100-120 and 120-200 mesh.

3.2.3 Purification of crude biodiesel

3.2.3.1 Purification of crude biodiesel using acid activated LSB

The acid activation LSBs were accurately weighed and added into crude biodiesel. Then the mixture was stirred for 10 min with stirring rate 200 rpm. After removing the adsorbents by gravity for 3 h, the percentage of residue soap removal and acid value were analyzed to calculate the biodiesel purity by titration method.

- Effect of acid concentration and solvent on precipitation of soap

Activated LSB was prepared in reaction bottles. The crude biodiesel was transferred into each of bottles. By means of activated LSB 0.10, 0.25, 0.50, 0.75 and 1.00 M H_2SO_4 in DI water, ethanol and isopropanol, respectively, as adsorbents were added into crude biodiesel. These bottles were stirred for 10 min with stirring rate 200 rpm. The purified biodiesel of each of the bottles were filtered and calculated percentage of residue soap removal and acid value by titration.

- Effect of particle size on precipitation of soap

Activated LSB was prepared in reaction bottles. The crude biodiesel was transferred into each of bottles. By means of activated LSB 0.10 M H_2SO_4 in DI water (0.10M/DI) and 0.25 M H_2SO_4 in DI water (0.25M/DI) particle size 60-80, 80-100, 100-120 and 120-200 mesh, respectively, as adsorbents were added into crude biodiesel. These bottles were stirred for 10 min with stirring rate 200 rpm. The purified biodiesel of each of the bottles were filtered and calculated percentage of residue soap removal and acid value by titration

- Effect of activating time on precipitation of soap

Activated LSB was prepared in reaction bottles. The crude biodiesel was transferred into each bottle. By means of activated LSB 0.25M/DI particle size 60-80 mesh (0.25M/DI 60-80) and 0.10M/DI particle size 120-200 mesh (0.10M/DI 120-200) activating time 1, 2, 6 and 12h, respectively, as adsorbents were added into crude biodiesel. These bottles were stirred for 10 min with stirring rate 200 rpm. The purified biodiesel of each of the bottles were filtered and calculated percentage of residue soap removal and acid value by titration

- Effect of amount of adsorbents on precipitation of soap

Activated LSB was prepared in reaction bottles. The crude biodiesel was transferred into each of bottles. By means of activated LSB 0.25M/DI 60-80 mesh activating time 1h (0.25M/DI/1h 60-80) and 0.10M/DI 120-200 mesh activating time 1h (0.10M/DI/1h 120-200) 1, 3, 5, 7 and 10 %wt of adsorbents, respectively, as adsorbents were added into crude biodiesel. These bottles were stirred for 10 min with stirring rate 200 rpm. The purified biodiesel of each of the bottles were filtered and calculated percentage of residue soap removal and acid value by titration [26].

3.2.3.2 Purification of crude biodiesel using commercial bentonite and LSB

Raw LSB, activated LSB and commercial bentonite were prepared in reaction bottles. The crude biodiesel was transferred into each of bottles. By means of a raw LSB 60-80, raw LSB 120-200, activated LSB 0.25M/DI/1h 60-80, activated LSB 0.10M/DI/1h 120-200 and commercial bentonite 1, 3 and 5 %wt of adsorbents, respectively, as adsorbents were added into crude biodiesel. These bottles were stirred for 10 min with stirring rate 200 rpm. The purified biodiesel of each of the bottles was filtered and calculated percentage of residue soap removal and acid value by titration.

3.2.3.3 Purification of crude biodiesel using water washing

The crude biodiesel was separated from the glycerin, It was purified by washing gently with warm water to remove residual impurities. This process was repeated to remove close to 100% of soaps until color clear. The finished product should have a pH of 7, checked with universal indicator [19].

3.2.4 Biodiesel analysis

3.2.4.1 Determination of the amount of soap by titration method

Five grams of biodiesel sample were dissolved in 100 ml of isopropanol with 2 ml of 1% phenol red as an indicator. The mixture was titrated with 0.01 M hydrochloric acid until the color of the solution changed from red to colorless. Then, 1 ml of 0.04% bromophenol blue was added into the mixture solution and titrated with 0.01 M hydrochloric acid until the color of the solution changed from blue to yellow. This amount of 0.01 M hydrochloric acid solution was referred as “B”. The amount of soap in the biodiesel was calculated by using equation below.

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

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

3.2.4.2 Determination of the acid value (ASTM D974)

Reagent

1. p-naphtholbenzein indicator solution
2. 0.10 M Alcoholic KOH solution
3. Titration solvent (250 ml toluene + 250 ml isopropanol)

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 titrated with 0.10 M of alcoholic KOH until the green color was occurred. Blank was determined and carried out same with the sample. The ml of acid solution was recorded. The acid value was calculated as follows:

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

A = titration of sample

B = titration of blank

N = normality of alcoholic KOH solution

Alcoholic KOH = 0.6 g of potassium hydroxide
dissolved in 100 ml of isopropyl alcohol

3.2.5 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 were determined with specific surface area analyzer using BET (Brunauer-Emmett-Teller) method. It could be carried out into two steps.

Step1, Pretreatment; 40 mg 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.

3.2.6 Adsorption isotherm

3.2.6.1 Adsorption/desorption isotherm

Raw and activated LSB were described the type of adsorption isotherm using the nitrogen adsorption isotherm at 77K and relative pressures (P/Po) ranging from 0.05-1.0. The determination method was performed the same as 3.2.5. Type of adsorption isotherm was obtained from this analysis.

3.2.6.2 Adsorption isotherm of soap

The adsorption isotherms were studied to describe how soap molecules interact with the adsorbent surface of raw and activated LSB. 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 results were calculated through two equations, Langmuir and Freundlich isotherms, for determination the nature of the adsorption.

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

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

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

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

K_L = Langmuir constant (l/mg)

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

Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Where ,

x/m = adsorption per gram of adsorbent which is obtained be dividing the amount of adsorbate (x) by the weight of the adsorbent (m).

P = Pressure

k and n = constants whose values depend upon adsorbent and gas at particular temperature.

Taking the logarithms of a first equation.

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 Preparation of crude biodiesel by transesterification of refined palm oil

The transesterification reaction was monitored by thin layer chromatography (TLC). As can be seen in Fig. 4.1, triglycerides were converted to methyl ester. There were traces 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.

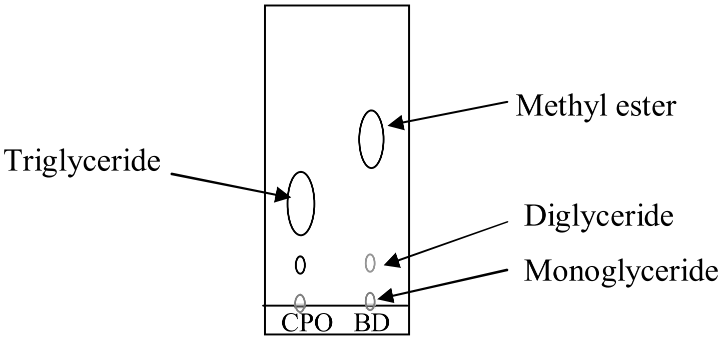


Figure 4.1 TLC of biodiesel when CPO: crude palm oil, BD: biodiesel and mobile phase: a mixture of hexane, ethyl acetate and acetic acid (90:10:1 v/v).

4.2 Purification of crude biodiesel

4.2.1 Purification of crude biodiesel using acid activated LSB

The most important parameters affecting the efficiency of an absorbent were solvent, sulfuric acid treatment, particle size, activating time and amount of adsorbents. The purified biodiesel was analyzed to determine percentage of residue soap removal.

- Effect of acid concentration and solvent on precipitation of soap

The acid concentration was effected to percentage of residue soap removal and acid value when the solvents were DI water, ethanol and isopropanol (Fig.4.2 and Fig. 4.3). The LSB was activated by using H_2SO_4 0.10, 0.25, 0.50, 0.75 and 1.00 M. Activated LSB with dilute H_2SO_4 in DI water was showed a higher performance than those of ethanol and isopropanol. The percentage of residue soap removal of 0.10 - 1.00 molar concentrations of acid in DI water were 54.57%, 56.56%, 61.62%, 68.42% and 69.34%, respectively. Due to proportion of acid value and acid strength which the acid value accordingly to ASTM D6751-02 was 0.50 mgKOH/g maximum. As a result, H_2SO_4 0.10, 0.25, 0.50, 0.75 and 1.00 M of acid value were 0.34, 0.47, 0.57, 0.62 and 0.71 mgKOH/gOil, respectively. The acid value was dramatically increased with increasing acid concentration. In this experimental condition, 0.10 and 0.25 M H_2SO_4 could be used to activate LSB and selected for further examination [47].

Table 4.1 Residue soap removal and acid value of effect of acid concentration and solvent

Activated condition		Low silica bentonite (LSB)					
		Residue soap removal (%)			Acid value (mgKOH/g)		
		DI water	Ethanol	Isopropanol	DI water	Ethanol	Isopropanol
Crude Biodiesel		0.00	0.00	0.00	0.17	0.17	0.17
Raw LSB		43.92	40.18	30.13	0.26	0.27	0.27
[H_2SO_4]	0.10 M	54.57	50.50	36.89	0.34	0.40	0.30
	0.25 M	56.56	49.82	40.31	0.47	0.54	0.43
	0.50 M	61.62	56.37	52.09	0.57	0.64	0.50
	0.75 M	68.42	70.47	54.69	0.62	0.71	0.54
	1.00 M	69.34	69.30	52.17	0.71	0.77	0.67

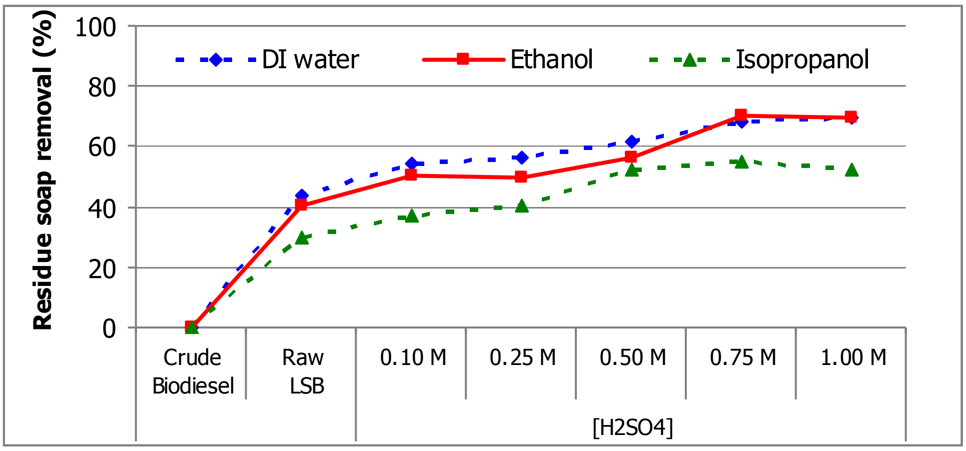


Figure 4.2 Residue soap removal of effect of acid concentration and solvent.

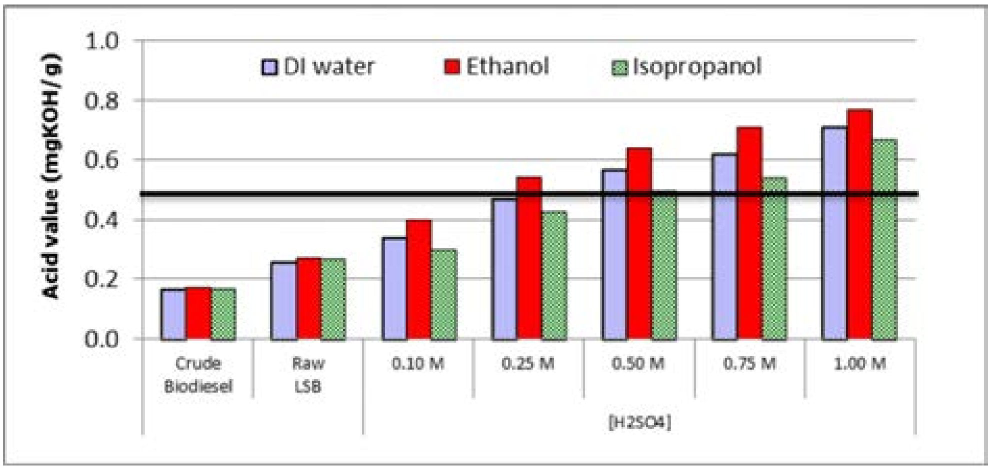


Figure 4.3 Acid value of effect of acid concentration and solvent.

- Effect of particle size on precipitation of soap

The effects of particle size of activated LSB bentonite at 0.10 and 0.25 M H_2SO_4 in DI water were determined by varying mesh size in the range of 60-80, 80-100, 100-120 and 120-200 mesh. As shown in Fig. 4.4, percentage of residue soap removal was increased when particle size decreased. In this study, acid activated LSB with 0.25 M H_2SO_4 in DI water (0.25M/DI) showed results of removing soap. They were 51.23%, 53.83%, 58.15% and 60.62%, respectively. The acid value was determined according to ASTM D6751-02. The acid value was 0.5 mgKOH/g maximum. As it seen in Fig.4.5, particle size 60-200 mesh of acid value was 0.44, 0.50, 0.54, and 0.47 mgKOH/g, respectively. As the results of acid value, 60 – 80 mesh was found to be an appropriate particle size for grinding LSB. Moreover, the removal of soap onto the acid activation of the bentonite sample with 0.10 M H_2SO_4 in DI water (0.10M/DI) was found 34.98%, 44.55%, 48.03% and 54.93%, respectively. As it was observed in Fig.4.5, acid value was 0.30, 0.27, 0.30 and 0.34 mgKOH/g, respectively. Significantly high adsorption at 0.10M/DI was achieved at 120-200 mesh. This can be explained by increasing of surface area with increasing acid concentrations.

Table 4.2 Residue soap removal and acid value of effect of particle size

Activated condition		Low silica bentonite (LSB)					
		Residue soap removal (%)			Acid value (mgKOH/g)		
		Raw LSB	0.10M/DI	0.25M/DI	Raw LSB	0.10M/DI	0.25M/DI
Crude Biodiesel		0.00	0.00	0.00	0.17	0.17	0.17
Particle size (mesh)	60-80	24.85	34.98	51.23	0.20	0.30	0.44
	80-100	35.90	44.55	53.83	0.24	0.27	0.50
	100-120	36.00	48.03	58.15	0.23	0.30	0.54
	120-200	43.86	54.93	60.62	0.26	0.34	0.47

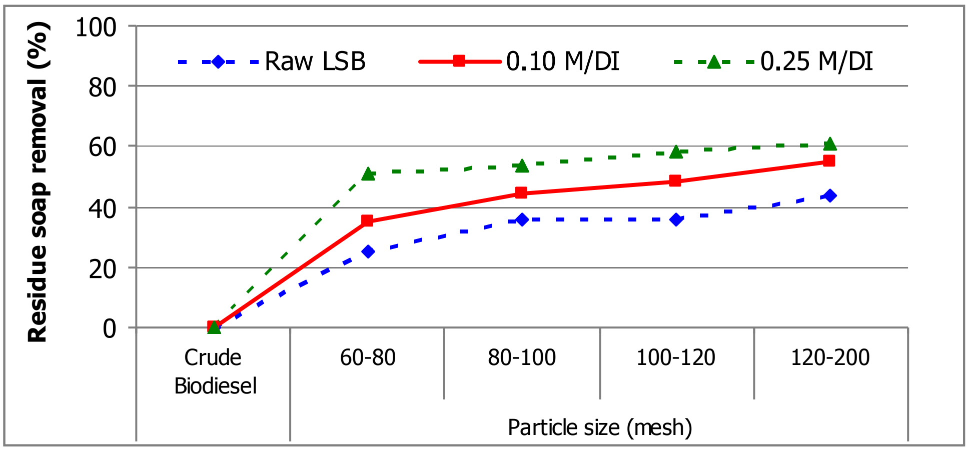


Figure 4.4 Residue soap removal of effect of particle size.

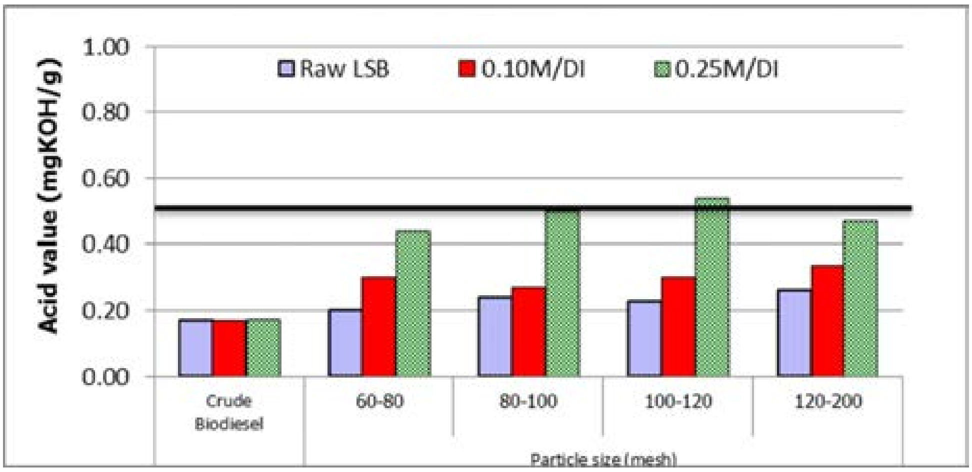


Figure 4.5 Acid value of effect of particle size.

- Effect of activating time on precipitation of soap

The influence of activating time 1, 2, 6 and 12h gave similar results of soap removal and acid value, As can be observed in Fig.4.6, percentage of residue soap removal of 0.10M/DI 120-200 mesh (0.10M/DI 120-200) was 47.00%, 48.71%, 50.33% and 49.59% whereas 0.25M/DI 60-80 mesh (0.25M/DI 60-80) was 49.63, 50.42, 52.21 and 52.34%, respectively. The acid value of 0.10M/DI 120-200 was 0.30, 0.34, 0.33 and 0.34 whereas 0.25M/DI 60-80 was 0.44, 0.44, 0.47 and 0.47 mgKOH/g, respectively. All samples were exhibited acid numbers not above the maximum limit of 0.50 mg KOH/g. Therefore, the activating time at 1, 2, 6 and 12h did not give significant different for soap removal. Activating time at 1 h was the most appropriate condition during the activated LSB purification.

Table 4.3 Residue soap removal and acid value of effect of activating time

Activated condition		Low silica bentonite (LSB)			
		Residue soap removal (%)		Acid value (mgKOH/g)	
		0.25M/DI 60-80	0.10M/DI 120-200	0.25M/DI 60-80	0.10M/DI 120-200
Crude Biodiesel		0.00	0.00	0.17	0.17
Activing time (h)	1 h	49.63	47.00	0.44	0.30
	2 h	50.42	48.71	0.44	0.34
	6 h	52.21	50.33	0.47	0.33
	12 h	52.34	49.59	0.47	0.34

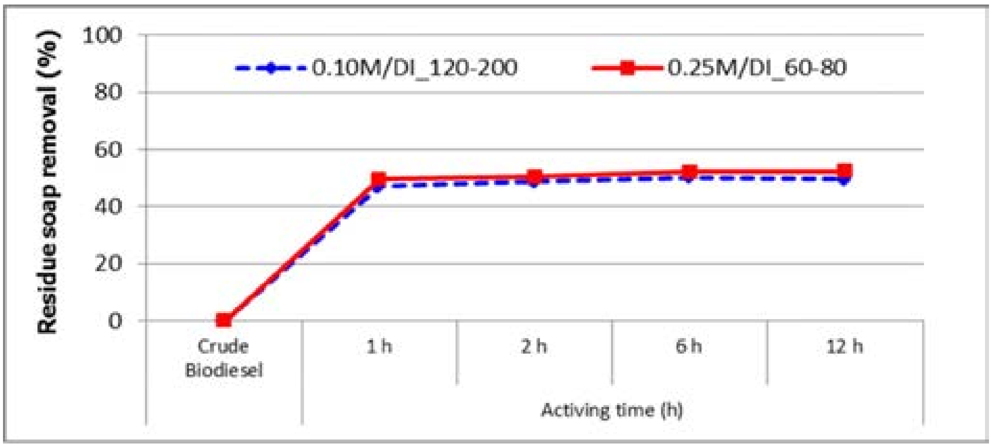


Figure 4.6 Residue soap removal of effect of activating time.

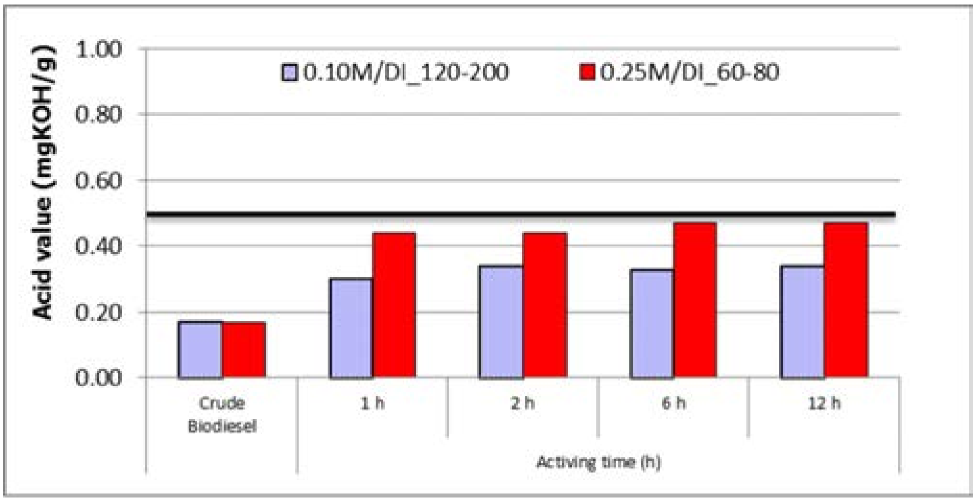


Figure 4.7 Acid value of effect of activating time.

- Effect of amount of adsorbents on precipitation of soap

The effect of adsorbents dosage was studied by increasing the amount of adsorbents from 1 to 10% activated LSB. At 0.10M/DI 120-200 activating time 1 h (0.10M/DI/1h 120-200), percentage of residue soap removal of adsorbent 1, 3, 5, 7 and 10% was 39.61, 42.20, 47.17, 48.99 and 50.14%, respectively. In Fig. 4.9, the acid value results were observed 0.30, 0.33, 0.34, 0.37 and 0.40 mgKOH/g, respectively. At 0.25M/DI 60-80 activating time 1 h (0.25M/DI/1h 60-80), the removing soap of adsorbent 1, 3, 5, 7 and 10% were 40.42, 43.75, 48.79, 49.47 and 52.18%, respectively. The acid value results were increased 0.40, 0.43, 0.44, 0.47 and 0.50 mgKOH/g, respectively. Both 0.10M/DI/1h 120-200 mesh and 0.25M/DI/1h 60-80 were showed 5% activated LSB greater than 1% activated LSB whereas 10% activated LSB nearly same 5% activated LSB. Therefore, the study was suggested that 5% activated LSB was suitable for use in adsorbents for removal of soap from crude biodiesel.

Table 4.4 Residue soap removal and acid value of effect of amount of adsorbents

Activated condition		Low silica bentonite (LSB)					
		Residue soap removal (%)			Acid value (mgKOH/g)		
		Raw LSB	0.25M/DI/1h 60-80	0.10M/DI/1h 120-200	Raw LSB	0.25M/DI/1h 60-80	0.10M/DI/1h 120-200
Crude Biodiesel		0.00	0.00	0.00	0.17	0.17	0.17
Amount of adsorbents (%)	1%	30.65	40.42	39.61	0.26	0.40	0.30
	3%	30.06	43.75	42.20	0.30	0.43	0.33
	5%	34.21	48.79	47.17	0.34	0.44	0.34
	7%	37.67	49.47	48.99	0.37	0.47	0.37
	10%	40.99	52.18	50.14	0.37	0.50	0.40

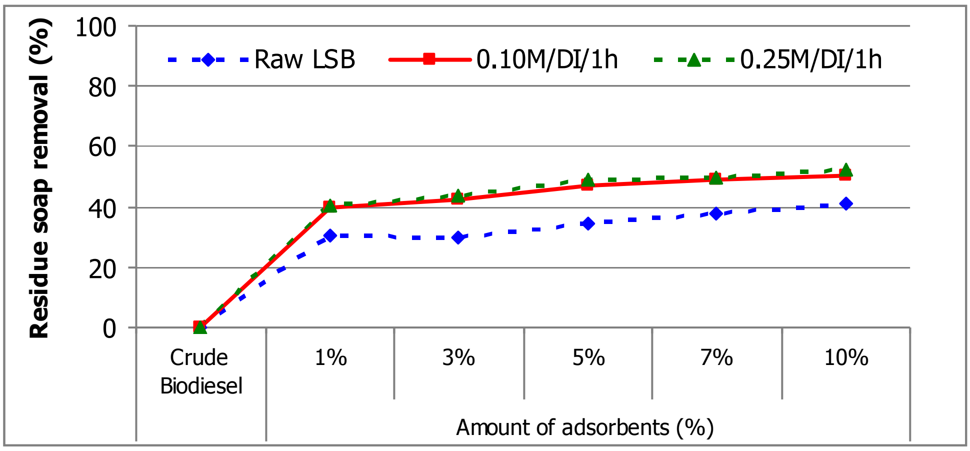


Figure 4.8 Residue soap removal of effect of amount of adsorbents.

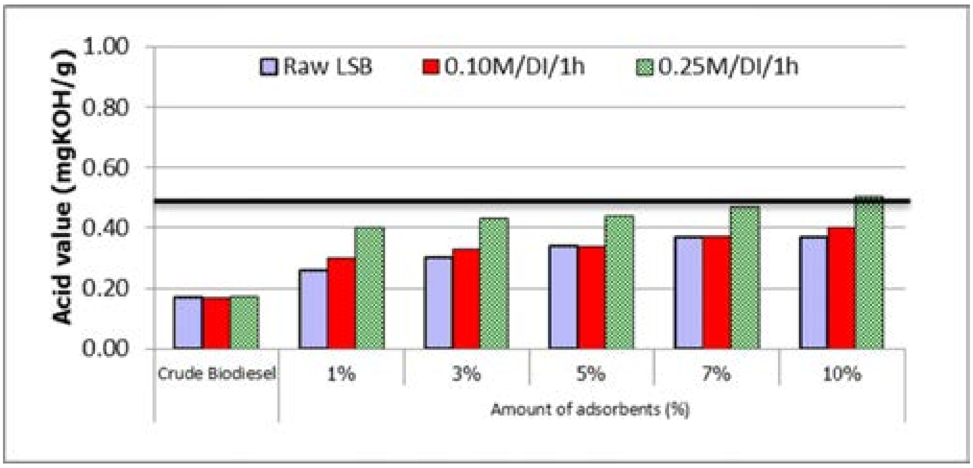


Figure 4.9 Acid value of effect of amount of adsorbents.

4.2.2 Purification of crude biodiesel using commercial bentonite and LSB

The acid activated LBS 0.10M/DI/1h 120-200 and 0.25M/DI/1h 60-80 mesh were done in order to verify their ability to removing soap from crude biodiesel. Their performances were compared with commercial bentonite. The results of percentage of residue soap removal and acid value were presented in Fig. 4.10 and Fig. 4.11. All amounts of adsorbents of acid activated LSB were showed values of acid value within the specification of biodiesel. According to the data, only samples purified by 1% of commercial bentonite (60-80 mesh and 120-200 mesh) showed values within specification, where the specification limit for acid number from ASTM D6751-02 was 0.50 mg KOH/g. Therefore, commercial bentonite 3% and 5% amount of adsorbents of acid number were above specification. It can be observed from the data, the percentage of residue soap removal in biodiesel for 1% commercial bentonite particle size 60-80 mesh and 120-200 mesh was 58.28% and 62.62%, respectively. However 5% of 0.25M/DI/1h 60-80 and 0.10M/DI/1h 120-200 were 57.22 % and 54.07%, respectively. Consequently, the ability of the 5% 0.25M/DI/1h 60-80 activated LSB was nearly same when compared with 1% commercial bentonite.

Table 4.5 Residue soap removal and acid value of crude and purified biodiesel

Adsorbent		Low silica bentonite (LSB)					
		Residue soap removal (%)			Acid value (mgKOH/g)		
		1% adsorbent	3% adsorbent	5% adsorbent	1% adsorbent	3% adsorbent	5% adsorbent
Crude Biodiesel		0.00	0.00	0.00	0.17	0.17	0.17
Raw LSB		30.77	30.28	32.57	0.27	0.30	0.34
Commercial	60-80 mesh	58.28	74.39	80.37	0.40	0.64	0.87
	120-200 mesh	62.62	78.68	88.08	0.47	0.74	0.94
Activated LSB	0.25M/DI/1h 60-80	43.78	47.05	57.22	0.44	0.43	0.44
	0.10M/DI/1h 120-200	40.72	42.94	54.07	0.30	0.33	0.34

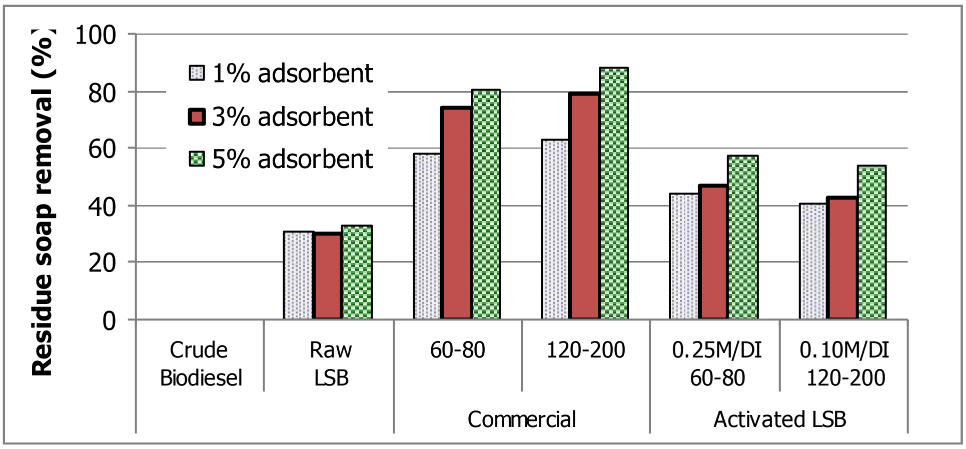


Figure 4.10 Residue soap removal of crude and purified biodiesel.

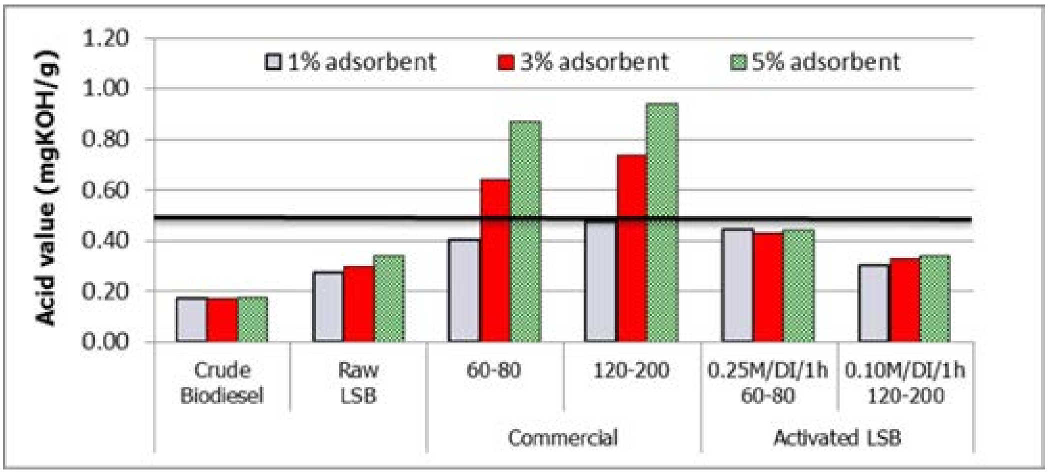


Figure 4.11 Acid value of crude and purified biodiesel.

4.2.3 Purification of crude biodiesel using water washing

The purified biodiesel properties of water washing and activated LSB washing were presented in Table 4.6. The acid value of water washing and dry washing with activated LSB 0.25M/DI/1h 60-80 and 0.10M/DI/1h 120-200 was 0.32, 0.44 and 0.34 mgKOH/g, respectively. Viscosity was 4.19, 3.88 and 3.93 cSt, respectively. All purified biodiesel samples were achieved standard (acid value < 0.5 mgKOH/g and viscosity 3.0-5.0 cSt.)

Table 4.6 Comparison of biodiesed properties between water washing and activated LSB washing

Biodiesel properties	**Standard value**	**Water washing**	**Dry washing 0.25M/DI/1h 60-80 LSB**
Acid value	<0.5 mgKOH/g	0.32	0.44
Viscosity	3.0 - 5.0 cSt	4.19	3.88
Free glycerol	<0.02	-	0.0017
Mono glycerol	<0.80	0.1892	0.3077
Di glycerol	<0.20	0.0179	-
Tri glycerol	<0.20	-	-
Total Glycerol	<0.25	0.0509	0.0802

4.3 Adsorption isotherm

4.3.1 Adsorption/desorption isotherm

Typical of adsorption isotherm of raw and acid activated LSB were measured by using the nitrogen adsorption/desorption isotherms at liquid nitrogen temperature and relative pressures (P/Po). The adsorption isotherm illustrated in Fig.4.12 – Fig.4.15

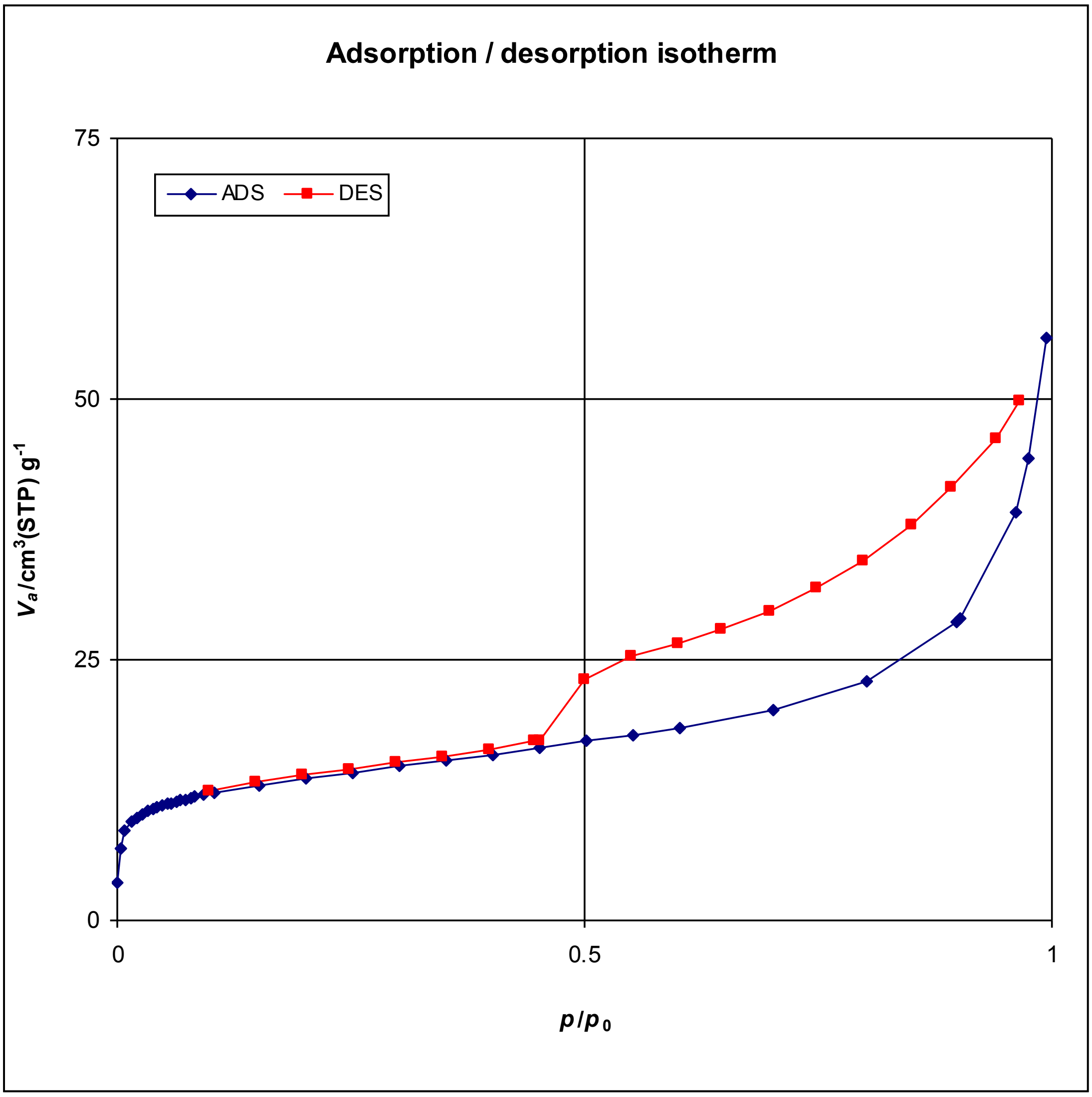


Figure 4.12 Adsorption isotherm Raw LSB 60-80 mesh when P: Pressure, P0 : Pressure saturated.

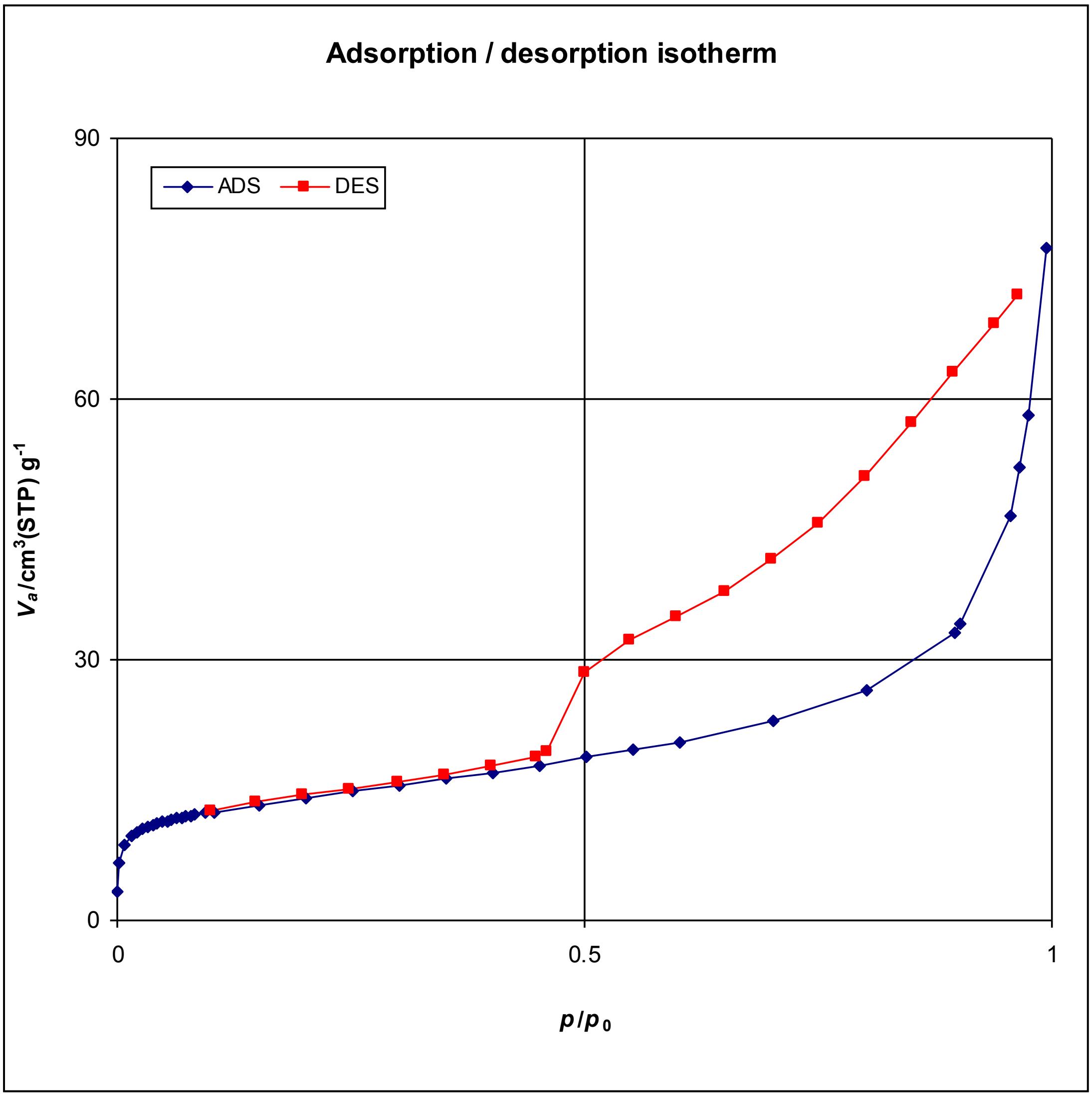


Figure 4.13 Adsorption isotherm activated LSB 0.25M/DI/1h 60-80 when P: Pressure, P0 : Pressure saturated.

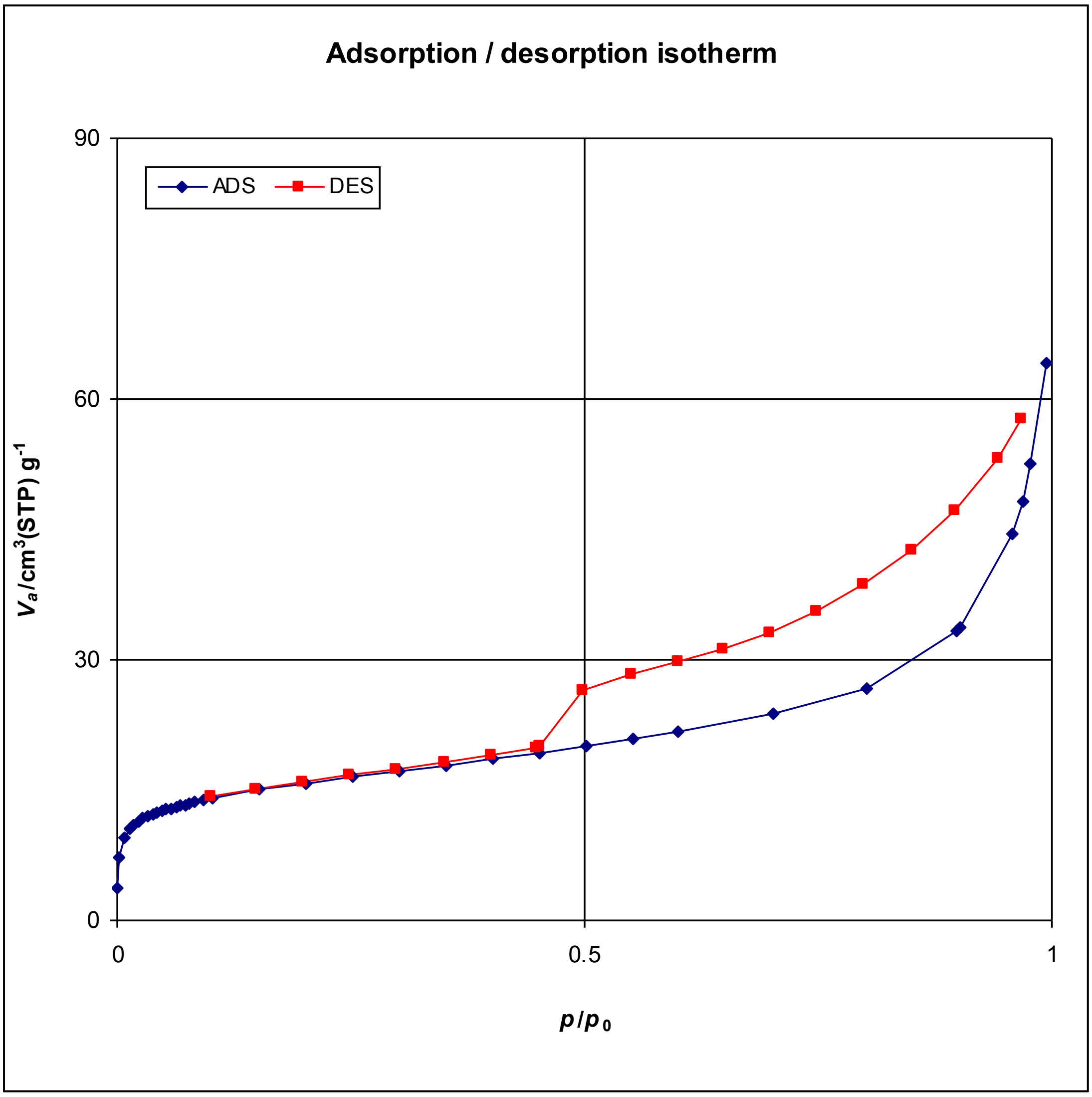


Figure 4.14 Adsorption isotherm Raw LSB 120-200 mesh when P: Pressure, P0 : Pressure saturated.

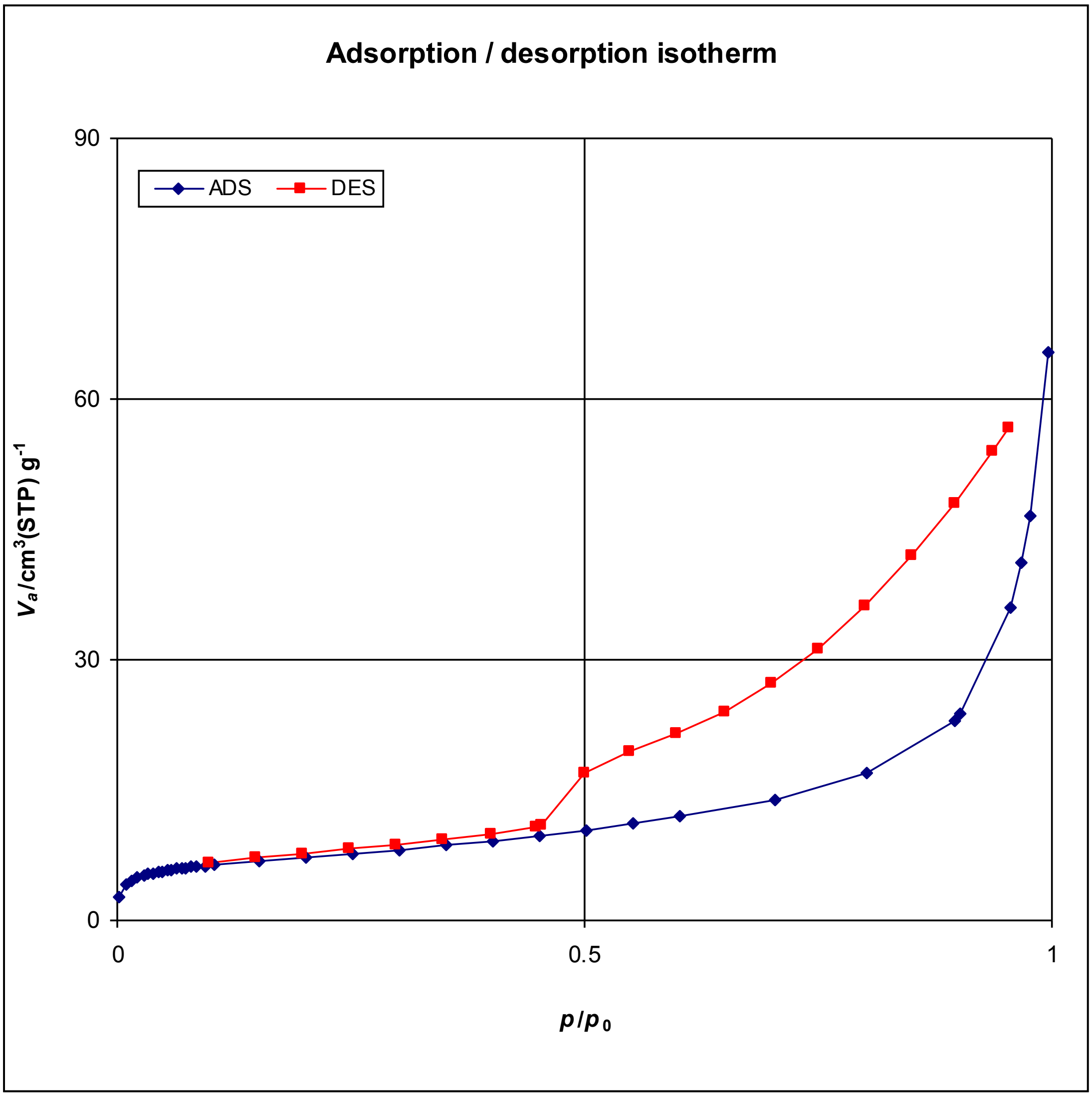


Figure 4.15 Adsorption isotherm activated LSB 0.10M/DI/1h 120-200 when P: Pressure, P0 : Pressure saturated.

From visual observation, the maximum adsorption/desorption capacity for the tested adsorption isotherm was reached in activated LSB 0.25M/DI/1h 60-80. The graphs of all LSBs were Type IV isotherm. They were hysteresis loop, which was associated with capillary condensation taking place in mesopores. The initial part of the Type IV isotherm was attributed to monolayer-multilayer adsorption since it followed the same path as the corresponding part of a Type II isotherm obtained with the given adsorption on the same surface area of the adsorbent. [35]

4.3.2 Adsorption isotherm of soap

The applicability of Langmuir and Freundlich adsorption isotherm equations was tested. Regarding adsorption isotherms, Fig. 4.16 and 4.17 showed a comparison of Langmuir and Freundlich isotherms of raw LSB. The experimental data was fit to Freundlich isotherm because the r^2 value (0.9942) was closer to 1. The values of their corresponding constants were determined from the slope and intercepts of their respective plots [34]. This adsorption behavior indicated that the adsorption took place on a heterogeneous surface. The overall adsorptive performance was dominated as a physical adsorption process.

Table 4.7 Adsorption parameters of Langmuir and Freundlich isotherm for the adsorption of soap molecule on Raw LSB

Bentonite weight (g)	concentration of soap at equilibrium C (mg/l)	Xf (mg)	Xi-Xf (mg)	X/m (mg/g)	1/C	1/(x/m)	logC	log(x/m)
Crude biodiesel	6.65	0.665	0.000	0.000	0.000	0.000	0.000	0.000
0.0102	6.02	0.602	0.062	6.111	0.166	0.164	0.780	0.786
0.0206	5.45	0.545	0.120	5.801	0.183	0.172	0.737	0.764
0.0304	5.04	0.504	0.161	5.286	0.198	0.189	0.702	0.723
0.0401	4.61	0.461	0.204	5.078	0.217	0.197	0.664	0.706
0.0502	4.29	0.429	0.235	4.688	0.233	0.213	0.633	0.671
0.0601	3.96	0.396	0.269	4.468	0.252	0.224	0.598	0.650
0.0703	3.63	0.363	0.301	4.287	0.275	0.233	0.560	0.632
0.0802	3.46	0.346	0.318	3.968	0.289	0.252	0.540	0.599
0.0901	3.22	0.322	0.343	3.803	0.310	0.263	0.508	0.580
0.1001	2.98	0.298	0.367	3.668	0.336	0.273	0.474	0.564

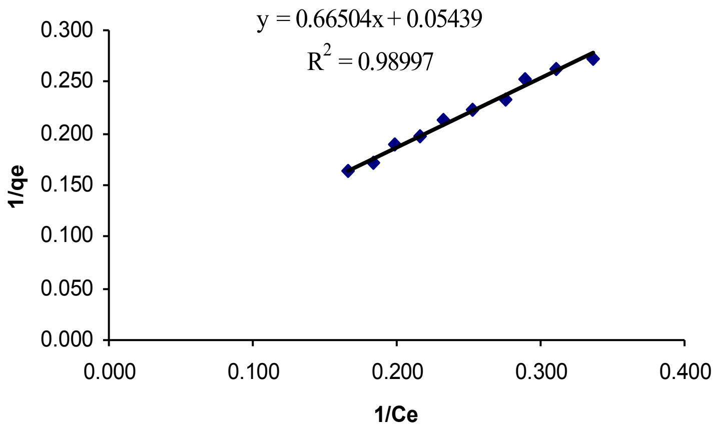


Figure 4.16 Adsorption Langmuir isotherms of raw LSB.

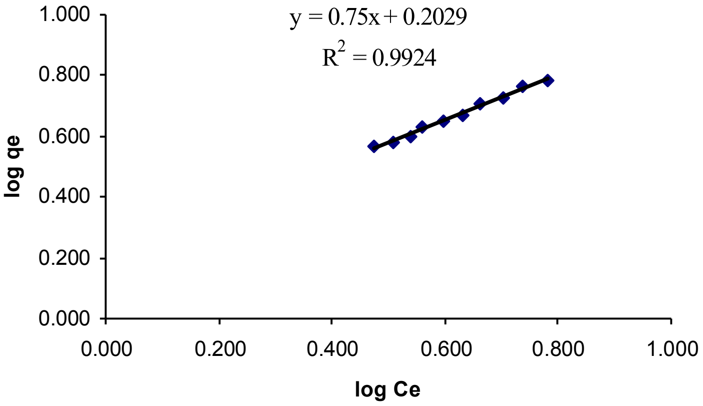


Figure 4.17 Adsorption Freundlich isotherms of raw LSB.

A plot of log x/m against log Ce gave a straight line. The slope and intercept were corresponded to 1/n and log K_F, respectively. The values of these constants were summarized in Tables 4.8 – 4.9

Table 4.8 Adsorption parameters of Freundlich isotherm for the adsorption of soap molecule on activated LSB 0.25M/DI/1h 60-80.

Bentonite weight (g)	concentration of soap at equilibrium C (mg/l)	Xf (mg)	Xi-Xf (mg)	X/m (mg/g)	logCe	log(x/m)
Crude biodiesel	5.62	0.562	0.000	0.000	0.000	0.000
0.0101	5.36	0.536	0.129	12.746	0.729	1.105
0.0202	4.45	0.445	0.220	10.878	0.648	1.037
0.0300	3.96	0.396	0.269	8.958	0.598	0.952
0.0402	3.47	0.347	0.318	7.904	0.540	0.898
0.0501	3.09	0.309	0.356	7.100	0.490	0.851
0.0602	2.66	0.266	0.399	6.623	0.425	0.821
0.0701	2.48	0.248	0.417	5.945	0.394	0.774
0.0803	2.26	0.226	0.439	5.464	0.354	0.737
0.0900	2.04	0.204	0.461	5.119	0.310	0.709
0.1001	1.94	0.194	0.471	4.703	0.288	0.672

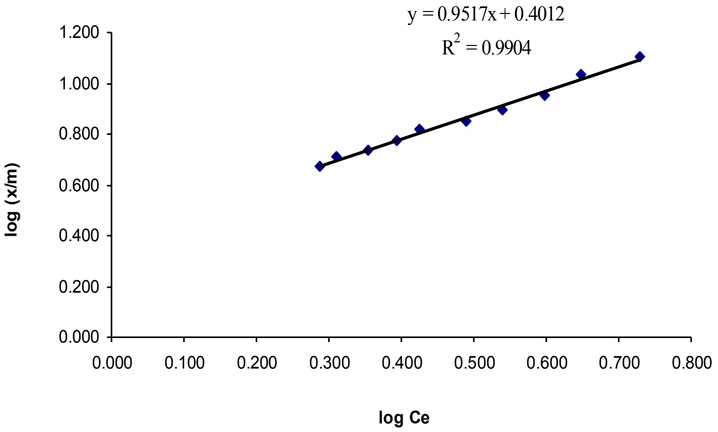


Figure 4.18 Adsorption Freundlich isotherms of activated LSB 0.25M/DI/1h 60-80.

Table 4.9 Adsorption parameters of Freundlich isotherm for the adsorption of soap molecule on and activated LSB 0.10M/DI/1h 100-200.

Bentonite weight (g)	concentration of soap at equilibrium C (mg/l)	Xf (mg)	Xi-Xf (mg)	X/m (mg/g)	logCe	log(x/m)
Crude biodiesel	6.10	0.610	0.000	0.000	0.000	0.000
0.0100	5.93	0.593	0.072	7.173	0.773	0.856
0.0201	5.31	0.531	0.134	6.653	0.725	0.823
0.0305	4.76	0.476	0.189	6.188	0.678	0.792
0.0403	4.38	0.438	0.227	5.626	0.641	0.750
0.0501	4.01	0.401	0.264	5.264	0.603	0.721
0.0600	3.70	0.370	0.295	4.912	0.568	0.691
0.0704	3.44	0.344	0.321	4.556	0.537	0.659
0.0805	3.18	0.318	0.347	4.307	0.502	0.634
0.0903	2.96	0.296	0.369	4.083	0.471	0.611
0.1000	2.69	0.269	0.396	3.957	0.430	0.597

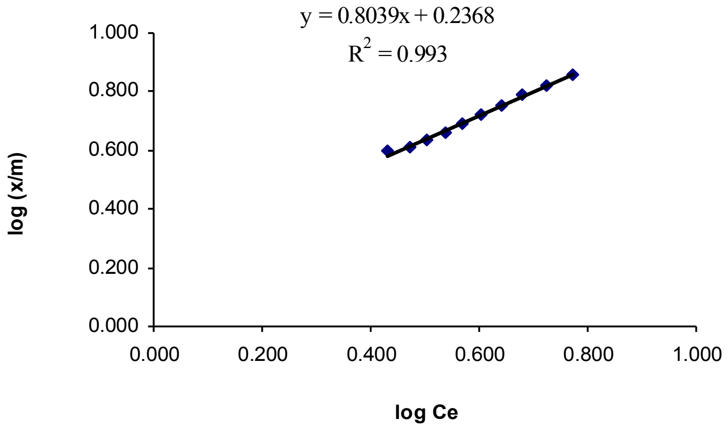


Figure 4.19 Adsorption Freundlich isotherms of activated LSB 0.1M/DI/1h 100-200.

The activated LSB samples were evaluated in order to verify their efficiency to remove soap from crude biodiesel. Their performances were compared with raw LSB. The favorable adsorption of the adsorption isotherm was determined from Freundlich constants. K_F was indicated of the adsorption capacity of the adsorbent. The result of K_F was determined in Table 4.10. The activated LSB 0.25 M/DI/1h 60-80 and 0.10M/DI/1h 120-200 (2.519 and 1.725 mg/g, respectively) were better than raw LSB (1.596 mg/g). Therefore, activated LSB was more adsorption capacity than raw LSB adsorption and 0.25 M/DI/1h 60-80 was sutiable for remove soap from crude biodiedel greater than 0.10M/DI/1h 120-200. The other Freundlich constant, n was measured of the deviation from linearity of the adsorption and used to verify types of adsorption. It was suggested that if n below unity indicated that adsorption was a chemical process; whereas, n above unity was associated with favourable adsorption and physical process. The results showed that n of raw LSB, activated LSB 0.25 M/DI/1h 60-80 and 0.10M/DI/1h 120-200 were 1.333, 1.051 and 1.244, respectively. Consequently, all LSB samples (n higher unity) were desired adsorption as a physical adsorption.

Table 4.10 Adsorption parameters of Freundlich isotherm for the adsorption of soap molecule on raw and activated LSB.

Adsorbent	Freundlich parameters		
	K_F (mg/g)	n	R^2
Raw LSB	1.596	1.333	0.9924
0.25M/DI/1h 60-80	2.519	1.051	0.9904
0.10M/DI/1h 120-200	1.725	1.244	0.9930

4.4 Characterization

For the better determination of these results, the raw LSB and acid activated LSB were analyzed in detail through BET, XRF and FTIR.

4.4.1 BET (Brunauer-Emmett-Teller)

The specific surface area (S_{BET}), pore volume (Vp) and pore diameter (dp) of raw and activated LSB were calculated using the BET method. The obtained value was shown in Table 4.11. The values of specific surface area and pore volume of raw LSB particle size 60-80 mesh were 25.398 m^2g^{-1} and 0.0912 cm^3g^{-1}respectively. After activated by 0.25M/DI 60-80 was increased 48.928 m^2g^{-1} and 0.1126 cm^3g^{-1} respectively whereas average pore diameter was decreased from 14.3610 to 9.2030 nm. After that decreased particle size to 120-200 mesh, The specific surface area of activated LSB after the treatment with H_2SO_4 0.10 M was increased from 47.559 to 56.889 m^2g^{-1} and pore volume from 0.0816 to 0.0942 cm^3g^{-1}. In contrast, average pore diameter was decreased from 6.8619 to 6.6294 nm. The results shown that the specific surface area and pore volume were increased by acid activation which improved the adsorption capacity due to acid dissolved cations (Mg^{2+}, Fe^{2+}, Al^{3+}) into the octahedral sheets by exchanged Al^{3+}, Fe^{3+} and Mg^{2+} with H^+ ions leading to destruction of montmorillonite layers and modification of the bentonite crystalline structure. Moreover, the formation in the porous bentonite was produces 2-50 nm mesopores. This formation can be explained by XRF and FT-IR. [49].

Table 4.11 Surface properties of raw LSB and activated LSB

Adsorbent		**S_{BET} [m^2 g^{-1}]**	**Vp [cm^3 g^{-1}]**	**dp (av) [nm]**
60-80 mesh	Raw LSB	25.398	0.0912	14.3610
	0.25M/DI/1h LSB	48.928	0.1126	9.2030
100-120 mesh	Raw LSB	47.559	0.0816	6.8619
	0.10M/DI/1h LSB	56.866	0.0942	6.6294

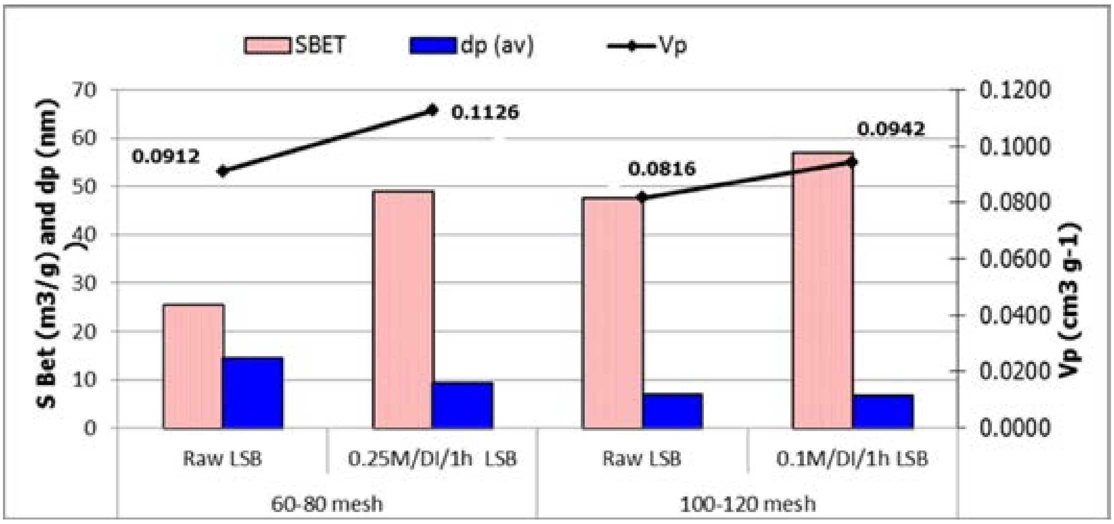


Figure 4.20 Surface properties of raw LSB and activated LSB.

4.4.2 XRF (X-Ray Fluorescence)

Chemical analysis was analyzed by XRF (X-Ray Fluorescence). The adsorption efficiency results of raw and acid activated LSB were given quantitatively in Table 4.12 and displayed in Fig.4.21, as % wt. of metal oxide. Acid activated dissolved the cations from the LSB during acid treatment. Two groups of cations were distinguished. First group contained Ca^{2+}, Na^{+}, K^{+} and second group included in Al^{3+}, Fe^{3+} and Mg^{2+}. The chemical composition of acid activated bentonite 0.25M/DI/1h and 0.10M/DI/1h shown the results in material with higher silica oxide content (SiO_2 were 43.24% and 41.04, respectively) and lower metal oxide (Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O and TiO_2). Due to the quantity of Ca^{2+}, Na^{+}, and K^{+} removal by acid treatment corresponds to the bentonite interlayer hydrated phase. Consequently, first group was dissolved under mild condition. Second group contains Al^{3+}, Fe^{3+} and Mg^{2+} which belonging to octahedral sheet. Dissolution of Al^{3+}, Fe^{3+} and Mg^{2+}cations was increased by acid activated. However, the Si^{4+} cations at tetrahedral of bentonite was not dissolved by acid treatment. Increasing of Si^{4+} correspond with quantity of these cations from the octahedral sheet and interlayer of the bentonite. The tetrahedral cations were normally the most resistant to acid attack while the octahedral cations exchangeable cations [44].

Table 4.12 Chemical analysis of raw LSB and activated LBS

Chemical analysis	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	Loss
Raw LSB	40.77	10.20	25.78	3.59	9.32	2.85	1.64	1.58	4.27
0.10M/DI/1h LSB	41.04	9.03	25.36	2.76	8.27	2.74	1.37	1.37	8.06
0.25M/DI/1h LSB	43.24	8.56	24.89	2.54	8.02	2.51	1.29	1.30	7.65

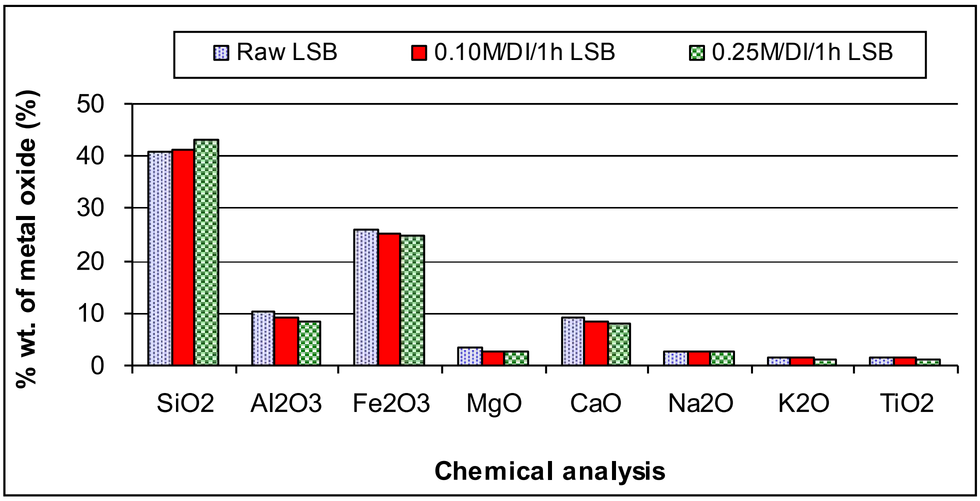


Figure 4.21 Chemical analysis of raw LSB and activated LBS.

4.4.3 FT-IR (Fourier Transform InfraRed)

FTIR spectra of characteristic of bentonite was two wavelength ranges 400–1800 cm^{-1} and 3000–4000 cm^{-1}. The IR spectra in wavelength range 600–4000 cm^{-1} was presented in Fig. 4.22 - 4.25. The characteristic of bentonite was identified at the wavenumber 3620 cm^{-1}, the band which corresponds to stretching vibrations of the Al–OH and Si–OH bonds was occured. The broad band was shown maximum at 3450 cm^{-1} corresponds to stretching vibrations of –OH, whereas bending vibration was deformed at 1640 cm^{-1}. The band at 1135 cm^{-1} was indicated presence of the Si–O vibrations behind the plane and the band at 529 cm^{-1}was related to bending vibrations Si–O, for Si–O–Al and Si–O–Si. The bands at 915 cm^{-1}, 875 cm^{-1}

and 844 cm^{-1} were originated from bending vibrations of Al–Al–OH, Al–Fe–OH and Al–Mg–OH. An appearance of absorption bands at 640–680 cm^{-1} was indicated the presence of the Si–O–Si bonds [50].

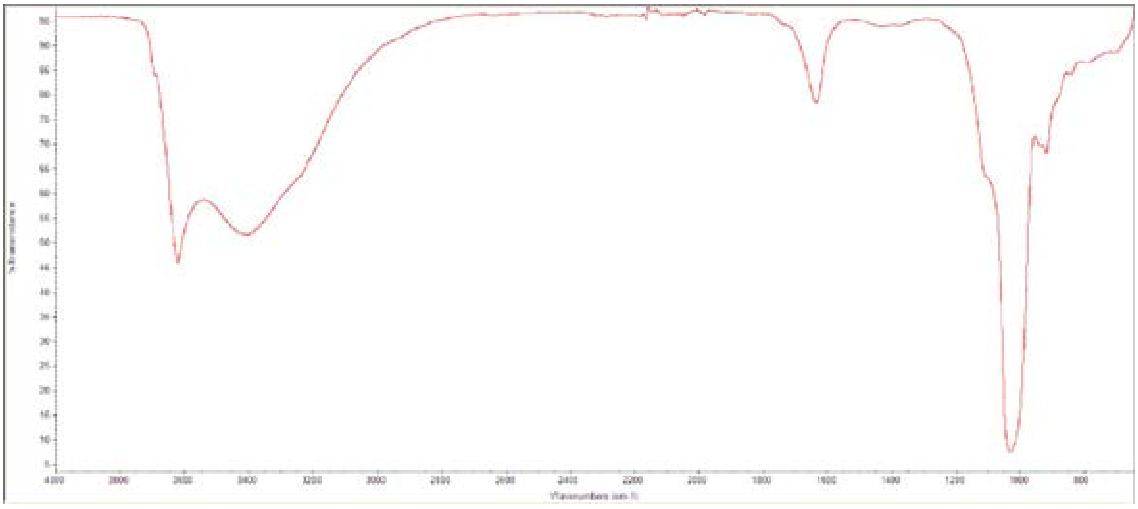


Figure 4.22 IR spectrum of raw LSB 60-80 mesh.

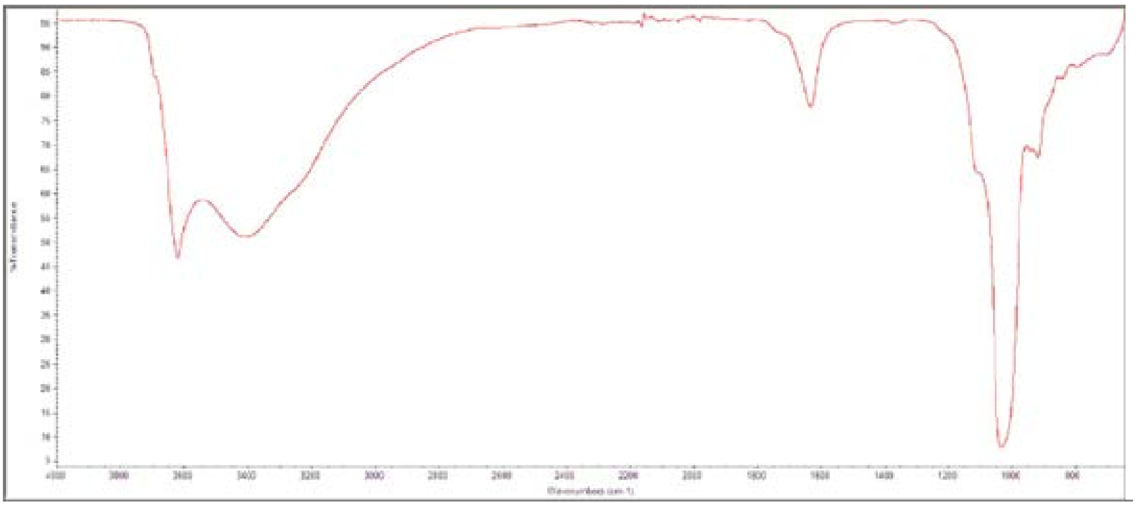


Figure 4.23 IR spectrum of activated LSB 0.25M/DI/1h.

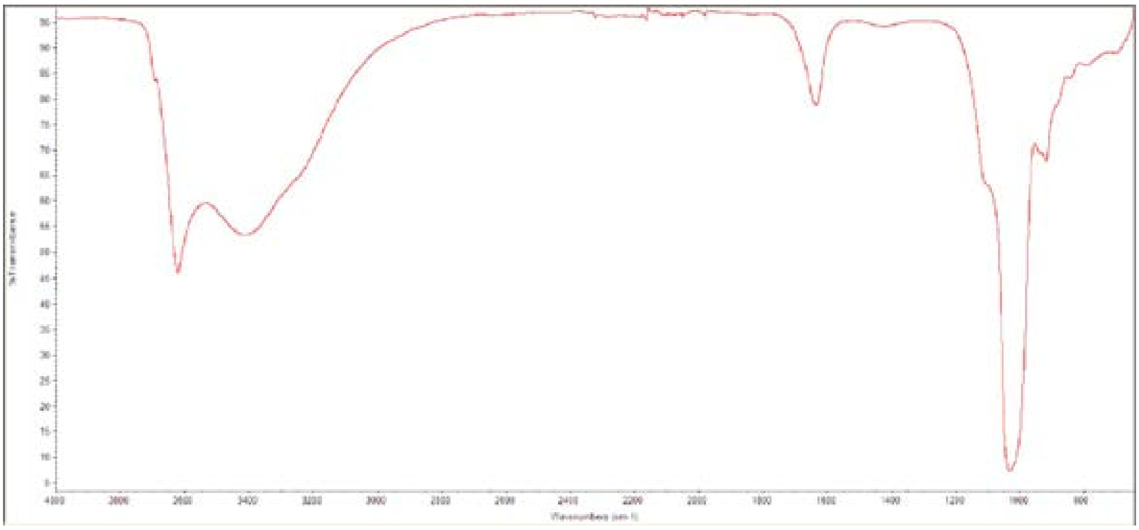


Fig 4.24 IR spectrum of raw LSB 120-200 mesh

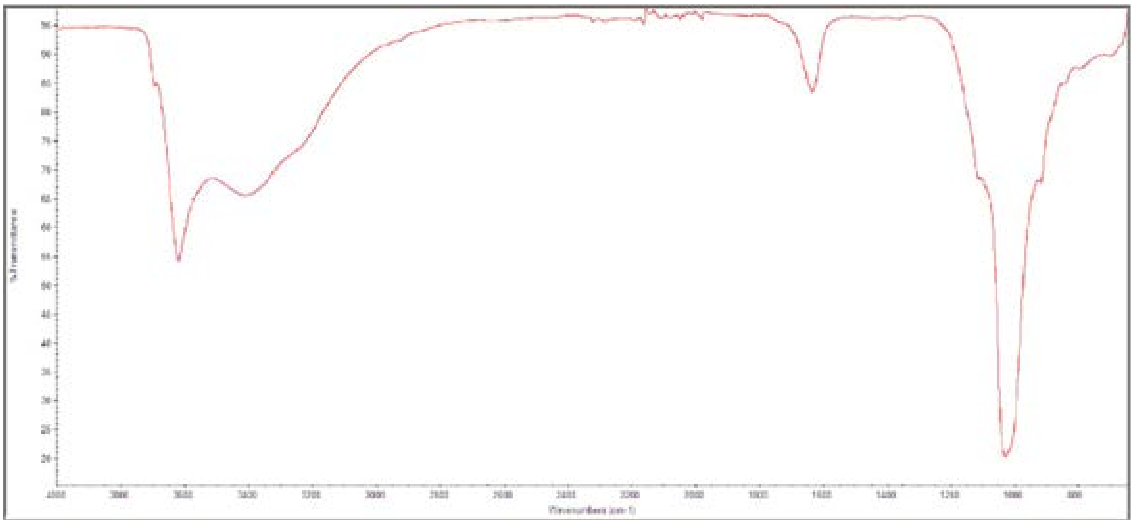


Figure 4.25 IR spectrum of activated LSB 0.10M/DI/1h.

The results from FTIR analysis showed that bands involving octahedral Al^{3+} were reduced in the montmorillonite structure. After the acid treatment, the only differences intensity of this band was decreased of the Al–Al–OH band at 915 cm^{-1} due to the loss of Al from it structure, as compared to intensity band of raw LSB.

CHAPTER V

CONCLUSION AND SUGGESTION

Purification of biodiesel by adsorption with activated low silica bentonite (LSB) was studied. This work was to investigate acid activated condition and the potential of acid-activated LSB for the removal of soap from crude biodiesel. Chemical composition and adsorptive properties of the acid activated LSB can be changed depending on the acid concentration, activating time, particle size and amount of adsorbents. The optimize adsorption capabilities of LSB were activated with 0.25 M H_2SO_4 in DI water reflux at 100 ^{0}C for 1 hour. Using of 5% of activated bentonite with 60-80 mesh size were presented about 57.22% average soap removal performances from crude biodiesel. The adsorption isotherm was agreed with Freundlich model that data indicated predominance the nature of physical. The physical and chemical characteristics of raw and acid activated LSB were analyzed by BET, XRF and FTIR. The results were showed that the adsorption efficiency of acid activated LSB improved and led to significant increase of surface area on the LSB from 25.398 to 48.928 m^2 g^{-1}. Because of destruction of the montmorillonite layers and formation of the SiO_2 rich reaction were described by XRF. Furthermore, acid activation increased the surface area of LSB that influenced by the adsorption efficiency. The consequent decomposition of montmorillonite structure could be seen by FTIR at 915 cm^{-1}. The overall chemical analysis and physical properties results contribute to the conclusion that the activated LSB can be converted into great adsorbent for adsorption soap from crude biodiesel. The dry washing was found to be appropriate method that can be used to replace water washing for biodiesel purification.

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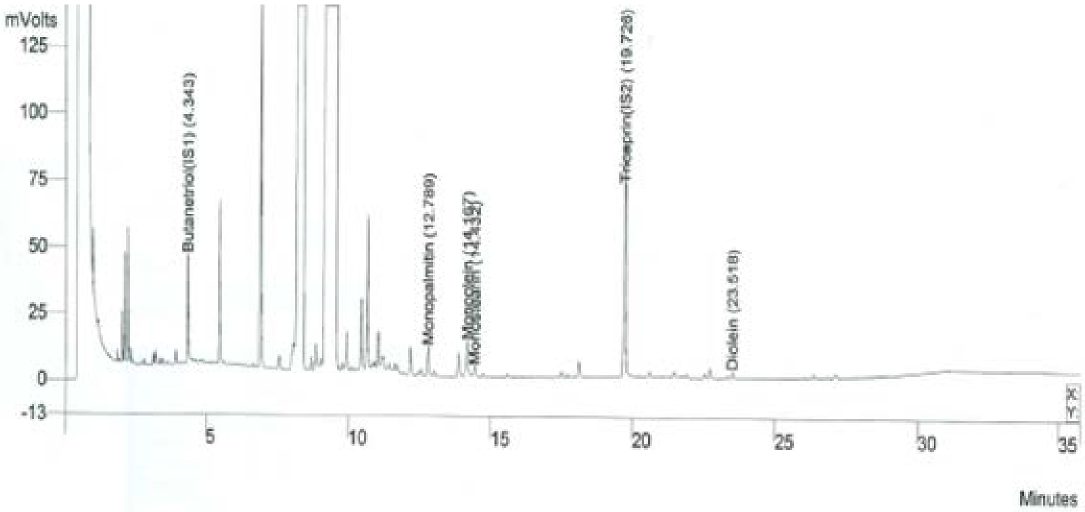
APPENDICES

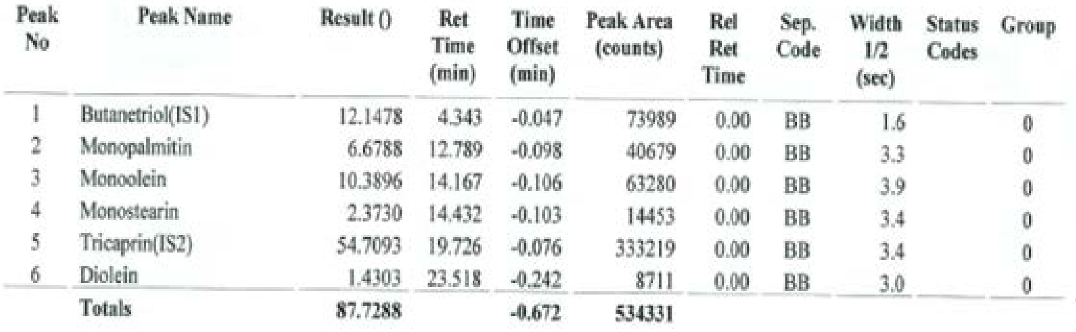
APPENDIX A

GC CHROMATOGRAM OF BIODIESEL

Appendix A

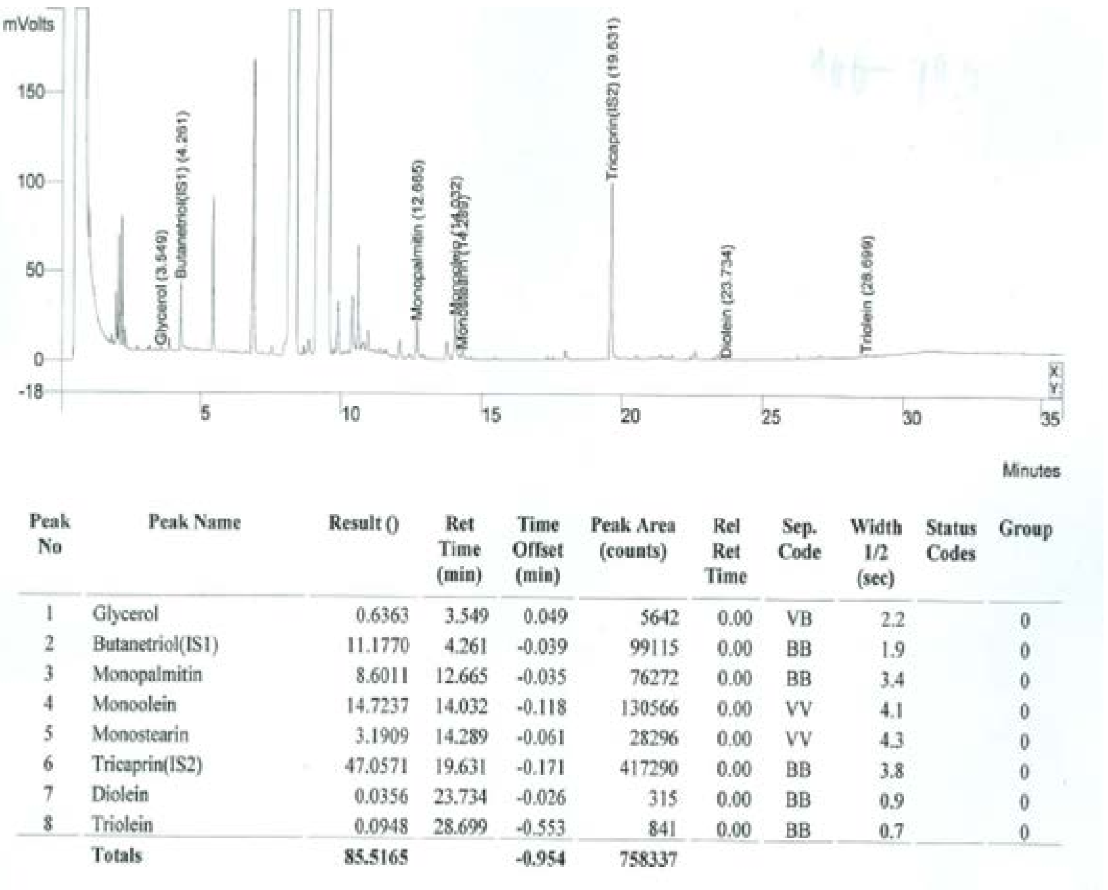
GC chromatogram





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

Figure A1 GC chromatogram of biodiesel treated with water.



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

Figure A2 GC chromatogram of biodiesel treated with 0.25M/DI/1h 60-80.

APPENDIX B

CALCULATIONS

Appendix B

CALCULATIONS

1. Calculation of soap content

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

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

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

W = weight of untreated biodiesel (g)

303.4 = average molecular weight of sodium oleate

Table B1 Residue soap removal of effect of acid concentration and solvent.

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
Crude biodiesel	1	5.0222	5.70	4948.27	5089.89	0.00
	2	5.0003	6.00	5231.52		
Activated LSB in DI water						
Raw LSB	1	5.0340	3.40	2944.68	2854.23	43.92
	2	5.0480	3.20	2763.78		
[H_2SO_4] 0.10 M	1	5.0374	3.20	2769.59	2312.09	54.57
	2	5.0714	3.10	1854.60		
[H_2SO_4] 0.25 M	1	5.0234	2.50	2169.77	2211.20	56.56
	2	5.0322	2.60	2252.62		
[H_2SO_4] 0.50 M	1	5.0226	2.30	1996.51	1953.45	61.62
	2	5.0208	2.20	1910.39		

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
[H_2SO_4] 0.75 M	1	5.0203	1.80	1563.20	1607.50	68.42
	2	5.0150	1.90	1651.79		
[H_2SO_4] 1.00 M	1	5.0340	1.90	1645.56	1560.56	69.34
	1	5.0230	1.70	1475.56		
Activated LSB in ethanol						
Raw LSB	1	5.0222	3.60	3125.22	3044.87	40.18
	2	5.0003	3.40	2964.53		
[H_2SO_4] 0.10 M	1	5.0295	2.80	2427.20	2519.49	50.50
	2	5.0079	3.00	2611.79		
[H_2SO_4] 0.25 M	1	5.0346	3.00	2597.94	2554.29	49.82
	2	5.0360	2.90	2510.64		
[H_2SO_4] 0.50 M	1	5.0026	2.50	2178.80	2220.77	56.37
	2	5.0097	2.60	2262.74		
[H_2SO_4] 0.75 M	1	5.0979	1.60	1368.36	1502.83	70.47
	2	5.0594	1.90	1637.29		
[H_2SO_4] 1.00 M	1	5.0151	1.70	1477.89	1562.84	69.30
	2	5.0272	1.90	1647.78		
Activated LSB in isopropanol						
Raw LSB	1	5.0334	4.00	3464.74	3556.22	30.13
	2	5.0200	4.20	3647.69		
[H_2SO_4] 0.10 M	1	5.0156	3.60	3129.33	3212.45	36.89
	2	5.0272	3.80	3295.56		
[H_2SO_4] 0.25 M	1	5.0298	3.50	3033.82	3037.99	40.31
	2	5.0160	3.50	3042.17		
[H_2SO_4] 0.50 M	1	5.0098	2.80	2436.74	2438.82	52.09
	2	5.0013	2.80	2440.89		
[H_2SO_4] 0.75 M	1	5.0107	2.70	2349.30	2306.29	54.69
	2	5.0085	2.60	2263.28		

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
[H_2SO_4] 1.00 M	1	5.0149	2.80	2434.27	2434.65	52.17
	2	5.0133	2.80	2435.04		

Table B2 Residue soap removal of effect of particle size

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
Crude biodiesel	1	5.0222	5.70	4948.27	5089.89	0.00
	2	5.0003	6.00	5231.52		
Raw LSB						
60-80 mesh	1	5.0177	4.20	3649.36	3824.93	24.85
	2	5.0132	4.60	4000.51		
80-100 mesh	1	5.0222	3.80	3298.85	3262.47	35.90
	2	5.0003	3.70	3226.10		
100-120 mesh	1	5.0295	3.80	3294.06	3257.63	36.00
	2	5.0079	3.70	3221.21		
120-200 mesh	1	5.0346	3.40	2944.33	2857.35	43.86
	2	5.0360	3.20	2770.36		
[H_2SO_4] 0.10 M in DI water						
60-80 mesh	1	5.0026	3.80	3311.77	3309.42	34.98
	2	5.0097	3.80	3307.08		
80-100 mesh	1	5.0151	3.40	2955.78	2822.13	44.55
	2	5.0272	3.10	2688.49		
100-120 mesh	1	5.0334	3.20	2771.79	2645.22	48.03
	2	5.0200	2.90	2518.64		
120-200 mesh	1	5.0726	2.70	2320.63	2293.83	54.93
	2	5.0002	2.60	2267.04		

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
[H_2SO_4] 0.25 M in DI water						
60-80 mesh	1	5.0098	2.90	2523.87	2482.33	51.23
	2	5.0013	2.80	2440.89		
80-100 mesh	1	5.0107	2.60	2262.28	2349.83	53.83
	2	5.0085	2.80	2437.38		
100-120 mesh	1	5.0149	2.30	1999.58	2130.34	58.15
	2	5.0133	2.60	2261.11		
120-200 mesh	1	5.0032	2.20	1917.11	2004.44	60.62
	2	5.0023	2.40	2091.77		

Table B3 Residue soap removal of effect of activating time

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
Crude biodiesel	1	5.0222	5.70	4948.27	5089.89	0.00
	2	5.0003	6.00	5231.52		
[H_2SO_4] 0.25 M in DI water 60-80 mesh						
1 h	1	5.0176	2.90	2519.85	2563.74	49.63
	2	5.0159	3.00	2607.62		
2 h	1	5.0050	2.80	2439.08	2523.43	50.42
	2	5.0156	3.00	2607.78		
6 h	1	5.0327	2.90	2512.29	2432.48	52.21
	2	5.0035	2.70	2352.68		
12 h	1	5.0328	2.90	2512.24	2425.86	52.34
	2	5.0317	2.70	2.339.49		

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
[H_2SO_4] 0.10 M in DI water 120-200 mesh						
1 h	1	5.0058	3.00	2612.88	2697.90	47.00
	2	5.0133	3.20	2782.91		
2 h	1	5.0053	3.10	2700.25	2610.40	48.71
	2	5.0162	2.90	2520.55		
6 h	1	5.0004	2.80	2441.33	2527.97	50.33
	2	5.0025	3.00	2614.61		
12 h	1	5.0182	2.80	2432.67	2565.78	49.59
	2	5.0078	3.10	2698.90		

Table B4 Residue soap removal of effect of amount of adsorbents

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
Crude biodiesel	1	5.0222	5.70	4948.27	5089.89	0.00
	2	5.0003	6.00	5231.52		
Raw LSB						
1%	1	5.0032	3.90	3398.51	3529.96	30.65
	2	5.0012	4.20	3661.40		
3%	1	5.0202	4.00	3473.85	3559.97	30.06
	2	5.0222	4.20	3646.09		
5%	1	5.0218	4.00	3472.75	3348.84	34.21
	2	5.0021	3.70	3224.94		
7%	1	5.0197	3.70	3213.63	3172.36	37.67
	2	5.0128	3.60	3131.08		
10%	1	5.0002	3.50	3051.78	3003.51	40.99
	2	5.0160	3.40	2955.25		

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
[H_2SO_4] 0.25 M in DI water reflux 1 h 60-80 mesh						
1%	1	5.0223	3.40	2951.54	3032.65	40.42
	2	5.0407	3.60	3113.75		
3%	1	5.0478	3.20	2763.89	2863.20	43.75
	2	5.0037	3.40	2962.51		
5%	1	5.0228	3.10	2690.84	2606.68	48.79
	2	5.0123	2.90	2522.51		
7%	1	5.0000	3.10	2703.11	2572.02	49.47
	2	5.0012	2.80	2440.93		
10%	1	5.0217	2.80	2430.97	2434.15	52.18
	2	5.0086	2.80	2437.33		
[H_2SO_4] 0.10 M in DI water reflux 1 h 120-200 mesh						
1%	1	5.0006	3.60	3138.72	3073.62	39.61
	2	5.0721	3.50	3008.52		
3%	1	5.0416	3.50	3026.72	2942.08	42.20
	2	5.0351	3.30	2857.45		
5%	1	5.0005	3.00	2615.65	2661.55	47.71
	2	4.9920	3.10	2707.44		
7%	2	5.0092	3.00	2611.11	2596.55	48.99
	1	5.0657	3.00	2581.99		
10%	1	5.0002	2.95	2572.21	2537.95	50.14
	2	5.0500	2.90	2503.68		

Table B5 Residue soap removal of crude and purified biodiesel

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
Crude biodiesel	1	5.0222	5.70	4948.27	5089.89	0.00
	2	5.0003	6.00	5231.52		
1% adsorbents						
Raw LSB	1	5.0222	3.90	3385.66	3523.86	30.77
	2	5.0003	4.20	3662.06		
Commercial 60-80	1	5.0357	2.30	1991.32	2123.58	58.28
	2	5.0250	2.60	2255.85		
Commercial 120-200	1	5.0340	2.20	1905.38	1902.74	62.62
	2	5.0480	2.20	1900.10		
0.25M/DI/1h 60-80	1	5.0234	3.30	2864.10	2861.60	43.78
	2	5.0322	3.30	2859.09		
0.10M/DI/1h 120-200	1	5.0374	4.00	3461.99	3017.25	40.72
	2	5.0714	4.30	2572.50		
3% adsorbents						
Raw LSB	1	5.0372	4.00	3462.13	3548.68	30.28
	2	5.0372	4.20	3635.23		
Commercial 60-80	1	5.0203	1.50	1302.67	1303.36	74.39
	2	5.0150	1.50	1304.05		
Commercial 120-200	1	5.0226	1.30	1128.46	1085.25	78.68
	2	5.0208	1.20	1042.03		
0.25M/DI/1h 60-80	1	5.0217	3.00	2604.61	2695.06	47.05
	2	5.0086	3.20	2785.52		
0.10M/DI/1h 120-200	2	5.0340	3.50	3031.29	2904.41	42.94
	1	5.0230	3.20	2777.53		

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average	%Soap removed
5% adsorbents						
Raw LSB	1	5.0228	4.00	3472.05	3432.20	32.57
	2	5.0123	3.90	3392.34		
Commercial 60-80	1	5.0295	1.20	1040.23	998.94	80.37
	2	5.0079	1.10	957.66		
Commercial 120-200	1	5.0478	0.80	690.97	606.88	88.08
	2	5.0037	0.60	522.80		
0.25M/DI/1h 60-80	1	5.0026	2.50	2178.80	2177.25	57.22
	2	5.0097	2.50	2175.71		
0.10M/DI/1h 120-200	1	5.0346	2.70	2338.14	2337.82	54.07
	2	5.0360	2.70	2337.49		

2. Determination of the acid value (ASTM D974)

Reagent

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

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

The acid value was calculated as follows:

Acid value = $[(A - B) \times N \times 56.1]$ / weight of sample
A = titration of sample
B = titration of blank
N = normality of alcoholic KOH solution
Alcoholic KOH = 0.6 g of potassium hydroxide dissolved in 100 ml of isopropyl alcohol

Table B6 Acid value of effect of acid concentration and solvent

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
Crude biodiesel	1	2.0106	0.100	0.05	0.134	0.17
	2	2.0048	0.125	0.05	0.202	
Activated LSB in DI water						
Raw LSB	1	2.0309	0.150	0.05	0.265	0.26
	2	2.0535	0.150	0.05	0.263	
[H_2SO_4] 0.10 M	1	2.0047	0.150	0.05	0.269	0.34
	2	2.0082	0.200	0.05	0.403	
[H_2SO_4] 0.25 M	1	2.0073	0.250	0.05	0.537	0.47
	2	2.0064	0.200	0.05	0.403	
[H_2SO_4] 0.50 M	1	2.0028	0.250	0.05	0.538	0.57
	2	2.0048	0.275	0.05	0.605	
[H_2SO_4] 0.75 M	1	2.0371	0.300	0.05	0.662	0.62
	2	2.0658	0.275	0.05	0.587	
[H_2SO_4] 1.00 M	1	2.005	0.325	0.05	0.739	0.71
	2	2.0038	0.300	0.05	0.673	

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
Activated LSB in ethanol						
Raw LSB	1	2.0115	0.125	0.05	0.201	0.27
	2	2.0063	0.175	0.05	0.336	
[H_2SO_4] 0.10 M	1	2.0064	0.200	0.05	0.403	0.40
	2	2.0032	0.200	0.05	0.404	
[H_2SO_4] 0.25 M	1	2.0012	0.250	0.05	0.539	0.54
	2	2.0085	0.250	0.05	0.537	
[H_2SO_4] 0.50 M	2	2.0082	0.300	0.05	0.671	0.64
	1	2.0036	0.275	0.05	0.605	
[H_2SO_4] 0.75 M	1	2.0042	0.300	0.05	0.672	0.71
	2	2.0032	0.325	0.05	0.740	
[H_2SO_4] 1.00 M	1	2.0054	0.350	0.05	0.807	0.77
	2	2.0002	0.325	0.05	0.741	
Activated LSB in isopropanol						
Raw LSB	1	2.0034	0.150	0.05	0.269	0.27
	2	2.0124	0.150	0.05	0.268	
[H_2SO_4] 0.10 M	1	2.0002	0.150	0.05	0.270	0.30
	2	2.0014	0.175	0.05	0.337	
[H_2SO_4] 0.25 M	1	2.0243	0.200	0.05	0.399	0.43
	2	2.0126	0.225	0.05	0.469	
[H_2SO_4] 0.50 M	1	2.0042	0.250	0.05	0.538	0.50
	2	2.0054	0.225	0.05	0.470	
[H_2SO_4] 0.75 M	1	2.0065	0.250	0.05	0.537	0.54
	2	2.0014	0.250	0.05	0.539	
[H_2SO_4] 1.00 M	1	2.0052	0.300	0.05	0.672	0.67
	2	2.0021	0.300	0.05	0.673	

Table B7 Acid value of effect of particle size

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
Crude biodiesel	1	2.0106	0.100	0.05	0.134	0.17
	2	2.0048	0.125	0.05	0.202	
Raw LSB						
60-80 mesh	1	2.0238	0.125	0.05	0.200	0.20
	2	2.0021	0.125	0.05	0.202	
80-100 mesh	1	2.0031	0.125	0.05	0.202	0.24
	2	2.0013	0.150	0.05	0.269	
100-120 mesh	1	2.0241	0.150	0.05	0.266	0.23
	2	2.0045	0.125	0.05	0.202	
120-200 mesh	1	2.0035	0.150	0.05	0.269	0.26
	2	2.0673	0.150	0.05	0.261	
[H_2SO_4] 0.10 M in DI water						
60-80 mesh	1	2.0015	0.150	0.05	0.269	0.30
	2	2.0066	0.175	0.05	0.336	
80-100 mesh	1	2.0094	0.150	0.05	0.268	0.27
	2	2.0072	0.150	0.05	0.269	
100-120 mesh	1	2.0074	0.175	0.05	0.336	0.30
	2	2.0054	0.150	0.05	0.269	
120-200 mesh	1	2.0042	0.175	0.05	0.336	0.34
	2	2.0012	0.175	0.05	0.337	

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
[H_2SO_4] 0.25 M in DI water						
60-80 mesh	1	2.0043	0.225	0.05	0.471	0.44
	2	2.0034	0.200	0.05	0.404	
80-100 mesh	1	2.0065	0.250	0.05	0.537	0.50
	1	2.0004	0.225	0.05	0.472	
100-120 mesh	1	2.0007	0.250	0.05	0.539	0.54
	2	2.0027	0.250	0.05	0.538	
120-200 mesh	1	2.0002	0.225	0.05	0.472	0.47
	2	2.0021	0.225	0.05	0.471	

Table B8 Acid value of effect of activating time

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
Crude biodiesel	1	2.0106	0.100	0.05	0.134	0.17
	2	2.0048	0.125	0.05	0.202	
[H_2SO_4] 0.25 M in DI water 60-80 mesh						
1 h	1	2.0027	0.225	0.05	0.471	0.44
	2	2.0054	0.200	0.05	0.403	
2 h	1	2.0192	0.200	0.05	0.400	0.44
	2	2.0017	0.225	0.05	0.471	
6 h	1	2.0025	0.225	0.05	0.471	0.47
	2	2.0054	0.225	0.05	0.470	
12 h	1	2.0322	0.225	0.05	0.464	0.47
	2	2.0092	0.225	0.05	0.470	

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
[H_2SO_4] 0.10 M in DI water 120-200 mesh						
1 h	1	2.0005	0.175	0.05	0.337	0.30
	2	2.0075	0.150	0.05	0.269	
2 h	1	2.0031	0.175	0.05	0.336	0.34
	2	2.0135	0.175	0.05	0.335	
6 h	2	2.0182	0.175	0.05	0.334	0.33
	1	2.0326	0.175	0.05	0.332	
12 h	1	2.0044	0.175	0.05	0.336	0.34
	2	2.0006	0.175	0.05	0.337	

Table B9 Acid value of effect of amount of adsorbents

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
Crude biodiesel	1	2.0106	0.100	0.05	0.134	0.17
	2	2.0048	0.125	0.05	0.202	
Raw LSB						
1%	1	2.0641	0.150	0.05	0.261	0.26
	2	2.0145	0.150	0.05	0.268	
3%	1	2.0075	0.175	0.05	0.336	0.30
	2	2.0073	0.150	0.05	0.269	
5%	1	2.0042	0.175	0.05	0.336	0.34
	2	2.0030	0.175	0.05	0.336	
7%	1	2.0067	0.175	0.05	0.336	0.37
	2	2.0034	0.200	0.05	0.404	
10%	1	2.0043	0.175	0.05	0.336	0.37
	2	2.0074	0.200	0.05	0.403	

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
[H_2SO_4] 0.25 M in DI water reflux 1 h 60-80 mesh						
1%	1	2.0038	0.200	0.05	0.404	0.40
	2	2.0032	0.200	0.05	0.404	
3%	1	2.0043	0.200	0.05	0.403	0.43
	2	2.0307	0.225	0.05	0.465	
5%	1	2.0065	0.200	0.05	0.403	0.44
	2	2.0074	0.225	0.05	0.470	
7%	2	2.0054	0.225	0.05	0.470	0.47
	1	2.0021	0.225	0.05	0.471	
10%	1	2.0055	0.250	0.05	0.538	0.50
	2	2.0021	0.225	0.05	0.471	
[H_2SO_4] 0.10 M in DI water reflux 1 h 120-200 mesh						
1%	1	2.0106	0.150	0.05	0.268	0.30
	2	2.0136	0.175	0.05	0.335	
3%	1	2.0057	0.175	0.05	0.336	0.33
	2	2.0228	0.175	0.05	0.333	
5%	1	2.0011	0.175	0.05	0.337	0.34
	2	2.0058	0.175	0.05	0.336	
7%	1	2.0031	0.175	0.05	0.336	0.37
	2	1.9985	0.200	0.05	0.405	
10%	1	2.0082	0.200	0.05	0.403	0.40
	2	2.0097	0.200	0.05	0.402	

Table B10 Acid value of crude and purified biodiesel

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
Crude biodiesel	1	2.0106	0.100	0.05	0.134	0.17
	2	2.0048	0.125	0.05	0.202	
1% adsorbents						
Raw LSB	1	2.0126	0.150	0.05	0.268	0.27
	2	2.0048	0.150	0.05	0.269	
Commercial 60-80	1	2.0010	0.200	0.05	0.404	0.40
	2	2.0036	0.200	0.05	0.404	
Commercial 120-200	1	2.0079	0.200	0.05	0.403	0.47
	2	2.0003	0.250	0.05	0.539	
0.25M/DI/1h 60-80	1	2.0083	0.225	0.05	0.470	0.44
	2	2.0024	0.200	0.05	0.404	
0.10M/DI/1h 120-200	1	2.0047	0.175	0.05	0.336	0.30
	2	2.0032	0.150	0.05	0.269	
3% adsorbents						
Raw LSB	1	2.0010	0.150	0.05	0.269	0.30
	2	2.0048	0.175	0.05	0.336	
Commercial 60-80	1	2.0071	0.275	0.05	0.604	0.64
	2	2.0188	0.300	0.05	0.668	
Commercial 120-200	1	2.0098	0.325	0.05	0.738	0.74
	2	2.0148	0.325	0.05	0.736	
0.25M/DI/1h 60-80	1	2.0279	0.225	0.05	0.465	0.43
	2	2.0026	0.200	0.05	0.404	
0.10M/DI/1h 120-200	2	2.0087	0.175	0.05	0.335	0.33
	1	2.0338	0.175	0.05	0.331	

Condition	Experiment	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
5% adsorbents						
Raw LSB	1	2.0010	0.175	0.05	0.337	0.34
	2	2.0053	0.175	0.05	0.336	
Commercial 60-80	1	2.0045	0.375	0.05	0.874	0.87
	2	2.0025	0.375	0.05	0.875	
Commercial 120-200	1	2.0078	0.400	0.05	0.940	0.94
	2	2.0062	0.400	0.05	0.941	
0.25M/DI/1h 60-80	1	2.0075	0.225	0.05	0.470	0.44
	2	2.0032	0.200	0.05	0.404	
0.10M/DI/1h 120-200	1	2.0054	0.200	0.05	0.403	0.34
	2	2.0031	0.150	0.05	0.269	

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

2.1 Free Glycerol

Table B11 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 B12 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
$\Sigma X = 3.576$	$\Sigma Y = 2.750$	$\Sigma X^2 = 2.113$	$\Sigma Y^2 = 1.297$	$\Sigma XY = 1.654$

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

From obtained data can calculate:

$$a_g = \frac{(N\times\Sigma XY)-(\Sigma X\times\Sigma Y)}{(N\times\Sigma X^2)-(\Sigma Y)^2} = \frac{(8\times1.654)-(3.576\times2.750)}{(8\times2.113)-1.297} = 0.8264$$

$$b_g = \frac{\Sigma Y-(a_g\times\Sigma X)}{N} = \frac{2.750-(0.8264\times3.576)}{8} = -\ 0.0256$$

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

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

$$= \frac{(8\times1.654)-(3.576\times2.750)}{\sqrt{(8\times2.113-12.787)\,(8\times1.297-7.563)}} = 0.9995$$

2.2 Monoglyceride

Table B13 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 B14 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
$\Sigma X = 11.007$	$\Sigma Y = 7.625$	$\Sigma X^2 = 18.707$	$\Sigma Y^2 = 9.023$	$\Sigma XY = 12.992$

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

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

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

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

2.3 Diglyceride

Table B15 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 B16 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
$\Sigma X = 3.019$	$\Sigma Y = 2.750$	$\Sigma X^2 = 1.529$	$\Sigma Y^2 = 1.297$	$\Sigma XY = 1.408$

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

$$a_d = \frac{(8\times1.408) - (3.019\times2.750)}{(8\times1.529) - 7.563} = 0.9489$$

$$b_d = \frac{2.750 - (0.9489\times3.019)}{8} = -\ 0.1429$$

$$r = \frac{(8\times1.408) - (3.019\times2.750)}{\sqrt{(8\times1.529 - 9.112)\ (8\times1.297 - 7.563)}} = 0.9999$$

2.4 Triglyceride

Table B17 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 B18 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
$\Sigma X = 2.296$	$\Sigma Y = 2.250$	$\Sigma X^2 = 0.889$	$\Sigma Y^2 = 0.859$	$\Sigma XY = 0.874$

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

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

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

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

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:

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

Where:

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

A_g = peak area of the glycerol

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

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

m = mass of sample (milligrams)

a_g and b_g = constants coming from regression method for glycerol

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

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

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

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

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

ΣA_{mi}, ΣA_{di}, ΣA_{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:

$$G\mathrm{T} = G + 0.255\,M + 0.146\,D + 0.103\,T$$

Where: $G\mathrm{T}$ = 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 B19 The percentage of free glycerol of biodiesel

Samples		Peak area (Sample)	Peak area (IS1)	Weight of sample (mg)	%Free
Water washing biodiesel	1	-	73989	100	-
0.25M/DI/1h 60-80 LSB	1	5642	99115	99.5	0.0017

Table B20 The percentage of monoglyceride of biodiesel

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Mono
Water washing biodiesel	1	118412	333219	100	0.1892
0.25M/DI/1h 60-80 LSB	1	235135	417290	99.5	0.3077

Table B21 The percentage of diglyceride of biodiesel

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Di
Water washing biodiesel	1	8711	333219	100	0.0179
0.25M/DI/1h 60-80 LSB	1	-	417290	99.5	-

Table B22 The percentage of triglyceride of biodiesel

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Tri
Water washing biodiesel	1	-	333219	100	-
0.25M/DI/1h 60-80 LSB	1	-	417290	99.5	-

Table B23 The percentage of total glycerin of biodiesel

Samples		Free glycerol	Mono	Di	Tri	Total glycerin
Water washing biodiesel	1	-	0.1892	0.0179	-	0.0509
0.25M/DI/1h 60-80 LSB	1	0.0017	0.3077	-	-	0.0803

APPENDIX C

VISCOSITY

Appendix C

VISCOSITY

1.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 Spass from the first to the second timing mark. The time of sample used was recorded.

The viscosity was calculated as follows:

viscosity = Ct

C = Constant of viscometer tube (mm^2/s^2)

time = measured flow times for $t1$ and $t2$, respectively(s)

Table C1 Viscosity of purified biodiesel by water washing and activated LSB dry washing

Purification method	Experiment	Time 1 (s)	Time 2 (s)	Constants of tube	Viscosity (cSt)	Average
Water Washing	1	289	289	0.01434	4.153	4.19
	2	295	295	0.01434	4.237	
0.25M/DI/1h 60-80 LSB	1	270	272	0.01434	3.886	3.88
	2	269	271	0.01434	3.872	
0.10M/DI/1h 120-200 LSB	1	274	276	0.01434	3.944	3.93
	2	273	274	0.01434	3.922	

APPENDIX D

ADSORPTION ISOTHERM

Appendix D

ADSORPTION ISORTHEM

1. Determination of the Adsorption isotherm of soap

The adsorption isotherms were studied to describe how soap molecules interact with the adsorbent surface of activated clay, diatomite and LSB. 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 ^{o}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.

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

Where:
x/m = the amount of soap adsorbed per unit of adsorbent at equilibrium (mg/g)
C_e = the concentration of soap at equilibrium(mg/l)
n = the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg/g)
K_L = Langmuir constant (l/mg)

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

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).

Table D1 Adsorption parameters of Langmuir and Freundlich isotherm for the adsorption of soap molecule on Raw LSB

Raw LSB weight (g)	Experiment	Weight of sample (g)	Titrant (mL)	concentration of soap at equilibrium C (mg/l)	Average
Crude biodiesel	1	5.0322	7.70	6.67	6.65
	2	5.0003	7.60	6.63	
0.0102	1	5.0032	7.00	6.10	6.02
	2	5.0620	6.90	5.94	
0.0206	1	5.0001	6.30	5.49	5.45
	2	5.0036	6.20	5.40	
0.0304	1	5.0050	5.80	5.05	5.04
	2	5.0230	5.80	5.03	
0.0401	1	5.0024	5.20	4.53	4.61
	2	5.0125	5.40	4.70	
0.0502	1	5.0524	4.90	4.23	4.29
	2	5.0032	5.00	4.36	
0.0601	1	5.0041	4.60	4.01	3.96
	2	5.0048	4.50	3.92	

Raw LSB weight (g)	Experiment	Weight of sample (g)	Titrant (mL)	concentration of soap at equilibrium C (mg/l)	Average
0.0703	1	5.0064	4.20	3.66	3.63
	2	5.0721	4.20	3.61	
0.0802	1	5.0657	4.00	3.44	3.46
	2	5.0091	4.00	3.48	
0.0901	1	5.0003	3.70	3.23	3.22
	2	5.0056	3.70	3.22	
0.1001	1	5.0045	3.40	2.96	2.98
	2	5.0764	3.50	3.01	

Table D2 Adsorption parameters of Freundlich isotherm for the adsorption of soap molecule on activated LSB 0.25M/DI/1h 60-80

Raw LSB weight (g)	Experiment	Weight of sample (g)	Titrant (ml)	concentration of soap at equilibrium C (mg/l)	Average
Crude biodiesel	1	5.0020	6.40	5.58	5.62
	2	5.0013	6.50	5.67	
0.0101	1	5.0021	6.20	5.40	5.36
	2	5.0001	6.10	5.32	
0.0202	1	5.0002	5.20	4.53	4.45
	2	5.0005	5.00	4.36	
0.0300	1	5.0004	4.60	4.01	3.96
	2	5.0268	4.50	3.90	
0.0402	1	5.0380	4.00	3.46	3.47
	2	5.0196	4.00	3.47	
0.0501	1	5.0047	3.60	3.14	3.09
	2	5.0182	3.50	3.04	

Raw LSB weight (g)	Experiment	Weight of sample (g)	Titrant (ml)	concentration of soap at equilibrium C (mg/l)	Average
0.0602	1	5.0010	3.00	2.62	2.66
	2	5.0021	3.10	2.70	
0.0701	1	5.0005	2.80	2.44	2.48
	2	5.0081	2.90	2.52	
0.0803	1	5.0230	2.50	2.17	2.26
	2	5.0002	2.70	2.35	
0.0900	1	5.0601	2.40	2.07	2.04
	2	5.0008	2.30	2.01	
0.1001	1	5.0312	2.20	1.91	1.94
	2	5.0632	2.30	1.98	

Table D3 Adsorption parameters of Freundlich isotherm for the adsorption of soap molecule on and activated LSB 0.1M/DI/1h 100-200

Raw LSB weight (g)	Experiment	Weight of sample (g)	Titrant (mL)	concentration of soap at equilibrium C (mg/l)	Average
Crude biodiesel	1	5.0020	7.10	6.19	6.10
	2	5.0013	6.90	6.02	
0.0100	1	5.0021	6.80	5.93	5.93
	2	5.0020	6.80	5.93	
0.0201	1	5.0003	6.20	5.41	5.31
	2	5.0087	6.00	5.22	
0.0305	1	5.0332	5.60	4.85	4.76
	2	5.0324	5.40	4.68	
0.0403	1	5.0531	5.10	4.40	4.38
	2	5.0023	5.00	4.36	

Raw LSB weight (g)	Experiment	Weight of sample (g)	Titrant (mL)	concentration of soap at equilibrium C (mg/l)	Average
0.0501	1	5.0025	4.60	4.01	4.01
	2	5.0035	4.60	4.01	
0.0600	1	5.0022	4.30	3.75	3.70
	2	5.0010	4.20	3.66	
0.0704	1	5.0030	4.00	3.49	3.44
	2	5.0085	3.90	3.39	
0.0805	1	5.0003	3.60	3.14	3.18
	2	5.0024	3.70	3.22	
0.0903	1	5.0005	3.40	2.96	2.96
	2	5.0061	3.40	2.96	
0.1000	1	5.0030	3.10	2.70	2.69
	2	5.0508	3.10	2.68	

VITA

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