รายงานการวิจัยฉบับสมบูรณ์

การดูดซับสิ่งปนเปื้อนที่มีขั้วออกจากไบโอดีเซลโดยใช้ตัวดูดซับแมกนีเซียมซิลิเกต
Adsorption of polar contaminates from biodesel by using Magnesium Silicate adsorbent

ดร.พรสวรรค์ อัศวแสงรัตน์

ได้รับทุนสนับสนุนงานวิจัยจากเงินงบประมาณเงินรายได้ ประจำปีงบประมาณ 2556

คณะวิศวกรรมศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

ชื่อโครงการ (ภาษาไทย) การดูดซับสิ่งปนเปื้อนที่มีขั้วออกจากไบโอดีเซลโดยใช้ตัวดูดซับแมกนีเซียมซิลิเกต
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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการดูดซับสิ่งเจือปนในน้ำมันไบโอดีเซล โดยใช้แมกนีเซียมซิลิเกต (Magnesium Silicate) เป็นตัวดูดซับ เพื่อศึกษาพฤติกรรมการดูดซับสิ่งเจือปนได้แก่ กรดไขมันอิสระ (Free fatty acid) สบู่ (Soap) กรีเซอรีนอิสระ (Free glycerin) และ กรีเซอรีนทั้งหมด (Total glycerin) ซึ่งสังเคราะห์ตัวดูดซับด้วยกระบวนการตกตะกอน (Precipitation) และทำการศึกษาหาสภาวะที่เหมาะสมในกระบวนการตกตะกอนของแมกนีเซียมซิลิเกต ประกอบด้วยการปรับเปลี่ยนประเภทของแหล่งซิลิกาได้แก่ (I) สารละลายโซเดียมซิลิเกต จากบริษัท Merck (SSM) (II) สารละลายซิลิกาที่สกัดจากเถ้าแกลบ (RHA) (III) ผลึกโซเดียม เมตะซิลิเกต จากบริษัท Rankem (SMR) และ (IV) บริษัท Aldrich (SMA) และอัตราส่วนความเข้มข้นของ Na_2SiO_3: $MgSO_4$ 0.5:1.5M, 0.5:0.5M และ 3.0:0.5M โดยศึกษาประสิทธิภาพของการดูดซับเปรียบเทียบกับแมกนีเซียมซิลิเกตทางการค้า อีกทั้งวิเคราะห์ลักษณะของตัวดูดซับโดยใช้วิธีการเรืองแสงของรังสีเอ็กซ์ (XRF) ศึกษาองค์ประกอบทางเคมี ตรวจวัดความเป็นผลึกของตัวดูดซับโดยวิธีการเลี้ยวเบนของรังสีเอ็กซ์ (XRD) ตรวจวัดพื้นที่ผิว (BET) และหาโครงสร้างของสารโดยการวิเคราะห์การดูดกลืนรังสีอินฟราเรด (FT-IR) จากการศึกษาพบว่า แมกนีเซียมซิลิเกตที่สังเคราะห์จาก SMA เป็นแหล่งซิลิกา ด้วยความเข้มข้นของ Na_2SiO_3: $MgSO_4$ เท่ากับ 3.0:0.5M นั้น มีประสิทธิภาพสูงที่สุดในการดูดซับสิ่งเจือปนในน้ำมันไบโอดีเซล โดยอัตราส่วน SiO_2/MgO เท่ากับ 2.04:1 จากนั้นได้ทำการศึกษาสภาวะสมดุลในการดูดซับ ได้แก่ ปริมาณตัวดูดซับ และ เวลาเข้าสู่สมดุล จากการศึกษาพบว่า ปริมาณตัวดูดซับและเวลาที่เข้าสู่สมดุลคือ 4 กรัมตัวดูดซับต่อไบโอดีเซล 150 กรัมและ 4 ชั่วโมง ตามลำดับ สามารถดูดกรดไขมันอิสระ, สบู่, กรีเซอรีนอิสระ และ กรีเซอรีนทั้งหมด ได้ 49.44, 0.76, 2.43 และ 109.43 mg/g ตามลำดับ

คำสำคัญ : การดูดซับ, ไบโอดีเซล, แมกนีเซียมซิลิเกต, เรซิน, กรดไขมันอิสระ

Research Title: Adsorption of polar contaminates from biodesel by using Magnesium Silicate adsorbent
Researcher: Dr. Pornsawan Assawasaengrat
Faculty: Engineering
Department: Chemical Engineering

ABSTRACT

This research aims to study the adsorption of contaminants in biodiesel by using magnesium silicate as an adsorbent. The contaminants in the biodiesel include free fatty acid, soap, free glycerin and total glycerin. The adsorbent was prepared by precipitation reaction between magnesium sulfate (VI) and four different sources of silica. The four different sources of silica; namely (I) solution of sodium silicate from Merck Company (SSM), (II) solution of silica was extracted from rice husk ash (RHA), (III) crystalline sodium metasilicate from Rankem (SMR) and (IV) Aldrich Company (SMA), were selected as a reactant. The efficiency of adsorbents in the purification of biodiesel was compared with commercial magnesium silicate. Magnesium silicate derived from SMA source had high adsorption capacities of contaminants with 0.76:1 SiO_2/MgO ratio. Thus, magnesium silicate derived from SMA source was further synthesized at three different concentration ratios of silica and magnesium sulfate(VI) (Na_2SiO_3: $MgSO_4$); 0.5:1.5M, 0.5:0.5M and 3.0:0.5M. The result presented increasing in efficiency of adsorption when silica concentration increased. The element analysis, the crystalline structures and surface area of the adsorbents were studied by X-ray fluorescence method (XRF), X-ray diffraction method (XRD) and Brunauer-Emmett-Teller technique (BET), respectively. FTIR technique was used to obtain infrared spectrum of the adsorbents. The effect of dosage amount to equilibrium adsorption capacities and equilibrium time were studied to find the optimum conditions for adsorption. The equilibrium was reached after 4 hours for 4 grams of synthesized magnesium silicate per 150 grams biodiesel. The highest capacity of contaminates adsorption with this condition was 49.44 mg/g for free fatty acid, 0.76 mg/g of soap, 2.43 mg/g of free glycerin and 109.43 mg/g of total glycerin.

Keywords : adsorption, biodiesel, magnesium silicate, resin, free fatty acid

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Dr. Pornsawan Assawasaengrat

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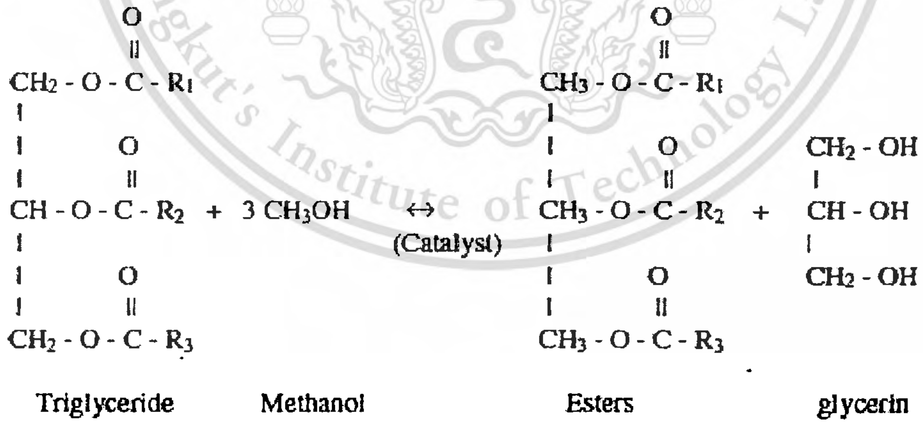
Chapter 1
Introduction

1.1 Motivation

Nowadays, the demand of energy, price of petroleum and environmental concerns about air pollution from gas cars are steadily increasing. Biodiesel is alternative fuel and a renewable fuel. It presents outstanding characteristics as non-toxicity, absence of sulfur, high energy content and biodegradability. Biodiesel consisting of mono-alkyl esters of long chain of fatty acid derived from vegetable oils or animal fats, including methyl ester or ethyl ester and glycerin with a chemical process called transesterification [1]. Transesterification is a chemical reaction relating triglycerides and alcohol using homogeneous or heterogeneous substances as catalyst to yield alkyl esters (biodiesel) and glycerol as by-product, as shown in Figure 1.1. The methyl ester has contaminants frequently that have effect on the quality of biodiesel. The amount glycerin also affects the quality of biodiesel as well [2], the high concentration of glycerol in biodiesel can be the cause of storage problem because biodiesel with high concentration of glycerol is easy to occurs separation of biodiesel phases. And using of that biodiesel, glycerol might accumulate in the nozzle of the engine [3]. The water content in biodiesel cause corrosion of system (such as fuel tubes and injector) or might react with glycerides got soap and glycerol as by-products [4]. In addition, soap and free fatty acids cause the deterioration of engine components. Therefore, the amount of water and free fatty acids affect to indicate the quality of biodiesel.



$$\begin{array}{l} CH_2-O-\overset{\overset{\large O}{\|}}{C}-R_1 \\ | \\ CH-O-\overset{\overset{\large O}{\|}}{C}-R_2 \\ | \\ CH_2-O-\overset{\overset{\large O}{\|}}{C}-R_3 \end{array} + 3\,CH_3OH \underset{(Catalyst)}{\leftrightarrow} \begin{array}{l} CH_3-O-\overset{\overset{\large O}{\|}}{C}-R_1 \\ CH_3-O-\overset{\overset{\large O}{\|}}{C}-R_2 \\ CH_3-O-\overset{\overset{\large O}{\|}}{C}-R_3 \end{array} + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Figure 1.1 Transesterification of vegetable oil with methanol

The purification of crude biodiesel is usually achieved via two notable techniques; wet and dry washings. Conventionally wet washing is the most employed technique to remove contaminants such as soap, catalyst, glycerol and residual alcohol from biodiesel. However, the major disadvantages in the use of water to purify biodiesel are emulsion formation, preventing the separation of the esters, allowing the formation of free fatty acids and soap, increase in cost and production time [5]. To avoid, the dry washing technique (ion exchange resins, magnesium silicate as adsorbent) was introduced to substitute wet washing to remove biodiesel contaminants. The use of adsorbents turns the process more rapid and there is not a formation of aqueous residues.

The adsorbent such as magnesium silicate has the potential of selectively adsorbing hydrophilic materials such as glycerol and mono-, diglycerides. Magnesium silicate surface consists of partially hydrophobic and partially hydrophilic. The hydrophobic part includes siloxane (≡Si–O–Si≡) groups and the hydrophilic portion contains isolated hydroxy groups (–Mg–OH), individual silanol groups (≡Si–OH) and hydrogen bonds formed due to close vicinity of hydroxy groups linked to neighboring silicon atoms. Surface modification is performed to augment hydrophobicity of silicate surface and, thus, to promote binding of several compounds. The modification takes place by introduction of new organofunctional groups to silicate surface [6].

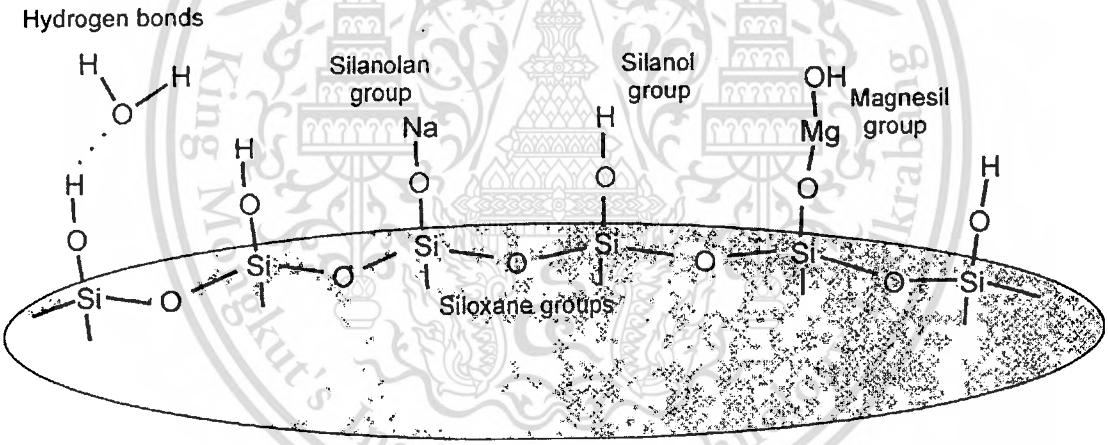


Figure 1.2 Magnesium silicate surface

In this research, the adsorption of contaminants in biodiesel by using magnesium silicate as an adsorbent was studied which the contaminants included free fatty acid, soap, free glycerin and total glycerin. The adsorbent, magnesium silicate, was synthesized by precipitation reaction between magnesium sulfate (VI) and four different source of silica as reactants. The efficiency of adsorbents in the purification of biodiesel was obtained and compared with commercial magnesium silicate. After that, the highest efficiency of source of silica was used for synthesize of magnesium silicate which varied in three different concentration ratios of silica and magnesium sulfate(VI) (Na_2SiO_3:$MgSO_4$). The element composition was obtained from X-ray fluorescence method (XRF). X-ray Diffractrometer method (XRD) was used to determine its crystallinity. And the FTIR technique was used to study infrared spectrum. The effect of dosage amount to equilibrium adsorption capacities were studied by adding different amount of magnesium silicate to 150 grams of biodiesel. In addition, the behavior of magnesium silicate adsorption was noticed by equilibrium time of adsorption and isotherm of adsorption.

1.2 Objectives

To test some commercial adsorbents on impurities removal from prewashed biodiesel.

1.3 Scopes of the study

1. To synthesize magnesium silicate as adsorbent in biodiesel.
2. To study the characters of the adsorbents prepared with the different sources of silica; (I) solution of sodium silicate from Merck Company (SSM), (II) solution of silica was extracted from rice husk ash (RHA), (III) crystalline sodium metasilicate from Rankem (SMR) and (IV) Aldrich Company (SMA).
3. To evaluate the effect of molecular ratio SiO_2/MgO by vary concentration ratios of silica and magnesium sulfate (VI) (Na_2SiO_3: $MgSO_4$); 0.5:1.5M, 0.5:0.5M and 3.0:0.5M to the efficiency of contaminants adsorption.
4. Characterization of magnesium silicate
   - 4.1 X-ray fluorescence method (XRF)
   - 4.2 X-ray Diffractrometer method (XRD)
   - 4.3 Fourier transforms infrared spectroscopy technique (FTIR)
   - 4.4 Brunauer-Emmett-Teller technique (BET)
5. To evaluate the effect of dosage amount to equilibrium adsorption efficiency.

1.4 Result

1. Gaining the techniques of biodiesel dry wash that can prevent loss and waste water
2. Publicize the techniques as a conference paper in ICEAST 2012 International Conference on Engineering, Applied Sciences and Technology. November 21-24, 2012 Bangkok, Thailand
3. The developed technique can be easily applied by biodiesel producers

Chapter 2

Theoretical Background and Literature Review

2.1 Adsorption process [7, 8, 9]

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). The molecules are attracted to the surface that is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term of sorption contains both processes, while desorption is the reverse process.

Mostly, solid adsorbents were used for adsorption, especially adjustable pore size adsorbents and high surface area adsorbents. Adsorption is effective in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. The adsorption is a consequence of surface energy liked surface tension. In a bulk material, all the bonding requirements; ionic, covalent or metallic bonds, of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

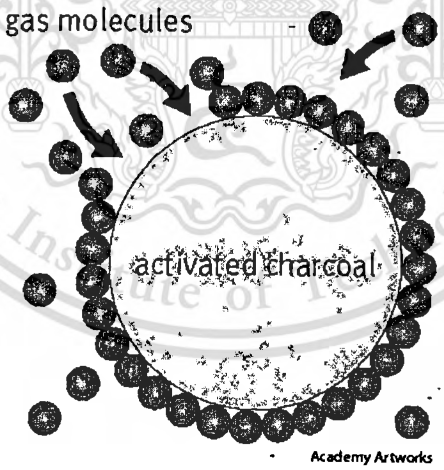


Figure 2.1 Adsorption process [10]

A solid material usually exhibits a heterogeneous distribution of surface energy. Gas, vapor, or liquid molecules may become bound to the surface if they approach sufficiently close to interact. The discussions in this paper are confined to the adsorption (and desorption) of gases or vapors on (or from) solid surfaces. The solid is called the *adsorbent*;

the gas or vapor molecule prior to being adsorbed is called the *adsorptive* and while bound to the solid surface, the adsorbate.

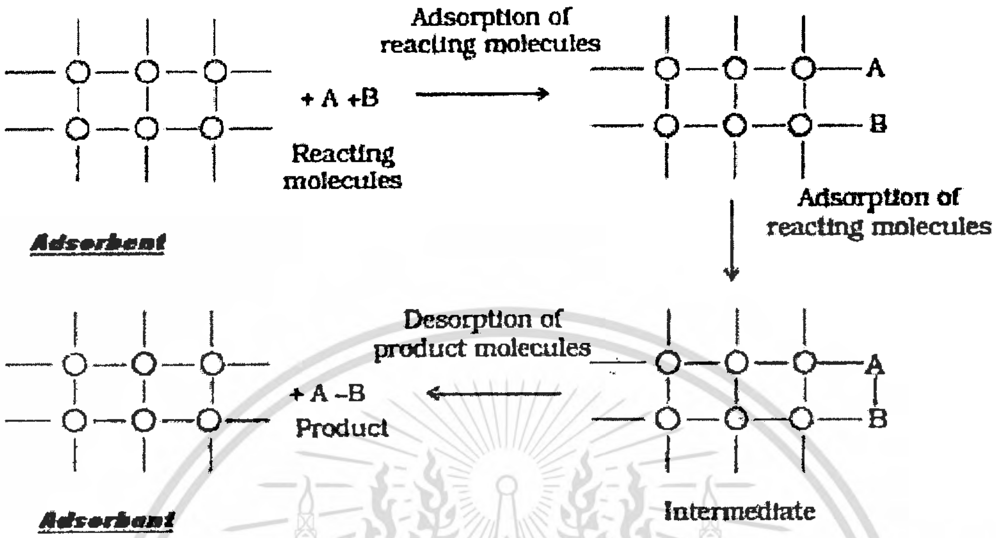


Figure 2.2 Mechanism of Adsorption Using Adsorbent [11]

2.1.1 Types of adsorption

Adsorption process was classified into 2 types which followed characteristic of molecule bonding; Physical adsorption and Chemical adsorption.

1. Physical adsorption [8, 12, 13]

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions. Even though the interaction energy is very weak (~10–100 meV) which are also responsible for the non-ideal behavior of real gases, physisorption plays an important role in nature. Adsorption energy usually not exceeding 80 kJ/mole, with typical energies being considerably less. Physically adsorbed molecules may diffuse along the surface of the adsorbent and typically are not bound to a specific location on the surface. Being only weakly bound, physical adsorption is easily reversed. Van der Waals forces originate from the interactions between induced, permanent or transient electric dipoles. In comparison with chemisorption, in which the electronic structure of bonding atoms or molecules is changed and covalent or ionic bonds form, physisorption, generally speaking, can only be observed in the environment of low temperature (thermal energy at room temperature ~26 meV) and the absence of the relatively strong chemisorptions. In practice, the categorization of a particular adsorption as physisorption or chemisorption depends principally on the binding energy of the adsorbate to the substrate. Physical adsorption takes place on all surfaces provided that temperature and pressure conditions are favorable.

2. Chemical adsorption [8,13]

Chemisorption or Chemical adsorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption. Chemisorption is highly selective and occurs only between certain adsorptive and adsorbent species and only if the chemically active surface is cleaned of previously adsorbed molecules. A chemical bond involves sharing of electrons between the adsorbate and the adsorbent and may be regarded as the formation of a surface compound. Due to the bond strength, chemical adsorption is difficult to reverse.

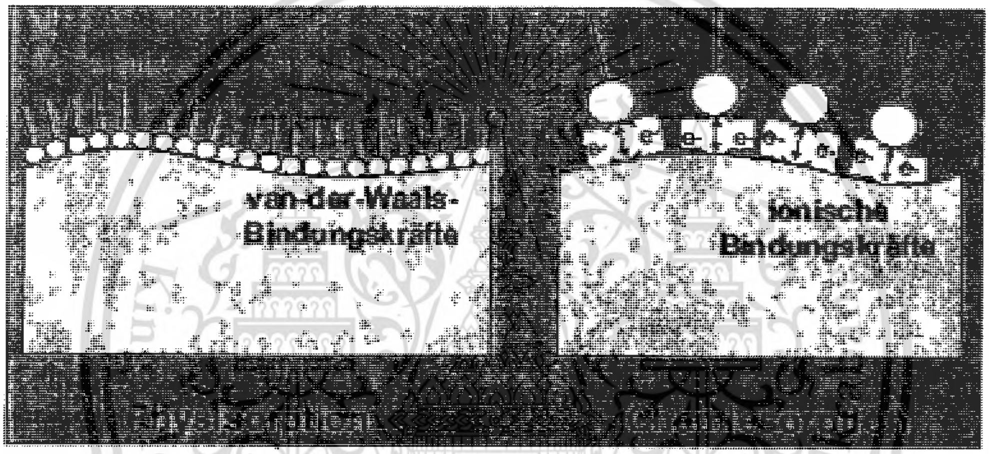


Figure 2.3 Physical adsorption and Chemical adsorption [14]

Under proper conditions, physical adsorption can result in adsorbed molecules forming multiple layers. Chemisorption, in the typical case, only proceeds as long as the adsorptive can make direct contact with the surface; it is therefore a single-layer process. Exceptions can exist if the adsorptive is highly polar such, NH3 being an example. Both physical and chemical adsorption may occur on the surface at the same time; a layer of molecules may be physically adsorbed on top of an underlying chemisorbed layer. The same surface can display physisorption at one temperature and chemisorption at a higher temperature.

Table 2.1 Comparison between Physisorption and Chemisorption [11]

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

2.1.2 Types of adsorbent [15]

Adsorbent was classified into 3 types as followed;

1. Non-polar adsorbent - It involving physical adsorption. The important of non- polar adsorbent is activated carbon or activated charcoal.

2. Polar adsorbent - This type of adsorbent relating chemical adsorption while the molecule structure of adsorbent was not changed. For instance, (I) oxide group adsorbent e.g. silica oxide, metal oxide (II) material of silica e.g. silica gel, fuller's earth

3. Chemical adsorbent - Its surface can react chemically with adsorbate. Chemical adsorbent included activated silica gel and activated manganese oxide etc.

2.1.3 The effects of adsorption [16,17]

1. Properties of adsorbent

- Surface area and pore structure

The pore structure with smaller pore sizes can increase the surface area, then surface area increasing when pore structure increased. And capacity of adsorption increased when surface area was increased.

- Adsorption size

The adsorbent without pore has more surface area when size of adsorbent decreased, so efficiency of adsorption was increased. However, the adsorption performance of porous adsorbent depended on amount of pores more than size of adsorbent.

2. Properties of adsorbate

- Solubility

In adsorption process, molecules of adsorbate were brought out from solvent to attach on adsorbent surface. Thus, solubility of adsorbate effects on pěrformance of adsorption; poor solubility can lead to high performance of adsorption, on the other hand, high solubility (strongly bonding with solvent molecule) has effect on efficiency of adsorption.

- Molecular weight and size of molecule

Increasing of molecular weight and size of molecule influenced on rising of adsorption. Because of solubility has decreased when molecular weight increased.

- Polarity

The performance of adsorption depended on solubility and then when polarity of adsorbate increased, the solubility was increased also.

3. Temperature

At high temperature, rate of adsorption was increased; however efficiency of adsorption was decreased because mostly adsorption process is exothermic reaction.

4. Time

Time is the important factor that effect on adsorption. However, it depends on individual adsorbent and adsorbate, then before usage, they were studied effect of time.

2.1.4 Applications of adsorption [11]

The principle of adsorption is employed,

1) In heterogeneous catalysis.
2) In gas masks where activated charcoal adsorbs poisonous gases.
3) In the refining of petroleum and discoloring cane juice.
4) In creating vacuum by adsorbing gases on activated charcoal.
5) In chromatography to separate the constituents' of a mixture.
6) To control humidity by the adsorption of moisture on silica gel.
7) In certain titrations to determinate the end point using an adsorbent as indicator (Example: Fluorescein).

2.2 Biodiesel

Biodiesel is a domestic, renewable fuel for diesel engines. Made from agricultural co-products and byproducts such as soybean oil, other natural oils, and greases, it is an advanced biofuel. To be called biodiesel, it must meet the strict quality specifications of ASTM D 6751. Biodiesel can be used in any blend with petroleum diesel fuel *[18].*

Biodiesel fuel is usually produced from virgin and used vegetable oils and animal fats. Presently several efforts are made to produce biodiesel from microalgae. Microalgae clearly offers a few advantages among others include: much higher biomass productivities than land plants (doubling times may be as short as 3.5 hours), some species can accumulate up to 20–50% triacylglycerols, while no high-quality agricultural land is necessary to grow the biomass, and even no land at all, offshore microalgae farming could be a reasonable alternative.[19]

The most common way to produce biodiesel is by transesterification. In this reaction, triglycerides, as the main components of vegetable oils, react with an alcohol to produce fatty acid monoalkyl esters and glycerol. Methanol is the most common alcohol because of its low price compared to other alcohols. In this case, the reaction is referred to as methanolysis. The stoichiometry of methanolysis reaction requires 3mol of methanol and 1mol of triglyceride to give 3mol of fatty acidmethyl ester and 1mol of glycerol. This reaction, in turn, consists of three consecutive reversible reactions with intermediate formation of diglycerides and mono- glycerides. After the reaction, the glycerol is separated by settling or centrifuging and the layer obtained is purified to be used in its traditional applications (the pharmaceutical, cosmetics and food industries) or in its recently developed applications (animal feed, carbon feedstock in fermentations, polymers, surfactants, intermediates and lubricants). The biodiesel phase is also purified before being used as diesel fuel in order to fulfill the EN 14214 Standard. [20]

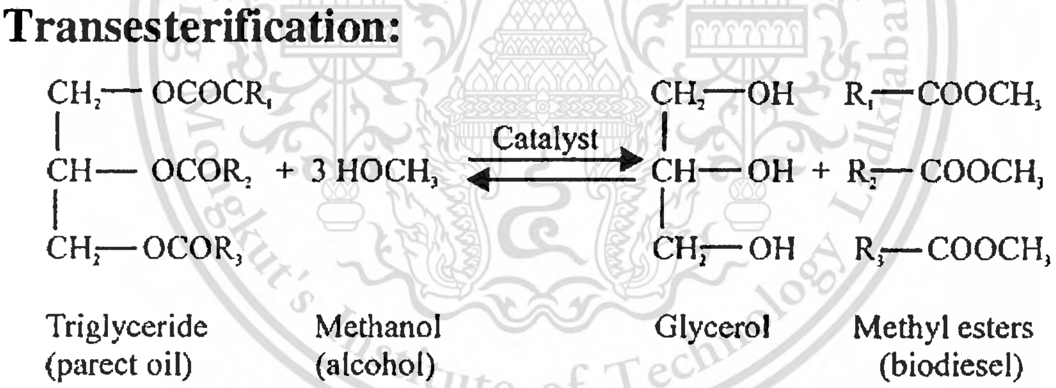


Figure 2.4 Transesterification process [21]

Table 2.2 Biodiesel Compared to Petroleum Diesel [22]

Advantages	Disadvantages
• Domestically produced from non-petroleum, renewable resources • Can be used in most diesel engines, especially newer ones • Less air pollutants (other than nitrogen oxides) • Less greenhouse gas emissions (e.g., B20 reduces CO_2 by 15%) • Biodegradable • Non-toxic • Safer to handle	• Use of blends above B5 not yet approved by many auto makers • Lower fuel economy and power (10% lower for B100, 2% for B20) • Currently more expensive • B100 generally not suitable for use in low temperatures • Concerns about B100's impact on engine durability • Slight increase in nitrogen oxide emissions possible in some circumstances

The methyl esters cannot be classified as biodiesel until the EN 14214 Standard specifications are fulfilled. Therefore, the purification stage is essential. The untreated biodiesel contains several impurities: free glycerol, soap, metals, methanol, free fatty acids (FFA), catalyst, water and glycerides. The engine life can be reduced by high levels of impurities. Table 3 shows the effect of each impurity. There are two generally accepted methods to purify biodiesel: wet and dry washing. The more traditional wet washing method is widely used to remove excess contaminants and leftover production chemical from biodiesel. However, the inclusion of additional water to the process offers many disadvantages, including increased cost and production time. Dry washing replaces water with an ion exchange resin or a magnesium silicate powder to neutralize impurities. Both dry washing methods are being used in industrial plants [20].

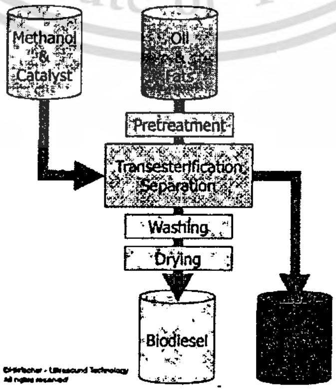


Figure 2.5 Biodiesel process [23]

Table 2.3 Negative effects of contaminants on biodiesel and engines.[19]

Contaminants	Negative effect
Methanol	Deterioration of natural rubber seals and gaskets, lower flash points (problems in storage, transport, and utilization, etc.), Lower viscosity and density values, Corrosion of pieces of Aluminum (Al) and Zinc (Zn).
Water	Reduces heat of combustion, corrosion of system components (such as fuel tubes and injector pumps) failure of fuel pump, hydrolysis (FFAs formation), formation of ice crystals resulting to gelling of residual fuel, Bacteriological growth causing blockage of filters, and Pitting in the pistons.
Catalyst/soap	Damage injectors, pose corrosion problems in engines, plugging of filters and weakening of engines.
Free fatty acids	Less oxidation stability, corrosion of vital engine components.
Glycerides	Crystallization, turbidity, higher viscosities, and deposits formation at pistons, valves and injection Nozzles.
Glycerol	Decantation, storage problem, fuel tank bottom deposits Injector fouling, settling problems, higher aldehydes and acrolein emissions, and severity of engine durability problems.

2.2.1 Factors Affecting Biodiesel Production [24]

- Effect of molar ratio of alcohol

Normally the transesterification reaction requires 3 mol of alcohol for one mol of triglycerides to three mol of fatty acid ester and one mol of glycerol. Excess amount of alcohol increases conversion of fats into esters within a short time. So the yield of biodiesel increases with increase in the concentration of alcohol up to certain concentration. However further increase of alcohol content does not increase the yield of biodiesel but it also increase the cost of alcohol recovery. In case the oil samples contain high free fatty acid (FFA) such reaction does not respond to alkali catalyst. In that situation acid catalyst will be effective to catalyze the reaction and the reaction requires higher amount of alcohol than alkali catalyst. This is due to the fact that acid catalyst tolerates the FFA content and water content present in the oil samples.

- Effect of water and FFA contents

The water and free fatty acid contents are critical factors for transesterification reaction. Base-catalyzed transesterification reaction requires water free and low acid value (<

1) raw materials for biodiesel production. If the oil samples have high FFA content (more than 1%) then the reaction requires more alkali catalyst to neutralize the FFA. Presence of water gives greater negative effect than that of FFAs because Water can cause soap formation and frothing which can cause increase in viscosity. In addition formation of gels and foams hinders the separation of glycerol from biodiesel. Free fatty acid and water always produce negative result during transesterification and causes soap formation and consumes the catalyst which leads to reduction of catalyst effect. Water and FFA also leads to the reduction of methyl ester. To overcome this problem, water has less influence in supercritical methanol method.

- Reaction time

The increase in fatty acid esters conversion when there is an increase in reaction time. The reaction is slow at the beginning due to mixing and dispersion of alcohol and oil. After that the reaction proceeds very fast. However the maximum ester conversion was achieved within < 90 min. Further increase in reaction time does not increase the yield product i.e. biodiesel/mono alkyl ester. Besides, longer reaction time leads to the reduction of end product (biodiesel) due to the reversible reaction of transesterification resulting in loss of esters as well as soap formation.

- Reaction temperature

Reaction temperature is another important factor that will affect the yield of biodiesel. For example higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. However, the increasing in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides. Usually the transesterification reaction temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation. The range of optimal reaction temperature may vary from 50°c to 60°c depends upon the oils or fats used.

- Catalyst concentration

Biodiesel formation is also affected by the concentration of catalyst. Most commonly used catalyst for biodiesel production is sodium hydroxide (NaOH) or Potassium hydroxide (KOH). However, the sodium methoxide would be more effective because mixing of sodium hydroxide with methanol produce little amount of water which inhibit the formation of end product (Biodiesel) due to the hydrolysis reaction. This is one of the reason for mixing of catalyst with methanol first and then added to the oil or fats. In addition to this when the concentration of catalyst is increases with oil samples, the conversion of triglycerides into biodiesel is also increases. On the other hand insufficient amount of catalyst leads to the incomplete conversion of triglycerides into fatty acid esters. However, optimal product yield (biodiesel) was achieved when the concentration of NaOH reaches 1.5 wt% at the same time further increase of catalyst concentration proved to have negative impact on end product yield. Because addition of excess amount of alkali catalyst react with triglycerides to form more soap.

- Agitation speed

Agitation speed plays an important role in the formation of end product (mono alkyl ester or biodiesel), because agitation of oil and catalyst mixture enhances the reaction. For example the mixing intensities chosen were 200 rpm, 400 rpm, 600 rpm and 800 rpm for 60 min while other parameters were kept constant. At 400 rpm higher conversion of end product were obtained. Because, lower stirring speed shows lower product formation. On the other hand higher stirring speed favors formation of soap. This is due to the reverse behavior of transesterification reaction.

2.2.2 Wet washing technique [25,26]

Biodiesel wet washing technique involves addition of certain amount of water to crude biodiesel and agitating it gently to avoid formation of emulsion. The process is repeated until colorless wash water is obtained, indicating complete removal of impurities. Wet washing processes usually require a lot of water, approximately water wash solution at the rate of 28% by volume of oil and 1 g of tannic acid per liter of water. The use of large quantity of water generates huge amount of wastewater and incur high energy cost. Production of 350,000 L/day of fatty acid esters (biodiesel) will result to no less than 70,000 L/day of contaminated wastewater. Wet washing is mostly conducted through washing with dionized water, washing with acid (5% phosphoric acid) and water and washing with organic solvent and water.

Water washing has been traditionally used to purify crude biodiesel after its separation from glycerol. The air was cautiously introduced into the aqueous layer, while gently stirring the mixture of crude biodiesel and water. This process was continued until the ester layer became cleared. In addition, after settling the aqueous solution was drained and water alone was added at 28% by volume of oil for the final washing process. [27]

2.2.3 Dry washing technique [19]

The dry washing technique commonly employed to purify crude biodiesel is usually achieved through the use of silicates (Magnesol or Trisyl), ion exchange resins (Amberlite or purolite), cellulosics, activated clay, activated carbon, and activated fiber, etc. These Adsorbents consist of acidic and basic adsorption (binding) sites and have strong affinity for polar compounds such as methanol, glycerin, glycerides, metals and soap. This technique is followed with the use of a filter to enable the process to be more effective and efficient as shown in figure 2.15. Therefore during washing process, the amount of glycerides and total glycerol in crude biodiesel are lowered to a reasonable level. Besides, the process has the advantage of being waterless, strong affinity to polar compounds, easy to integrate into existing plant, significantly lower purification time, no wastewater, total surface area coverage of wash tank is minimized, solid waste has alternate uses, saves space, and improves fuel quality.

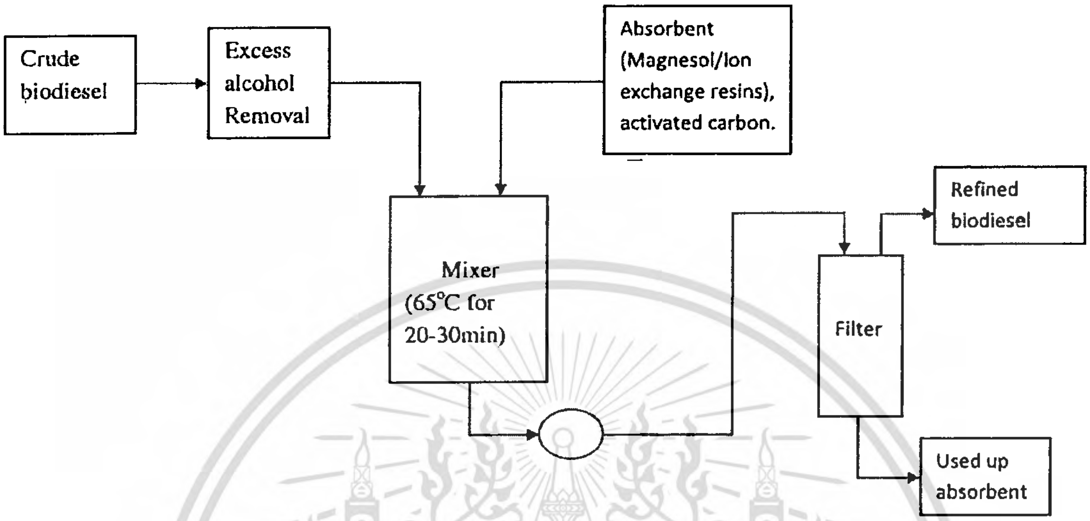


Figure 2.6 Schematic diagram of biodiesel dry washing process

2.3 Free fatty acid (FFA) [28]

The FFA are generally degradation products of the vegetable oil, with the FFA breaking away from the triglycerides (hence, the name "free"). In other words, a triglyceride molecule under exposure to prolonged heat will become a di-glyceride and one FFA, or a mono-glyceride and two free fatty acids, or potentially three FFA.

Vegetable oils with as little as 1-2 percent free fatty acid have been observed to cause difficulties with biodiesel production and/or separation. Although some biodiesel reaction systems are designed to convert free fatty acids to biodiesel using an acid-catalyzed esterification reaction, the most common biodiesel systems lack this capability. Most often, a homebrew biodiesel system or first-generation commercial system designed to handle virgin vegetable oils, uses a base-catalyzed reaction to convert the triglycerides to biodiesel and glycerin.

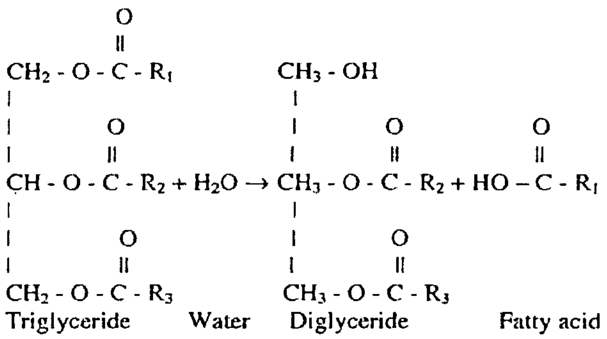


Figure 2.7 Hydrolysis of a triglyceride to form free fatty acids [29]

This reaction is particularly prevalent in deep fryers, and is the primary reason used cooking oil contains free fatty acids. It can also happen during biodiesel processing. The presence of a base catalyst facilitates this reaction in a similar way as it facilitates transesterification, except the end result is soap. [30]

However, with free fatty acids present, a portion (perhaps all if there is enough free fatty acid) of the basic catalyst will react with the free fatty acid to create a soap. This depletes the base used to catalyze the transesterification reaction or requires the addition of a larger amount of base to overcome the free fatty acid reaction and can cause problems with soap formation and the separation of products after the reaction is complete. In extreme cases, the soaps mix with water from the fuel wash stage to create an emulsion that can greatly lengthen or even prevent settling of the wash water layer from the fuel layer.

There are several ways to compensate for the free fatty acids present in the vegetable oil:

1. Using great care and equipment designed for strong acids, add sulfuric acid or another strong acid with alcohol to the oil assuming a certain level of free fatty acids (some users suggest using 1 mL of acid per liter of oil. Adding excess acid will increase your chemical costs, both in terms of the acid used and the base necessary to neutralize the excess acid prior to the base-catalyzed transesterification reaction.
2. Test the free fatty acid content, and if it is low enough (less than 1 percent), ignore it and take care with washing to prevent the formation of an emulsion.
3. Test the free fatty acid content and add the appropriate amount of strong acid to convert the free fatty acids to biodiesel. This approach requires the most skill, but will increase your yield of biodiesel fuel while minimizing your chemical costs and washing/separation problems.

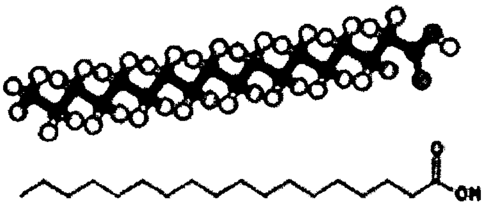


Figure 2.8 Structure of free fatty acid [31]

2.4 Soap [32]

Saponification is a chemical reaction that involves the production of a metal salt or soap. The reaction involves the attack on a methyl ester, free fatty acid, triglyceride, or other glyceride by a hydroxide ion, ^{-}OH.

The hydroxide ion implies the presence of water in the system. If water could be eliminated, then there would be no soap formation. However, this is a practical impossibility. There is always some water present, and there will always be some soap formed when biodiesel is made.

The exception to this is when a solid (heterogeneous) catalyst is used which does not provide the free metal ions needed to form soap. These catalysts should provide biodiesel and glycerin that are free of soap. In reality, many of these supposed heterogeneous catalysts leach metals ions into the liquid and thus require some clean-up of the reaction products.

Soap forms when the base catalyst reacts with FFAs in the feed stocks. Soap production gives rise to the formation of gels, increases viscosity and greatly increases product separation cost. The alcohol and catalyst must also comply with rigorous specifications. The alcohol as well as the catalyst must be essentially anhydrous (total water content must be 0.1-0.3 wt% or less). This is required since it is assumed that the presence of water in the feedstock promoted hydrolysis of the alkyl ester to FFA and consequently, soap formation.

Figure 2.9 Formation of soap

Soap must be removed from biodiesel after the reaction, and this can be done by either water washing, using a solid adsorbent mixed with the liquid, or by passing the liquid through a packed bed of ion exchange resin. And soap is not formed when biodiesel is manufactured using a supercritical technology that does not require a catalyst. [33]

The negative effects of excessive soap formation include amongst others; consumption of the catalyst, reduction of catalyst effectiveness, difficulty in glycerol separation, and prevention of crude biodiesel purification. So, the soap titration can be performed again after washing to see if the biodiesel is of enough quality for use in your diesel engine.

ASTM Standards call for no more than 41 PPM of soap when NaOH is used as your catalyst and 66 PPM when KOH is used. If the fuel tests at or below these standards, you have quality fuel. ASTM standards do not usually need to be met for clean operation, but are required for commercial use of the fuel. See the chart below for generally accepted values for home-brewers.

Fuel which is around or above 300 PPM of soap should be washed more before use. It is important to be sure your biodiesel is low enough in soap content to preserve your fuel filters and prevent long-term engine damage.

Table 2.4 Analyzing the quality of Biodiesel based on soap content chart [34]

Soap Content	Fuel Quality
at or below 41 PPM (NaOH) or 66 PPM (KOH)	Within ASTM standards
Above ASTM Standards but Below 200 PPM	Should not pose any threat to a fuel filter or engine
200-300 PPM	maximum soap content which should be allowed in fuel
300-400 PPM	May clog fuel filters, not recommended, wash more
400-500 PPM	High soap content, not recommended, wash more
Above 500 PPM	Can possibly leave ash in your engine and cause longterm damage, not recommended, wash more

2.5 Glycerin [35]

FAMEs are manufactured from various triglyceride feedstocks, including soy, rape seed, and palm oils. Triglycerides have three aliphatic unbranched fatty acids bonded to one molecule of glycerol, each by an ester linkage. The triglycerides undergo a transesterification reaction, with excess methanol and potassium hydroxide as the catalyst, to generate three molecules of free FAMEs and one molecule of glycerol byproduct. The glycerol, excess alcohol, and base are then separated from the FAMEs. The alcohol and base are recycled for another transesterification reaction, whereas the glycerol is refined and sold for use in industrial and medicinal syrup pharmaceutical products. Glycerin forms during the fat splitting process (Figure 2.19) and transersterification(Figure 2.13). Glycerol is an undesirable byproduct in biodiesel and therefore must be removed from the FAMEs. Free glycerol and bound glycerol from unconverted triglycerides cause negative effects on the diesel engine, such as clogging fuel filters, fouling fuel injectors, and forming a deposit on the bottom of fuel storage tanks.5 Additionally, the sub-freezing temperatures common in many winter climates affect unconverted triglycerides (bound glycerol) more than that typically observed in diesel. The most common effects are fuel separation and increased fuel viscosity, which results in poor fuel injection and engine lockup.

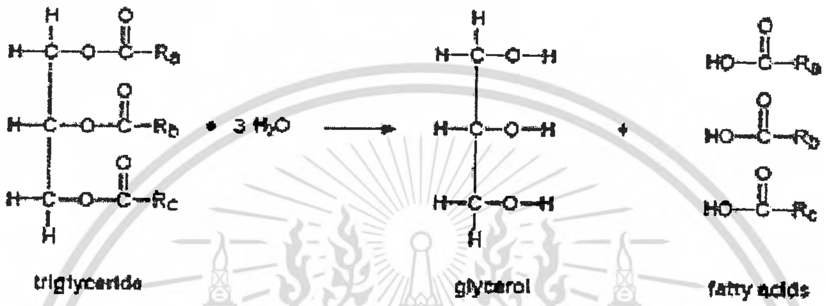


Figure 2.10 Fat splitting process [36]

Total glycerol, defined as free glycerol plus bound glycerol (unconverted triglycerides), is determined by base- hydrolysis to convert the bound glycerol to free glycerol. To minimize the problems caused by free and bound glycerol, sustain production of biofuels, and provide quality control criteria to this developing industry, the ASTM and other regulatory organizations have established limits of 0.02 wt % free glycerol and 0.24 wt % total glycerol (ASTM D6751) in B100 biofuels used to prepare B2–B20 blends. Therefore, accurate and sensitive methods are needed for the determination of free and total glycerol in biodiesel.

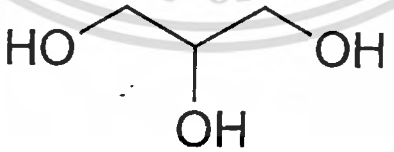


Figure 2.11 Structure of glycerin [37]

2.6 Magnesium silicate

Silicates belong to the widest spread minerals on the Earth making about 25% of all known minerals. The rocks-forming silicates include: quartz, amphiboles, pyroxenes and micas. Besides their rock-forming role, silicates are the sources of many valuable metals such as nickel, zinc, zircon and lithium and form deposits of many important minerals [38]. And silicate raw materials are of enormous technological importance. They are regarded to represent the most important mineral raw materials in the ceramic industry as well as, directly or indirectly, in other industries, like in the iron and steel, electrochemical, chemical, metallurgical, construction, radiochemical, and electronic industries[39].

Magnesium silicate may be used as a filler and pigment in dispersive paints, as an adsorbent in affinity chromatography, and as a component of anti-epileptic drugs. It could be used in the treatment of alimentary intoxication, indigestion, inflammatory conditions of the small intestine, gastric peracidity and peptic ulcers. Magnesium silicate is also used in the production of confectionery as an antiadhesive and anti-caking agent (molding powder or a component of anti-glitter paste). As far as whiteness is concerned, its white color may easily compete with titanate-based pigments, which permits us to eliminate partially or totally titanium dioxide.

Magnesium silicate exhibits strong sedimentation interactions in an organic medium such as linseed oil. The interactions increase with increasing amounts of applied modifying compounds, which the improve physicochemical properties of the product. The surface of magnesium silicate carries free hydroxyl groups (silanol groups), the most reactive groups on the surface. They provide the site for physical adsorption of organic particles and easily react chemically with multiple substituents. Being substituted with new atom groups, they provide potential for surface modification. The surface of magnesium silicate may be presented as illustrated by Figure 2.21

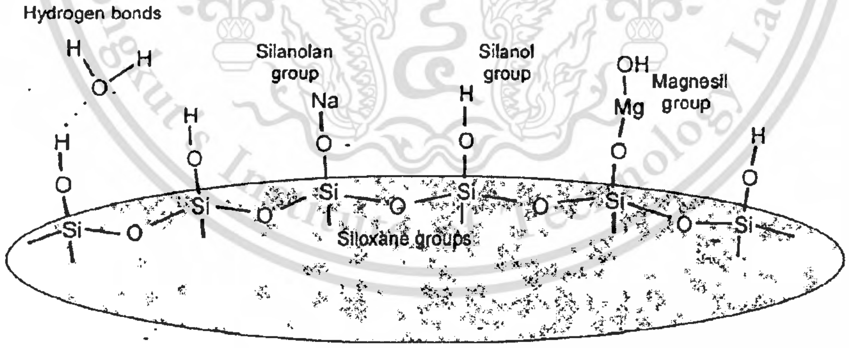


Figure 2.12 Magnesium silicate surface

Increasing demand for synthetic silicates of special parameters and properties has stimulated development of new technologies of their production. One of the best known of silica gel production is the solgel method. It needs relatively low temperatures and gives products of high purity and homogeneity. This method belongs to wet ones and requires hydrolysis and condensation of metal alkoxides and inorganic salts. Another well-known method is based on the ion exchange between the basic ions and protons contained in $\equiv$Si-

OH, which permits formation of ≡Si-O-A type bonds (where A is the alkaline metal e.g. Na). The course of hydrolysis and ion exchange depend on the concentration of protons and basic ions in the reaction mixture and influence the concentration of ≡Si-O-A bonds in oligomers. The amorphous Na_2OSiO_2 powder obtained by the ion-exchange method is the initial product for synthesis of magnesium silicate. The ion exchange between alkali earth ions and sodium in Na_2O-SiO_2 leads to formation of ≡Si-O-M (where M stands for magnesium or calcium ions). Quite often used are the methods of obtaining synthetic silicates in water systems. One of them is the standard reaction of precipitation from water-soluble alkaline silicates, e.g. sodium silicate, by addition of a reagent such as mineral acid or magnesium hydroxide.

2.7 Isotherm adsorption [40]

The process of adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature. Different adsorption isotherms have been Freundlich and Langmuir theory.

In the process of adsorption, adsorbate gets adsorbed on adsorbent.

$$\text{Adsorbate} + \text{Adsorbent} \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Adsorption}$$

$$A + B \rightleftharpoons AB \qquad (2.1)$$

According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored.

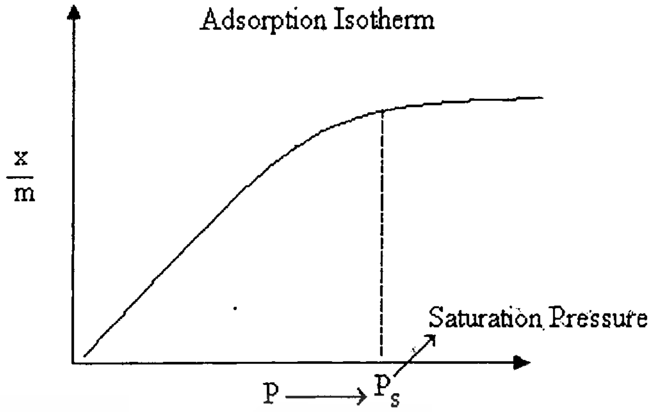


Figure 2.13 Adsorption isotherm

From the graph, we can predict that after saturation pressure Ps, adsorption does not occur anymore. This can be explained by the fact that 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.

2.7.1 Langmuir Adsorption Isotherm

In 1916 Langmuir proposed another Adsorption Isotherm known as Langmuir Adsorption isotherm. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A(g) + B(S) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB \tag{2.2}$$

Where .A(g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

$$\theta = \frac{KP}{1 + KP} \tag{2.3}$$

Where θ the number of sites of the surface which are covered with gaseous molecule, P represents pressure and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase .The basic limitation of Langmuir adsorption equation is that it is valid at low pressure only.

At lower pressure, KP is so small, that factor (1+KP) in denominator can almost be ignored. So Langmuir equation reduces to

$$\theta = KP \tag{2.4}$$

At high pressure KP is so large, that factor (1+KP) in denominator is nearly equal to KP. So Langmuir equation reduces to

$$6 = \frac{KP}{KP} = 1 \tag{2.5}$$

2.7.2 Freundlich Adsorption Isotherm

In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm.

$$\frac{x}{m} = kP^{\frac{1}{n}} \tag{2.6}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, 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.

2.7.3 Type of Adsorption Isotherm

Five different types of adsorption isotherm and their characteristics are explained below.

1. Type I Adsorption Isotherm

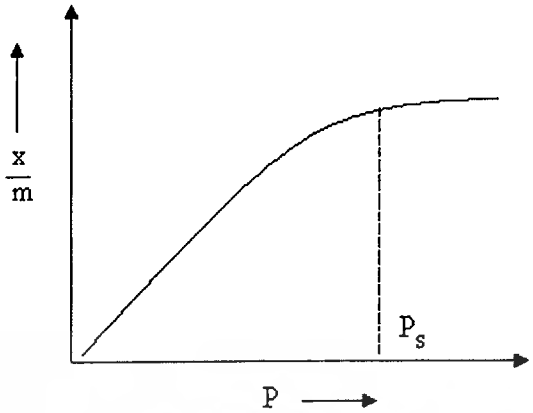


Figure 2.14 Type I adsorption isotherm

Type I Adsorption Isotherm

- The above graph depicts Monolayer adsorption.
- 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 and Type I Adsorption Isotherm is obtained.
- Examples of Type-I adsorption are Adsorption of Nitrogen (N2) or Hydrogen (H) on charcoal at temperature near to -1800C.

2. Type II Adsorption Isotherm

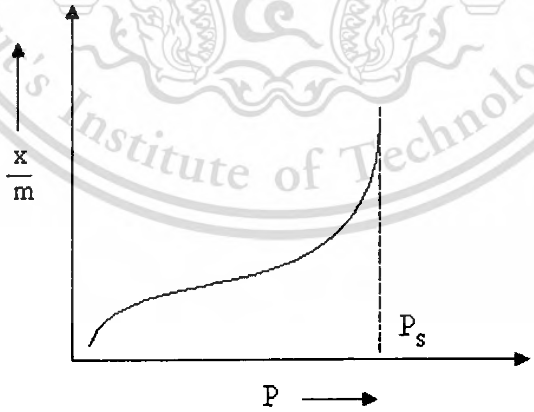


Figure 2.15 Type II adsorption isotherm

Type II Adsorption Isotherm

- Type II Adsorption Isotherm shows large deviation from Langmuir model of adsorption.
- The intermediate flat region in the isotherm corresponds to monolayer formation.
- In BET equation, value of C has to be very large in comparison to type I.
- Examples of Type-II adsorption are Nitrogen (N2 (g)) adsorbed at -1950C on Iron (Fe) catalyst and Nitrogen (N2 (g)) adsorbed at -1950C on silica gel.

3. Type III Adsorption Isotherm

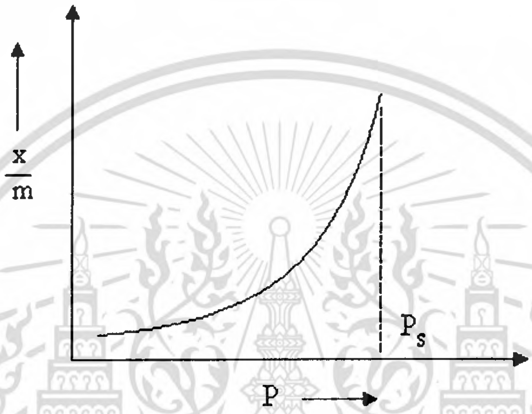


Figure 2.16 Type III adsorption isotherm

Type III Adsorption Isotherm

- Type III Adsorption Isotherm also shows 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 (Br2) at 790C on silica gel or Iodine (I2) at 790C on silica gel.

4. Type IV Adsorption Isotherm

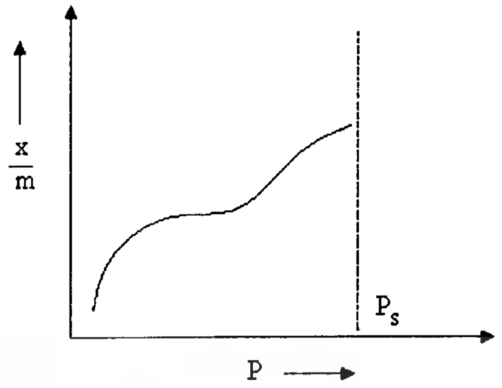


Figure 2.17 Type IV adsorption isotherm

Type IV Adsorption Isotherm

- At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer.
- 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 (PS) 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.

5. Type V Adsorption Isotherm

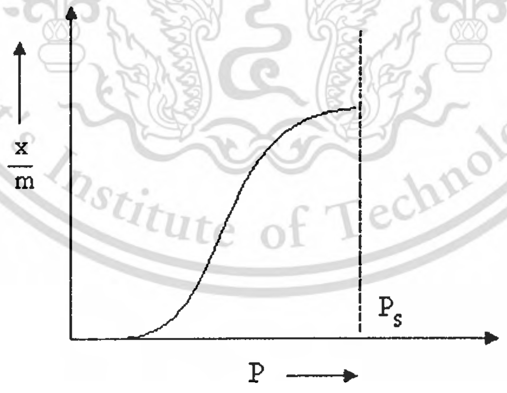


Figure 2.18 Type V adsorption isotherm

Type V Adsorption Isotherm

- Explanation of Type V graph is similar to Type IV.
- 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.

2.8 Literature review

Warod Patrungsee et al. studied about magnesium silicate with various silica and magnesium oxide ratios (SiO_2/MgO ratios) was used as the adsorbent for a study of adsorption of free fatty acid (FFA) in crude palm oil (CPO). Magnesium silicate was prepared from magnesium nitrate or magnesium sulfate solution precipitated with a solution of sodium silicate derived from rice husk. SiO_2/MgO ratios of the magnesium silicate synthesized from magnesium nitrate and magnesium sulfate were 3.93, 3.75, 2.74, 2.40, 1.99 and 3.96, 3.61, 3.51, 2.91, 2.69, respectively. FFA adsorption on the magnesium silicate was carried out by adding 1 gram of the adsorbent to 50 grams of CPO and shaking for 1 hour at 50°C. It was found that SiO_2/MgO prepared from magnesium nitrate ratio of 1.99 had the highest adsorption capacities of 185 mg of FFA per gram of adsorbent. In addition, increasing of SiO_2/MgO ratios of magnesium silicate was found to reduce the adsorption capacities due to decreasing of FFA chemisorption. The effect of dosage amount to equilibrium adsorption capacities were carried out by adding different amount of magnesium silicate (SiO_2/MgO ratio of 1.99) to 50 grams of CPO. The result showed that efficiency decreased when dosage increased. The Fruendlich and Langmuir isotherm were applied to describe this absorption system. The values of maximum sorption capacity (Q_0) and Langmuir's sorption affinity (b) in the Langmuir equation obtained by linear-regression were minus values which were physically meaningless. Thus, FFA adsorption on magnesium silicate was both physisorption and chemisorption and well represented by the Fruenlich isotherm [9].

The precipitation of highly dispersed magnesium silicate were studied by Andrzej Krysztafkiewicz et al. that solutions of sodium metasilicate and of magnesium salts [chloride, sulfate(VI) or nitrate(V)] were employed. The chemical reaction of silicate precipitation was corrected by supplementation of the system with diluted (5–15 wt%) solutions of sodium hydroxide. Optimum parameters of the precipitation process were established. The precipitated magnesium silicates were comprehensively examined. Their chemical composition and principal physicochemical properties were established, including bulk density, capacities to absorb water, dibutyl phthalate and paraffin oil as well as the sedimentation rate in linseed oil. Moreover, their morphology, microstructure and particle size distribution were studied, using scanning electron microscopy and dynamic light scattering technique. The obtained products manifested variable physicochemical properties. The presence of sodium hydroxide solution in the course of precipitation proved to significantly affect the quality of the obtained magnesium silicates [39].

Research of Marcia Cardoso Manique et al. studied about the purification of biodiesel from waste frying oil (WFO) using rice husk ash (RHA) at concentrations of 1%, 2%, 3%, 4% and 5% (w/w) was studied and compare it with two other different purification methods, the traditional acid solution (1% aqueous H_3PO_4) and with the commercial adsorbent Magnesol 1% (w/w). The structure and composition of the RHA were studied to better understand its properties as an adsorbent. In a concentration of 4%, the RHA showed excellent results for removal impurities from biodiesel. The high concentration of silica in its composition and the presence of meso and macropores can explain its high capacity of adsorption. Thus, the RHA, that is a byproduct of the rice processing, can appear as an alternative material for biodiesel purification [41].

From M. Berrios et al., in order to meet the very high purity requirements laid down on the European Standard for biodiesel fuel (EN 14214), a significant amount of post transesterification purification is needed. Until recently the preferred method was water washing but considerable interest is now being shown in purification by ion exchange resins and the use of magnesium silicate as a solid adsorbent. The three methods have been tested under several reaction conditions (temperature, concentration, agitation rate, etc.) in order to compare which gives better results. It has been found that it is necessary a previous methanol removal to avoid the saturation of the adsorbents. Glycerol and soap content have been removed in all the processes. Not many differences have been found on the other tested parameters [20].

The efficiency of different adsorbents in the purification of biodiesel produced by alkaline transesterification of soybean oil (Methanol/KOH) was studied by Candice Schmitt Faccini et al. The proposed methodologies were based on the use of Magnesol®, silica, Amberlite BD10 DRY® and Purolite PD 206® as adsorbents and were developed by adsorption at 65 °C. The response of each adsorbent was measured through the residual potassium, alcohol, water and soaps dissolved in the purified biodiesel. As a result, we observe that Magnesol® and silica showed better adsorption properties than Amberlite BD10 DRY® and Purolite PD 206®, especially for removing soap, free and bonded glycerol and potassium. In comparison to the conventional acid water washing, these matrices were found to be equally appropriate for the removal of inorganic and organic contaminant species from biodiesel. The main results found for these two adsorbents (Magnesol® 1% and silica 2%) were values below 0.17 mg KOH g-1 for acid number, 1 mg kg-1 of K, 61 ppm of soap, 500 mg kg-1 of water, 0.22% of methanol and 0.03% of free glycerol [42].

Chapter 3

Experimental details

This chapter describes a comprehensive research on synthesis magnesium silicate as adsorbent by precipitation method and adsorption process in five sections: section 1 describes how to synthesize magnesium silicate by precipitation method with four different sources of silica and magnesium sulfate (VI) as reactants. In section 2, synthesis of magnesium silicate varies in concentration ratio of the best source of silica from section1 and magnesium sulfate (VI). For section 3, the optimum conditions for adsorption of the highest efficiency magnesium silicate from section 2 were studied, i.e. amount of absorbent and time to equilibrium. The characterization of magnesium silicate were describes in details in section 4 and the determination contaminates in biodiesel; free fatty acid, soap, free glycerin and total glycerin, were explained in section 5. Resins preparation and packed-bed fabrication were explained in details in section 6. The dry wash method by resins was also given.

3.1 Instruments and apparatus for magnesium silicate part

1) 250 mL, 500 mL and 1L – Beaker
2) 100 mL, 500 mL and 1000 mL – Volumetric flask
3) 50 mL – Buret
4) 5 mL and 10 mL – Pipette
5) 10 mL and 100 mL – Cylinder
6) 125 ml and 250 mL – Erlenmeyer flask
7) Stirring rod
8) Magnetic bar
9) Desiccator
10) Whatman® Filtered-paper No.42
11) pH meter
12) Pestle
13) Sieve ASTM standard #80
14) Glass funnel
15) Filtration machine GAST DOA-P504-BN
16) Oven - REDLINE by Binder 9090-0001
17) Centrifuge - GEMMY PLC-012 series
18) Incubator shaker - Zhicheng Analytical Instruments Manufacturing Co.,Ltd Model: ZHWY-100B
19) Hotplate stirrer – IKA® C-MAG HS7
20) Analytical balance Mettler Toledo – AX 205

3.2 Chemicals for magnesium silicate part

1) Sodium metasilicate Analytical grade Produced by Rankem Company
2) Sodium metasilicate Analytical grade Produced by Aldrich Company
3) Solution of sodium silicate Analytical grade Produced by Merck Company
4) Rice husk ash
5) Magnesium sulfate Analytical grade Produced by Fisher Company
6) Magnesol D60 Produced by Dallas group America
7) Hydrochloric acid Analytical grade Produced by Labscan Asia Company
8) Sodium hydroxide Analytical grade Produced by Merck Company
9) Sodium fluoride Analytical grade Produced by Ajax Finechem
10) Methyl alcohol commercial grade
11) Sodium periodate Analytical grade Produced by Fisher Company
12) Ethanodiol Analytical grade Produced by Merck Company
13) Acetone Analytical grade Produced by Labscan Asia Company
14) Methyl red indicator
15) Bromophenol blue indicator from Loba Chemie Company
16) Phenolphthalein indicator
17) Phenol red indicator
18) Distilled water

3.3 Procedure for magnesium silicate part

Section1 and 2

3.3.1 Extraction solution of silica from rice husk ash

1) Boil rice husk ash (RHA) with 3M hydrochloric acid for 30 minutes.
2) Wash with distilled water until pH = 7.
3) Dry in an oven at 100°C for 24 hours.
4) Heat 10g of rice husk ash with 1 M sodium hydroxide at 70-80°C for 24 hours.
5) Filter the solution with Whatman® filtered-paper No.42.
6) Titrate silica content of silicate solution from RHA.

3.3.2 Synthesis of Magnesium silicate by precipitation method

1) Add solution of sodium silicate drop-wise into magnesium sulfate (VI) solution at room temperature with stirrer speed of 200 rpm. The details are shown in the table 3.1-3.2.
2) Keep the mixture at room temperature for 5-10 minutes
3) Separate the precipitate by centrifuge 2000 rpm. for 20 minutes
4) Filter the product and wash several times with distilled water.
5) Dry in an oven at 105°C for 24 hours.

6) Mash and sieve the magnesium silicate powder.
7) Keep the magnesium silicate powder in desiccator.

Table 3.1 The composition of mixture for section 1

Source of silica	Concentration ratio of silica and magnesium sulfate (VI)	Weight of silica	Weight of magnesium sulfate (g)
SSM	0.5:0.5	17.4 mL	12.324
RHA	0.5:0.5	25.0 mL	12.324
SMR	0.5:0.5	6.103 g	12.324
SMA	0.5:0.5	6.103 g	12.324

Table 3.2 The composition of mixture for section 2

Source of silica	Concentration ratio (Na_2SiO_3:$MgSO_4$)	Weight of SMA (g)	Weight of magnesium sulfate (g)
SMA	0.5:1.5	6.103	36.96
SMA	0.5:0.5	6.103	12.324
SMA	3.0:0.5	36.618	12.324

Section3

3.3.3 Comparison of adsorptive capacity between synthetic magnesium silicate with different silica source and commercial magnesium silicate

1) Add 50 g of biodiesel into 250 mL erlenmeyer flask.
2) Add 1 g of magnesium silicate into the same erlenmeyer flask.
3) Put the mixture into incubator shaker at 60°C, 200 rpm for 2 hours.
4) Separate the biodiesel and adsorbent by centrifuge 2000 rpm for 20 minutes.
5) Analyze remaining contaminates in biodiesel.

3.3.4 Study effect of Na_2SiO_3:$MgSO_4$ concentration ratio on adsorptive capacity

Repeat experiment as topic 3.3.3 by using the highest adsorptive capacities of silica source (from 3.3.3) with three different Na_2SiO_3:$MgSO_4$ concentration ratio; 0.5:1.5, 0.5:0.5 and 3.0:0.5. And the adsorptive conditions are 1, 2 and 3 grams per 150 mL biodiesel.

3.3.5 Study effect of dosage amount of magnesium silicate and time to equilibrium adsorption capacities

Repeat experiment as topic 3.3.3 by using the highest adsorptive capacities of Na_2SiO_3:$MgSO_4$ concentration ratio (from 3.3.4) with different dosage amount of magnesium silicate; 1, 2, 3, 4, 5 and 6 gram per 150 mL biodiesel. After that, effect of time to equilibrium was studied by using **the highest adsorptive capacities of** dosage amount of adsorbent at every hour until 7 hours.

Section4

3.3.6 Characterization of magnesium silicate

3.3.6.1 X-ray fluorescence (XRF)

It is used to study elements that present in a material by measuring the emission of X-ray fluorescence from a material that has been excites by bombarding with high-energy X-ray.

3.3.6.2 X-ray diffractometer (XRD)

It is used to identify the different phases in the catalyst as well as examine its crystalline structure by using Cu K_α radiation. The intensity data were collected over a 2Θ range of 5-70 degree

3.3.6.3 Brunauer-Emmett-Teller (BET)

It is used to explain the physical adsorption by measurement of the specific surface area (m^2/g), pore volume (cc/g) and pore size (A^0) of magnesium silicate.

3.3.6.4 Fourier transforms infrared spectrometry (FITR)

It is used to observe materials as it can reveal their molecular structure. It allows one to record infrared spectra. Infrared light is guided through an interferometer and then through the sample. A moving mirror inside the apparatus alters the distribution of infrared light that passes through the interferometer. The signal directly recorded represents light output as a function of mirror position. A data-processing turns this raw data into the desired result (the sample's spectrum): Light output as a function of infrared wavelength range of --- wavenumbers.

Section5

3.3.7 Determination contaminates in biodiesel

3.3.7.1 Free fatty acid

1) Mix biodiesel with MeOH as follow table 3.3. In this case, biodiesel has % free fatty acid about 0.2-1.0% w/w.
2) Add 1% concentration of phenolphthalein indicator 2-3 drops.
3) Titrate with 0.1M NaOH solution until the mixture turns pink color (still pink color at least 30 minutes).
4) Calculate % free fatty acid in the sample follow this equation:

$$\%FFA = \frac{C_{NaOH} \times V_{NaOH} \times 256 \times 100}{W_{oil} \times 1000} \qquad (3.1)$$

where %FFA is concentration of free fatty acid (%wt), C_{NaOH} is normality of the NaOH titration solution (0.1M), V_{NaOH} is volume in mL of NaOH titration solution and W_{oil} is weight of the sample of oil in grams.

Table 3.3 Ratio of weight of sample, volume of alcohol **and concentration of base in every range of % free fatty acid**

Free fatty acid (% w/w)	Weight of sample (g)	Volume of alcohol (mL)	Concentration of NaOH (M)
0.0 – 0.2	56.4 ± 0.2	50	0.1
0.2 – 1.0	28.2 ± 0.2	50	1.0
1.0 – 30.0	7.05 ± 0.05	75	0.25
30.0 – 50.0	7.05± 0.05	100	0.25 or 1.0
50.0 - 100	3.252 ± 0.001	100	1.0

3.3.7.2 Soap

1) Prepare a solvent of 980 mL of acetone and 20 mL of distilled water.
2) Mix 10 g of sample to 20 mL of solvent into 125 mL Erlenmeyer flask.
3) Add 4-5 drops of bromophenol blue indicator.
4) Titrate the mixture with 0.01M HCl solution until it reaches the yellow endpoint.
5) Calculate soap in parts per million in the sample follow this equation:

$$S = \frac{C_{HCl} \times V_{HCl} \times 304.4 \times 10^{6}}{W_{oil} \times 1000} \qquad (3.2)$$

where S is amount of soap in biodiesel (ppm), C_{HCl} is normality of the HCl titration solution (0.01M), V_{HCl} is volume in mL of HCl titration solution and W_{oil} is weight of the sample of oil in grams.

3.3.7.3 Free glycerin

1) Weigh the biodiesel 50 g into a 250 mL Erlenmeyer flask.
2) Extraction of glycerin from the biodiesel by washing:
    a) Put the flask in a water bath (60-65°C) and stir.
    b) Add 20 mL of HCl 5wt% stir approximately 15 minutes.
    c) Transfer carefully to a separatory funnel.
    d) Separate and place the aqueous phase in 250 mL Erlenmeyer flask.

   e) Put the biodiesel phase in the flask and repeat the washing using 20 mL of HCl 2.5 wt%.
   f) Separate and collect the aqueous phase into the Erlenmeyer flask.
   g) Repeat steps e and f but using distilled water instead of HCl 2.5 wt%.
   h) Rinse the flask with distilled water (20 mL approx.) and add it to the separatory funnel containing the biodiesel phase. Transfer the aqueous phase to the Erlenmeyer containing the previous washings.

3) Analyze the glycerin content in the aqueous phase:
   a) Add 5 drops of phenol red indicator.
   b) Add NaOH 2M to turn to fuchsia.
   c) Add HCl 5 wt% to turn to yellow, and then add 0.5 mL of HCl 5 wt% to make acid solution.
   d) Boil 3 minutes (with porous material to prevent violent boiling) to remove dissolve CO_2.
   e) Cool the mixture to room temperature.
   f) Add NaOH 0.1M until turning point (pink color).
   g) Add 15 mL of $NaIO_4$ (6 g/ 100 mL recently prepared), mix and leave 5-10 minutes in the darkness. Glycerin will react with $NaIO_4$ and produce formic acid.
   h) Add 2 mL ethanodiol (ethylene glycol) to get rid of remaining $NaIO_4$, wash the walls of the Erlenmeyer with distilled water, mix, and leave 5-10 minutes in the darkness.
   i) Titrate with 0.1 M NaOH

4) Calculate % Free glycerin in the sample follow this equation:

$$\%FG = \frac{C_{NaOH} \times V_{NaOH} \times 0.0921 \times 100}{W_{oil}} \tag{3.3}$$

where %FG is gram of glycerin per 100 g of sample, C_{NaOH} is normality of the NaOH titration solution (0.1M), V_{NaOH} is volume in mL of HCl titration solution and W_{oil} is weight of the sample of oil in grams.

3.3.7.4 Total glycerin

1) Weigh the biodiesel 50 g into a 250 mL Erlenmeyer flask.
2) Reaction of residual glycerides; transesterification. The reaction is carried out in a batch reactor with reflux:
   a) Put the flask in water bath (60-65°C) on a magnetic stirrer, and stir vigorously.
   b) Add 20 mL of sodium methoxide solution (0.7 g NaOH/ 40 mL methanol)
   c) Keep the temperature and the stirring during 30 minutes at 60°C
3) Extraction of glycerin from reacting media by washing:

Repeat step 2 in 3.3.7.3

4) Analyze the glycerin content in the aqueous phase:

Repeat step 3 in 3.3.7.3

5) Calculate % Free glycerin in the sample follow the equation as shown in step 5 of 3.3.7.3

Chapter 4
Results and Discussion

This research aims to synthesize and characterize the magnesium silicate as adsorbent in contaminated biodiesel with different conditions to determine adsorptive capacity. The synthesis was varied in sources of silica and concentration ratio to compare adsorptive capacity with commercial magnesium silicate. For adsorption, effect of dosage amount and time to reach equilibrium adsorption were studied by adding different amount of magnesium silicate at every hour for 7 hours of adsorption. Adsorbate characterization methods included XRF, XRD, BET and FTIR.

The results were discussed in the term of the comparison of adsorptive capacity in the different sources of silica and molecular ratio of SiO_2/MgO with commercial magnesium silicate, the optimum conditions of adsorption to equilibrium state.

Impurities of prewashed biodiesel were determined and removed by a packed-bed of resins as would be discussed later on.

4.1 The characterization of magnesium silicate

The synthetic magnesium silicate was prepared by precipitation method between different sources of silica and magnesium sulfate (VI).The magnesium silicates were characterized by XRF and FTIR technique. Magnesium silicate synthesized from SMA source, the highest adsorptive capacity, was studied by varying Na_2SiO_3: $MgSO_4$ concentration ratios and characterized by XRF, XRD, BET and FTIR technique.

4.1.1 The chemical compositions by the X-ray fluorescence (XRF)

The synthetic magnesium silicate was the fine white powder. Table 4.1 shows the components of commercial magnesium silicate and magnesium silicate derived from SMA and SMR as source of silica; 1.48:1, 0.76:1 and 0.004:1 molecular ratio of SiO_2/MgO, respectively. Obviously, the difference of silica source has effect on SiO_2/MgO ratio by SMR provided magnesium silicate precipitates with lower SiO_2/MgO ratio due to the limitation of SMR solubility in water. When, SMA could be able to prepare the desired SiO2/MgO molar ratio of magnesium silicate with high SiO_2 content. And the commercial Magnesium silicate was exhibited the highest molar ratio of SiO_2/MgO magnesium silicate.

Table 4.2 exhibited the chemical composition of synthetic magnesium silicate which was synthesized by varying Na_2SiO_3: MgSO4 concentration ratio. The molecular ratio of SiO_2/MgO in synthetic magnesium silicate was 0.36:1, 0.76:1 and 2.04:1 according to the Na_2SiO_3: $MgSO_4$ concentration ratio of 0.5:1.5, 0.5:0.5 and 3.0:0.5, respectively. Na_2SiO_3: $MgSO_4$ concentration ratio of 3.0:0.5 exhibited highest molecular ratio of SiO_2/MgO, while the concentration ratio of 0.5:1.5 showed lowest molecular ratio of SiO_2/MgO. Thus, the molar ratio of synthetic magnesium silicate was in agreement with the used concentration ratio.

Table 4.1 Chemical compositions of commercial magnesium silicate and magnesium silicate devised from various sources of silica.

Source of silica	% wt			Molecular ratio of SiO_2/MgO
	SiO_2	MgO	Other	
SMR	0.41	96.11	3.48	0.004:1
SMA	43.18	56.81	0.01	0.76:1
Commercial magnesium silicate	48.00	32.40	19.60	1.48:1

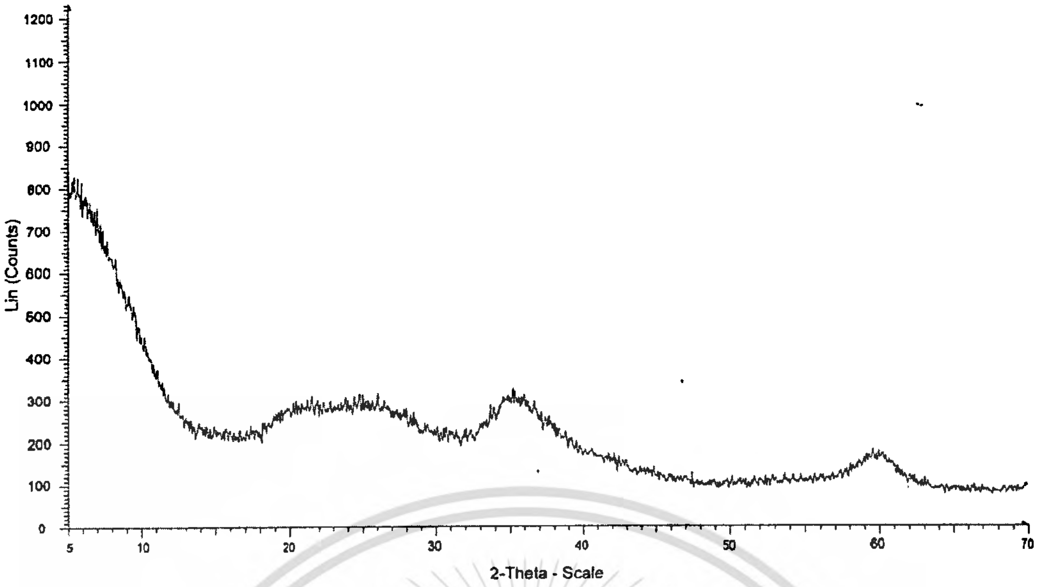
Table 4.2 Chemical compositions of synthetic magnesium silicate devised from SMA silica source by various Na2SiO3: MgSO4 concentration ratios.

Na_2SiO_3: $MgSO_4$ concentration ratios	% wt			Molecular ratio of SiO_2/MgO
	SiO_2	MgO	Other	
0.5:1.5	26.34	72.31	1.35	0.36:1
0.5:0.5	43.18	56.81	0.01	0.76:1
3.0:0.5	52.88	25.85	21.27	2.04:1

4.1.2 The crystalline structures by the X-ray diffractometer (XRD)

The synthesized magnesium silicate which was devised from different molecular ratio of SiO_2/MgO and commercial magnesium silicate were characterized and identified the crystalline structure by the X-ray diffraction technique. Cu Kα radiation was used and the intensity data were collected at 25°C over a 2Θ range of 5-70° and scan step of 0.02° (2Θ).

The diffraction patterns from the X-ray diffractometer were shown in Figure 4.1. The crystallinity of magnesium silicate was very weak, suggesting that magnesium silicate were amorphous [43-45].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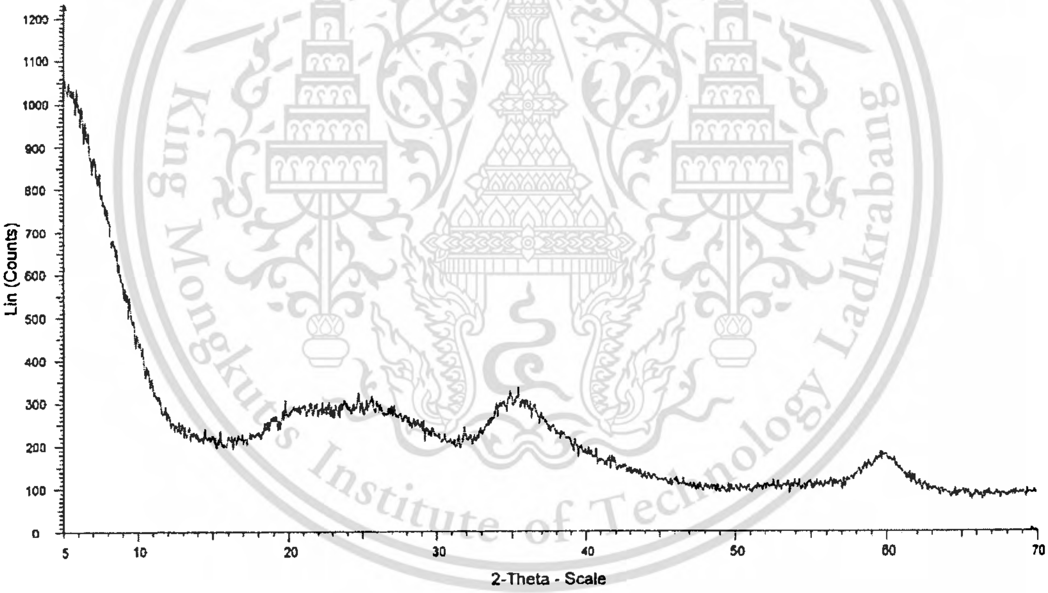
2-Theta - Scale

(a)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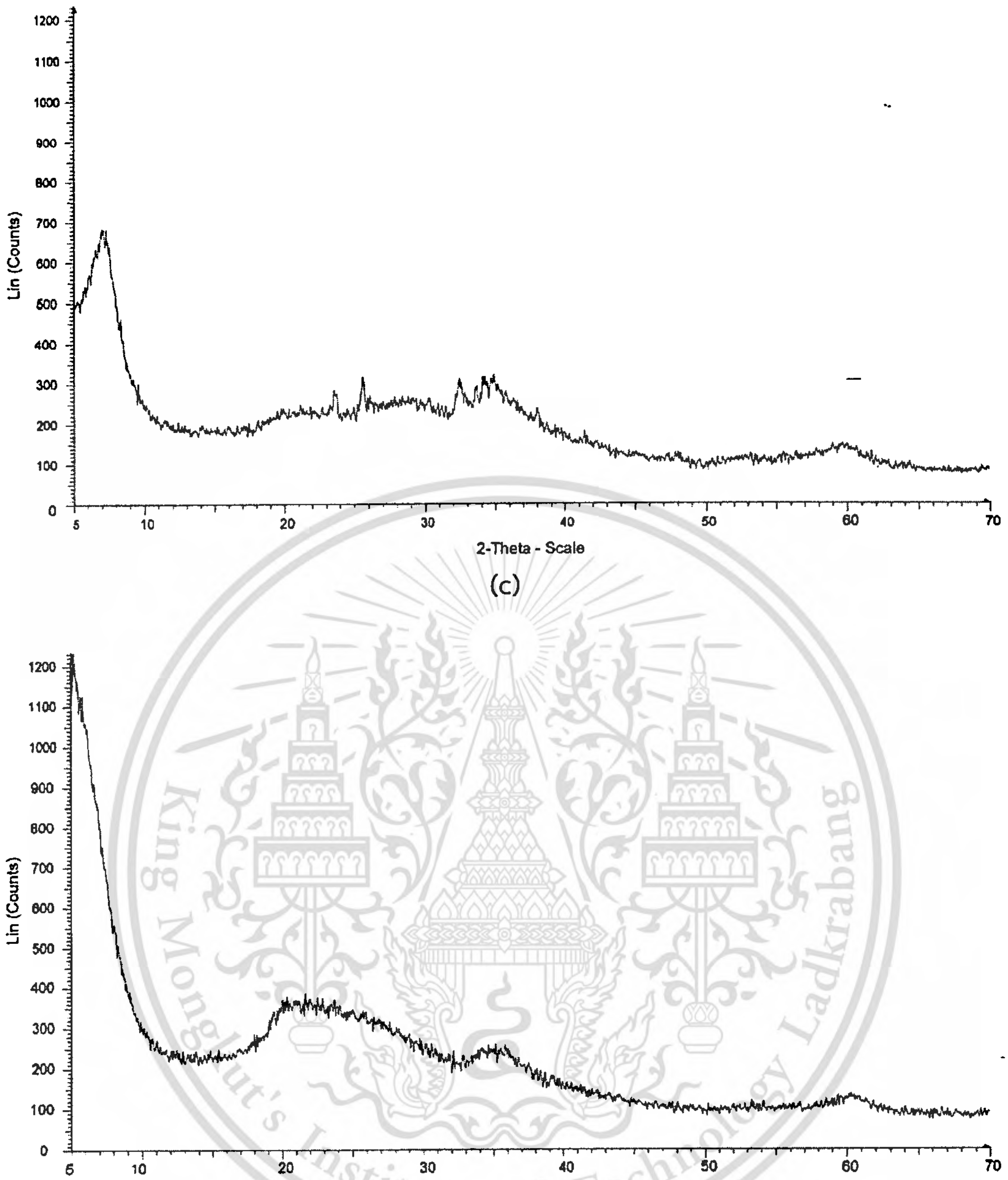
2-Theta - Scale

(b)



(c)

(d)

Figure 4.1 The XRD patterns of magnesium silicate with different molecular ratio of SiO_2/MgO: (a) 0.36:1, (b) 0.76:1, (c) 2.04:1 and (d) commercial magnesium silicate

4.1.3 The surface area and pore size by Brunauer-Emmett-Teller (BET)

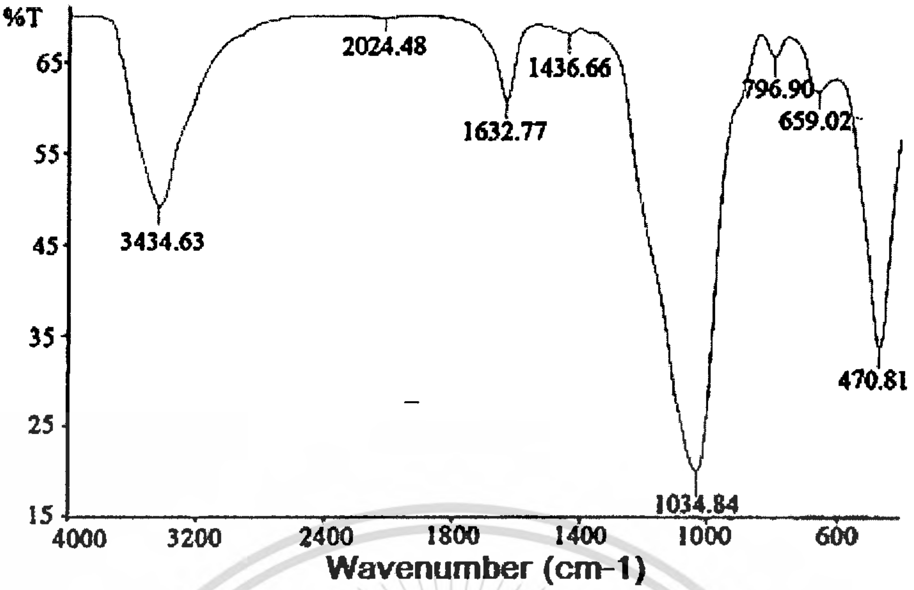
Table 4.3 lists the average surface area, pore volume and pore size of synthesized magnesium silicate and commercial magnesium silicate that were characterized by BET method. The results of synthesized magnesium silicate exhibited range of surface area between 15-58 m^2/g. And the average pore sizes were 50-105 A^0 which could describe that magnesium silicate was mesopore formation. From the results, the 2.04 : 1 molecular ratio of SiO_2/MgO of magnesium silicate had the biggest pore size than others, 105 A^0, which related to contaminates adsorption. Noticeably, the structure size of concerned contaminates were large so the pore size of adsorbents should play a significant role on adsorptivity of structure size of adsorbate.

Table 4.3 Average surface area, pore volume and pore size of magnesium silicate

Molecular ratio of SiO_2/MgO	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (A^0)
0.36 : 1	15.1	0.0192	50.88
0.76 : 1	67.19	0.1098	65.34
2.04 : 1	57.77	0.1516	105
Commercial magnesium silicate	425.4	0.7966	74.9

4.1.4 The infrared spectrum by the Fourier transforms infrared spectroscopy (FTIR)

The FT-IR spectra of magnesium silicate which were varied with silica source, SMR and SMA, are shown in Figure 4.2. These spectra were obtained from scanning in the range of 400-4000 cm-1. The band represented Si-O stretching vibration of magnesium silicate from commercial magnesium silicate, SMR and SMA were shown at 1034.84, 1129.89 and 1025.18 cm-1, respectively [41]. The hydroxyl stretching band (-OH) shows shoulders between 3300-3450 cm-1 [46]. Magnesium silicate from commercial magnesium silicate, SMR and SMA were exhibited the bands at 470.81, 451.56 and 446.26 cm-1, due to Mg–O stretching vibration, respectively [47]. From Figure 4.2, the band of magnesium silicate which derived from SMR represented hardly stretching vibration of Si-O which related with XRF result.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45
35
25
15
4000
3200
2400
1800
1400
1000
600
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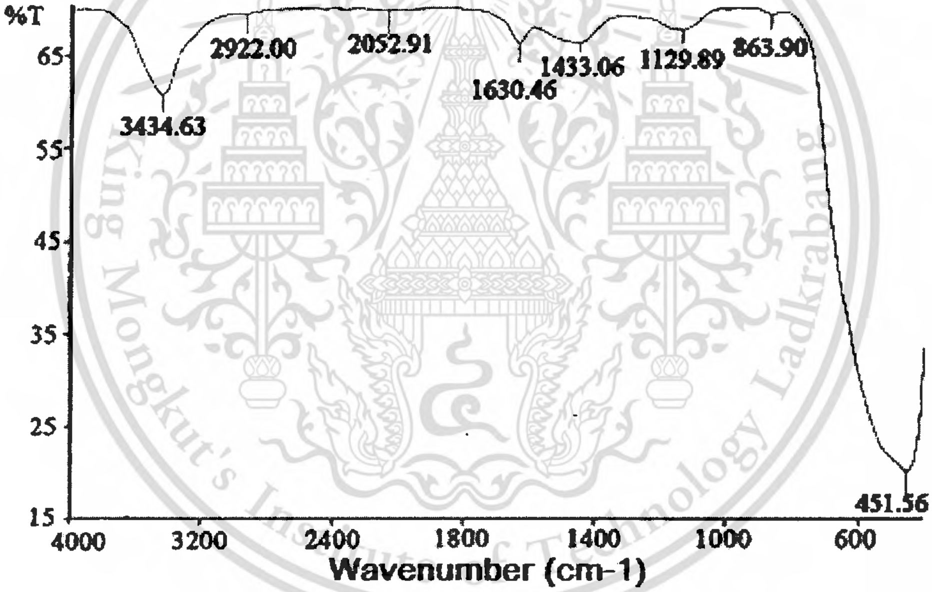
470.81

(a)


%T
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25
15
4000
3200
2400
1800
1400
1000
600
Wavenumber (cm-1)
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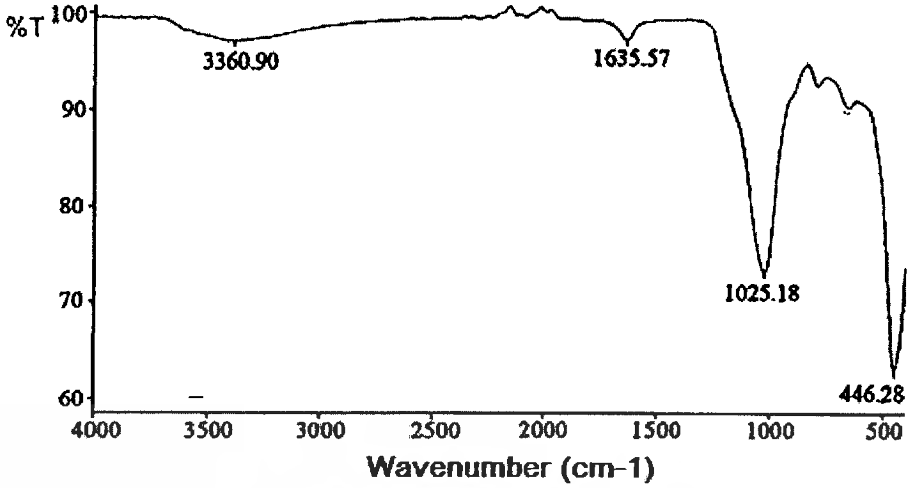
451.56

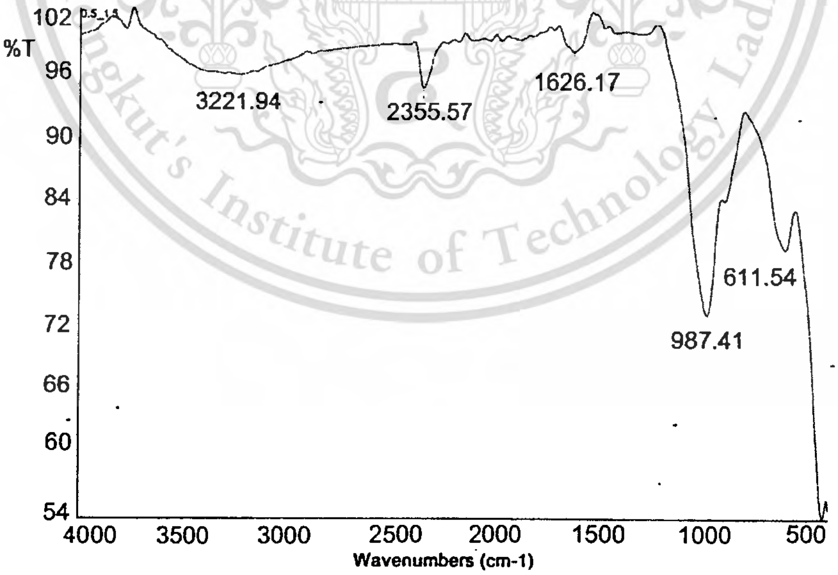
(b)



(c)

Figure 4.2 FT-IR spectra of magnesium silicate; (a) commercial magnesium silicate (b) SMR as source of silica and (c) SMA as source of silica

From Figure 4.3, the bands in 950-1100 cm-1 are due to Si-O stretching vibrational modes, the bands at 400-450 cm-1 is attributed to Mg-O stretching vibration and the bands at 3200-3800 cm-1 are assigned to deformation of hydroxyl stretching (-OH) [41,47]. The bands present at 1400-2000 cm-1 are due to the Si-O vibration because of combination and overtones of Si-O [46]. Therefore, the infrared analysis indicates that magnesium silicate adsorbents are a material with high content of SiO_2 and MgO.



(a)

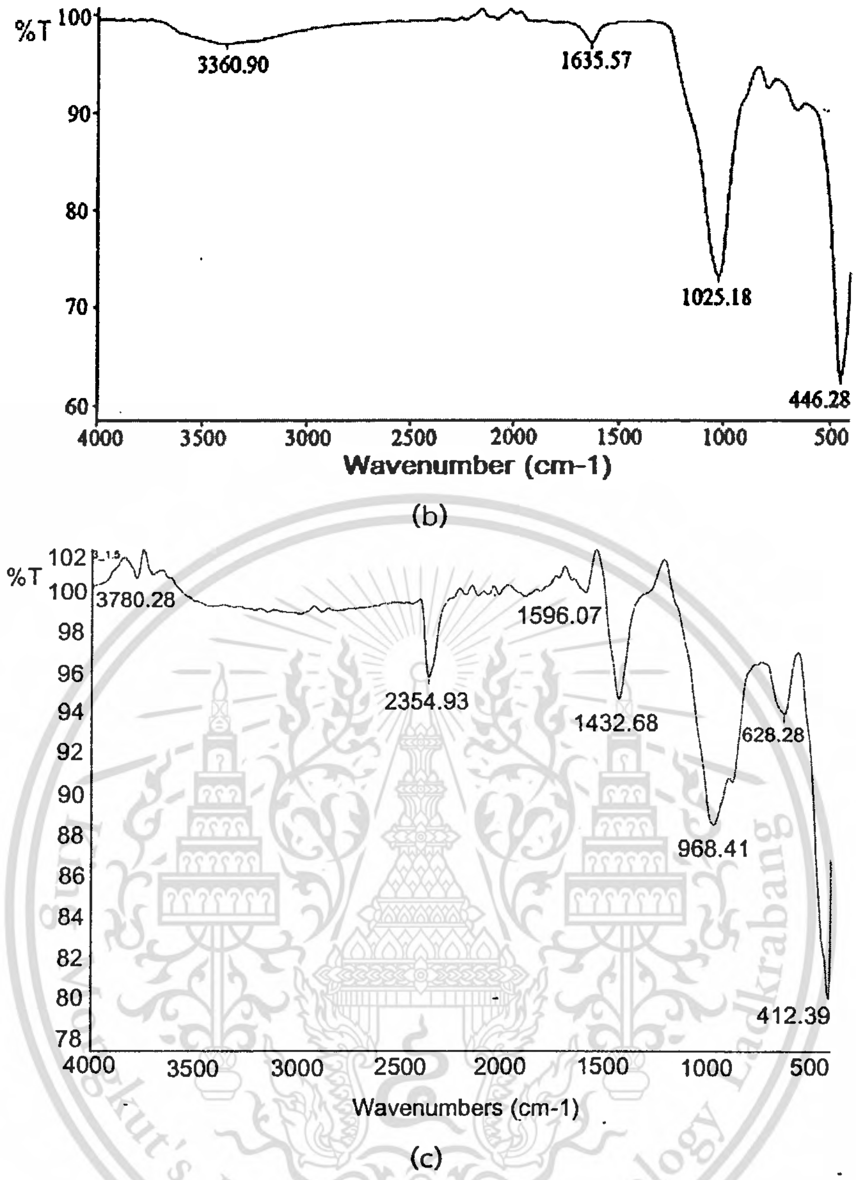


Figure 4.3 FT-IR spectra of magnesium silicate with different molecular ratios of SiO_2/MgO (a) 0.36:1, (b) 0.76:1 and (c) 2.04:1

4.2 The adsorption in contaminated biodiesel by synthesized magnesium silicate with different silica source compare with commercial magnesium silicate

The adsorption of contaminates in biodiesel by synthesized magnesium silicate, which RHA, SMA, SSM and SMR as source of silica, were studied and compared with commercial magnesium. The concerned contaminants in the biodiesel included free fatty acid, soap and free glycerin. The adsorption studied was observed under these conditions; 0.5:0.5M concentration ratio of silica and magnesium sulfate (VI), 50 grams biodiesel per 1 gram adsorbent of adsorbed ratio, 60°C and 2 hours.

4.2.1 The adsorption of free fatty acid

Figure 4.4 demonstrates adsorption efficiency comparison of FFA from different sources of silica and commercial magnesium silicate. Adsorption efficiency of commercial magnesium silicate was 29.34%, while magnesium silicate which derived from RHA, SMA, SSM and SMR as silica source had 78.76%, 91.90%, 66.61% and 23.18% adsorption efficiency, respectively. For the FFA adsorption capacity (qe) of magnesium silicate which derived from RHA, SMA, SSM and SMR as silica source and commercial magnesium silicate were 239.74, 287.25, 215.23, 73.83 and 96.07 mg/g, respectively. Thus, magnesium silicate which derived from SMA as source of silica had the highest adsorption efficiency of FFA.

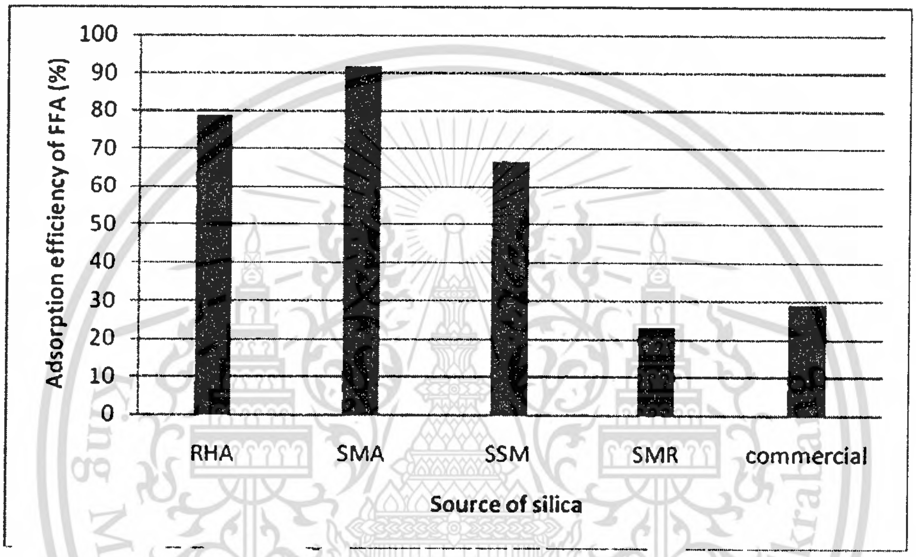


Figure 4.4 Comparison of adsorption efficiency of FFA from different sources of silica and commercial magnesium silicate.

4.2.2 The adsorption of soap

Adsorption efficiency of soap with different adsorbents was shown in Figure 4.5. For the figure, both of SMA and SSM as source of silicate show similarly high value of soap adsorption efficiency. Magnesium silicate which derived from SSM as silica source exhibited highest adsorption efficiency of soap at 44.29% and for SMA as adsorbent showed adsorption efficiency at 42.02%. For the soap adsorption capacity (qe) presented 1.62 mg/g of RHA, 2.137 mg/g of SMA, 2.141 mg/g of SSM, 0.49 mg/g of SMR and 0.75 mg/g of commercial magnesium silicate, when soap of unwash biodiesel was 475.83 ppm.

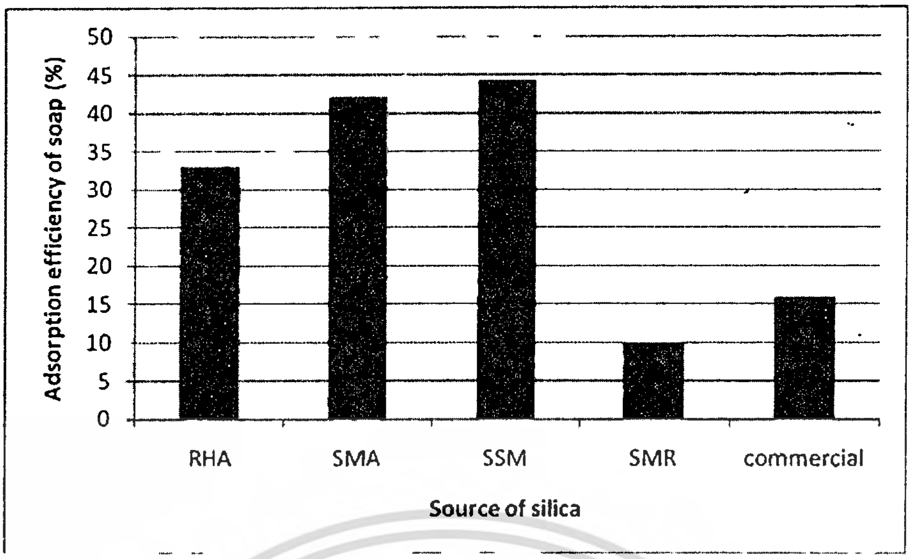


Figure 4.5 Comparison of adsorption efficiency of soap from different sources of silica and commercial magnesium silicate.

4.2.3 The adsorption of free glycerin

In figure 4.6, the comparison of efficiency on adsorption of free glycerin was exhibited. It presents that magnesium silicate which derived from SMA as source of silica had the best adsorption efficiency; 90.78%, when SSM had adsorption efficiency at 79.06%. When, the adsorption capacity (qe) of magnesium silicate which derived from RHA, SMA, SSM and SMR as silica source and commercial magnesium silicate were 9.59, 16.11, 14.08, 7.26 and 7.93 mg/g, respectively which free glycerin of unwash biodiesel was 0.051%.

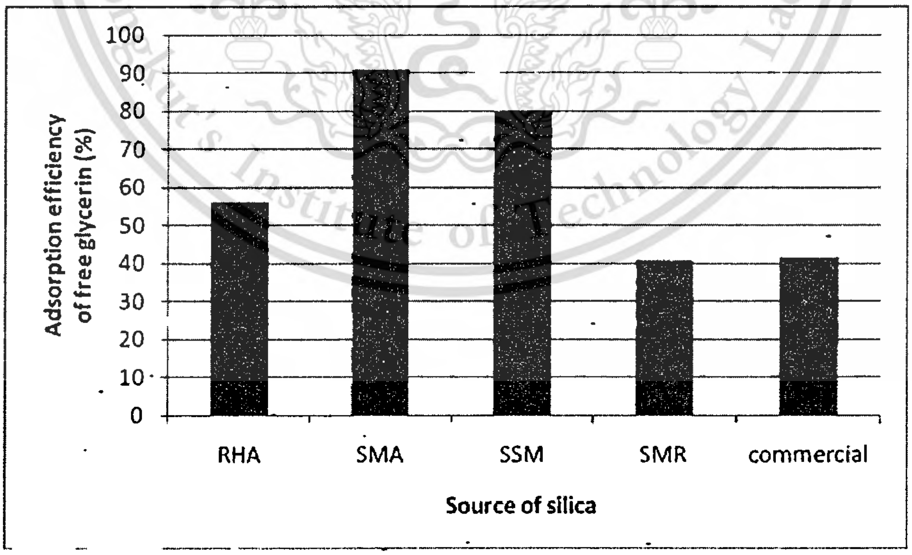


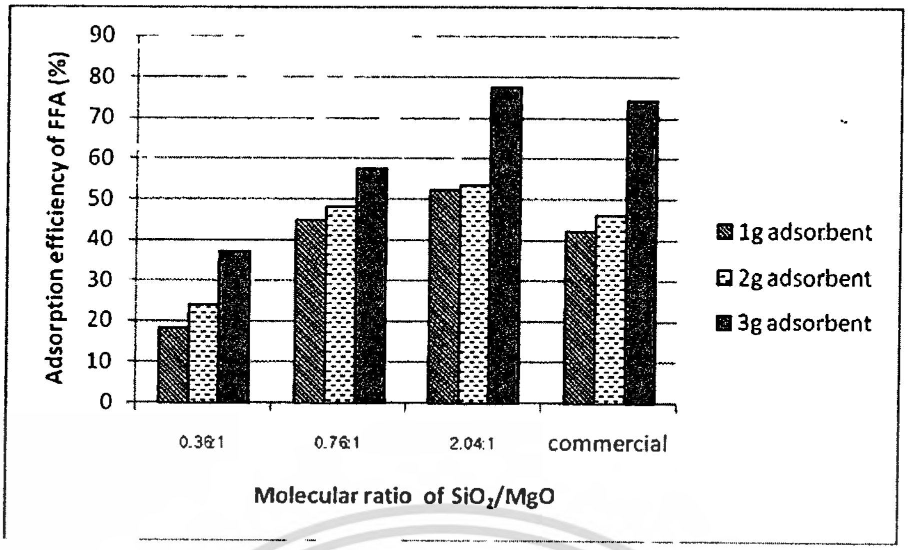
Figure 4.6 Comparison of adsorption efficiency of free glycerin from different sources of silica and commercial magnesium silicate.

From the result, SMR exhibited lowest adsorption efficiency of contaminates in biodiesel because of the limitation of SMR solubility with $Na_2SiO_3 \cdot 7H_2O$ of formula. Whereas SMA presented highest adsorption efficiency of contaminates in biodiesel because of it had structure without water; Na_2SiO_3 and had more solubility than SMR.

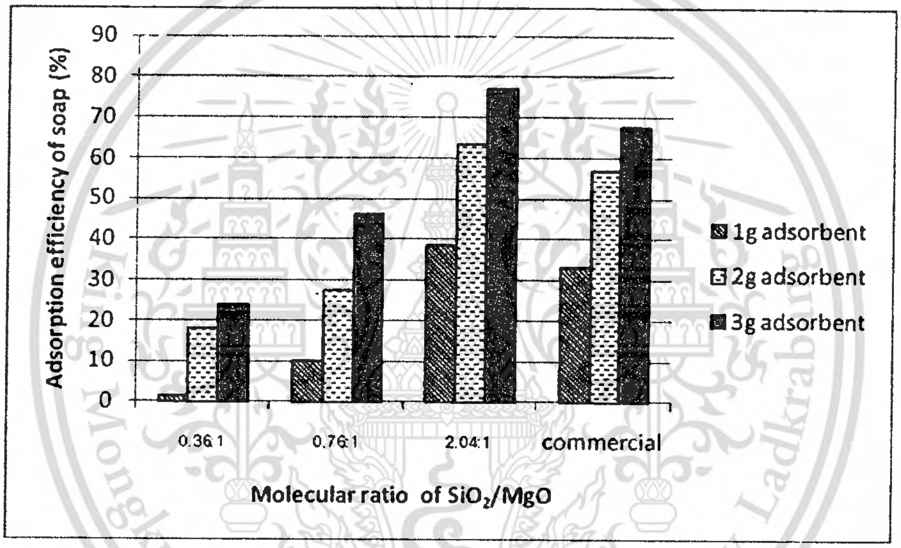
From behavior of adsorption of free fatty acid, soap and free glycerin, magnesium silicate which derived from SMA as source of silica showed high adsorption efficiency which SiO_2/MgO molar ratio of magnesium silicate is 0.76:1. Because of magnesium silicate surface is partially hydrophobic and partially hydrophilic. The hydrophobic part includes siloxane (≡Si–O–Si≡) groups and the hydrophilic portion contains isolated hydroxy groups (–Mg–OH), individual silanol groups (≡Si–OH). For the modification of magnesium silicate surface can carry out by increase hydrophobicity part of silicate surface to promote binding of several compounds [48]. And both structure of free fatty acid and soap are partially polar and non-polar, while glycerin presents non- polar structure. Thus, it related with the results of XRF analysis, magnesium silicate from SMA and commercial were exhibited high content of SiO_2/MgO molar ratio and FTIR result that clearly represented vibration of siloxane bonding; Si-O-Si.

4.3 The adsorption of contaminates in biodiesel by synthesized magnesium silicate from SMA silica source with different molecular ratios of SiO_2/MgO compare with commercial magnesium silicate

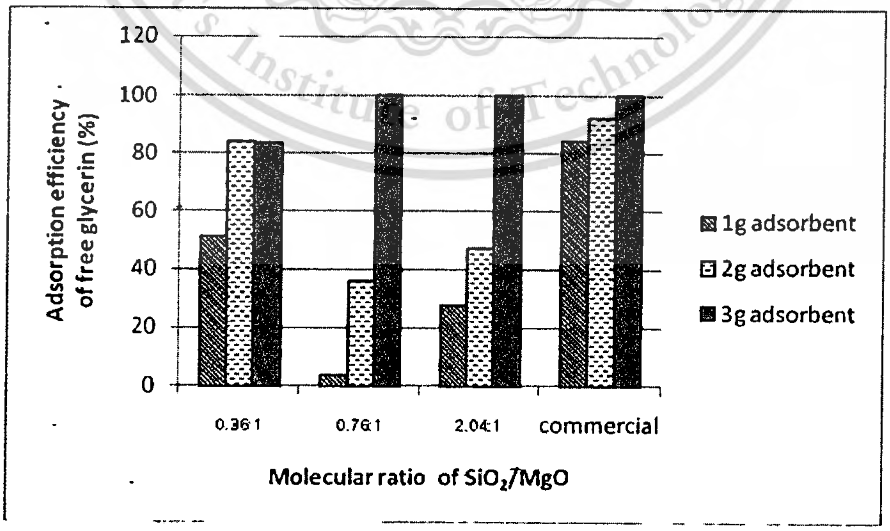
This topic studied adsorbed trend of free fatty acid, soap, free glycerin and total glycerin in biodiesel by synthesized magnesium silicate, which different Na_2SiO_3: $MgSO_4$ concentration ratios: 0.5:1.5M, 0.5:0.5M and 3.0:0.5M; 0.36:1, 0.76:1 and 2.04:1 molecular ratio of SiO_2/MgO respectively, compare dosage amount of adsorbents between 1g, 2g and 3g per 150 grams of biodiesel. The adsorbed study was noticed under these conditions; magnesium silicate which derived from SMA as silica source, adsorbed at 60°C for 5 hours.


Adsorption efficiency of FFA (%)
0
10
20
30
40
50
60
70
80
90
0.36:1
0.76:1
2.04:1
commercial
Molecular ratio of SiO_2/MgO
▨ 1g adsorbent
⊟ 2g adsorbent
■ 3g adsorbent

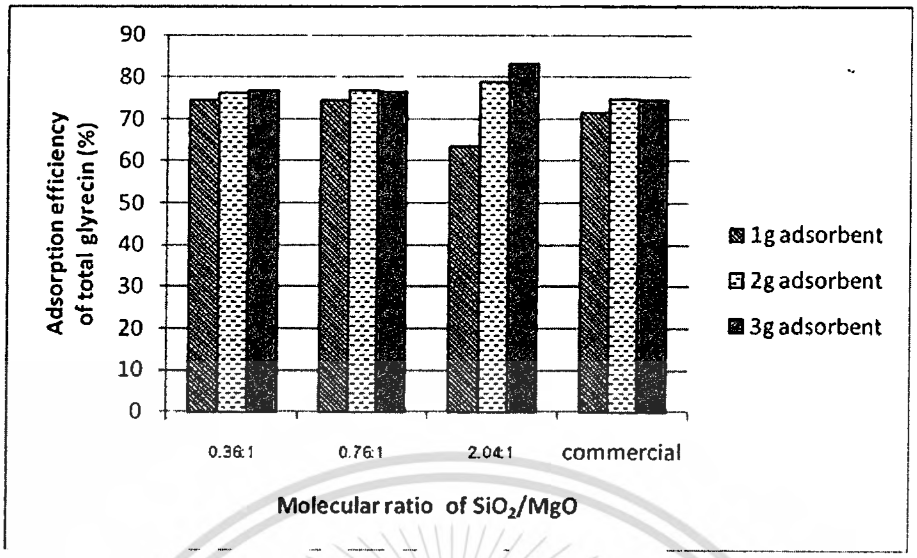
(a)


Adsorption efficiency of soap (%)
0
10
20
30
40
50
60
70
80
90
0.36:1
0.76:1
2.04:1
commercial
Molecular ratio of SiO_2/MgO
▨ 1g adsorbent
⊟ 2g adsorbent
■ 3g adsorbent

(b)


Adsorption efficiency of free glycerin (%)
0
20
40
60
80
100
120
0.36:1
0.76:1
2.04:1
commercial
Molecular ratio of SiO_2/MgO
▨ 1g adsorbent
⊟ 2g adsorbent
■ 3g adsorbent

(c)



(d)

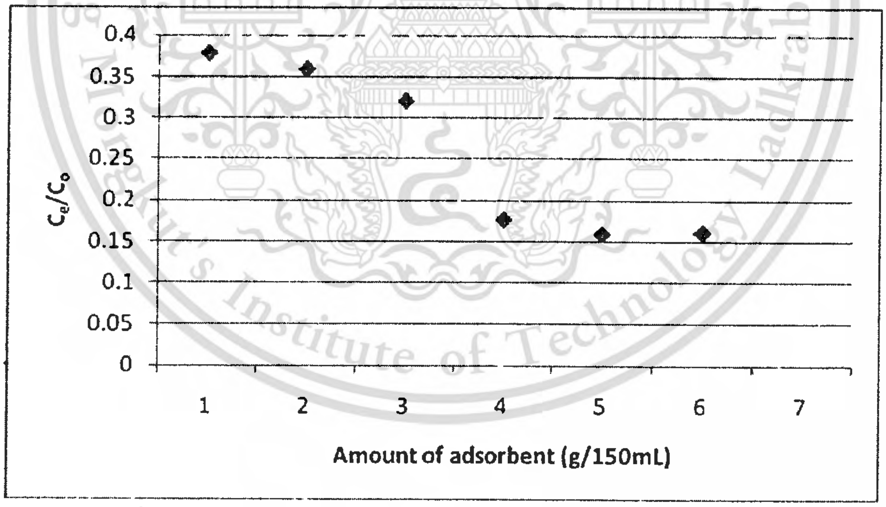
Figure 4.7 Comparison of adsorption efficiency of contaminates from different molecular ratios of SiO_2/MgO and commercial magnesium silicate; (a) free fatty acid, (b) soap, (c) free glycerin and (d) total glycerin

The comparison of contaminates adsorption efficiency between molecular ratios of SiO_2/MgO: 0.36:1, 0.76:1 and 2.04:1 and commercial magnesium silicate were presented in figure 4.7. From the results, dosage amount of adsorbent had direct variation with efficiency of contaminates adsorption and trends of FFA, soap, free glycerin and total glycerin adsorption with magnesium silicate which 2.04:1 molecular ratios of SiO_2/MgO show highest efficiency of adsorption; 77.39%, 77.11%, 100% and 82.92% respectively, while the adsorption capacity average, between 1g, 2g and 3g of adsorbent amount, was shown 70.73 mg/g of FFA adsorption, 1.62 mg/g of soap adsorption, 2.29 mg/g of free glycerin adsorption and 265.01 mg/g of total adsorption. On the other hand the trends of magnesium silicate, 0.36:1 molecular ratio of SiO_2/MgO, present low adsorbed efficiency of contaminates. This is because 2.04:1 molecular ratios of SiO_2/MgO of magnesium silicate had high silica content than other concentration ratios of magnesium silicate which related to XRF result. It means silica content in magnesium silicate effect on efficiency of contaminates adsorption, in other words, contaminates adsorption efficiency was increased when silica content in magnesium silicate increased because of siloxane groups in magnesium silicate (hydrophobic part) increasing. And in physical terms, BET results presented largest pore size of 2.04:1 SiO_2/MgO molecular ratio of magnesium silicate which involved adsorption efficiency; free fatty acid, soap, free glycerin and total glycerin have large size of structures. Therefore, pore size of magnesium silicate relates to structure size of adsorbate which effect on adsorption efficiency.

4.4 The study of effect on dosage amount of synthesized magnesium silicate with efficiency of contaminates adsorption in biodiesel

The effect on dosage amount of synthesized magnesium silicate with efficiency of contaminates adsorption in biodiesel by 3.0:0.5 M synthesized magnesium silicates, 2.04:1 molecular ratio of SiO_2/MgO, which derived from SMA as source of silica, were studied. The adsorption was observed to equilibrium state by the amount of absorbents were varied at 1, 2, 3, 4, 5 and 6 grams per 150 grams of biodiesel. The study of adsorption was noticed at 60°C for 5 hours.

The effect on dosage amount of absorbents were exhibited in figure 4.8 which the concentration ratio of contaminates before and after adsorption were plotted with amount of adsorbent for study the adsorption equilibrium of amount of adsorbent. The adsorption of soap, free glycerin and total glycerin show that the variation of contaminates amount decreased obviously at 1, 2grams and adsorption equilibrium was found at 3 grams adsorbent per 150 grams biodiesel, while adsorption equilibrium of FFA was found at 4 grams adsorbent per 150 grams biodiesel . For the efficiency of contaminates adsorption at 3 grams adsorbent were 61.46% of soap, 100% of free glycerin and 73.00% of total glycerin. For adsorption efficiency of FFA presents adsorption equilibrium at 4 grams adsorbent per 150 grams biodiesel, which were 82.37% of FFA adsorbed efficiency.



(a)

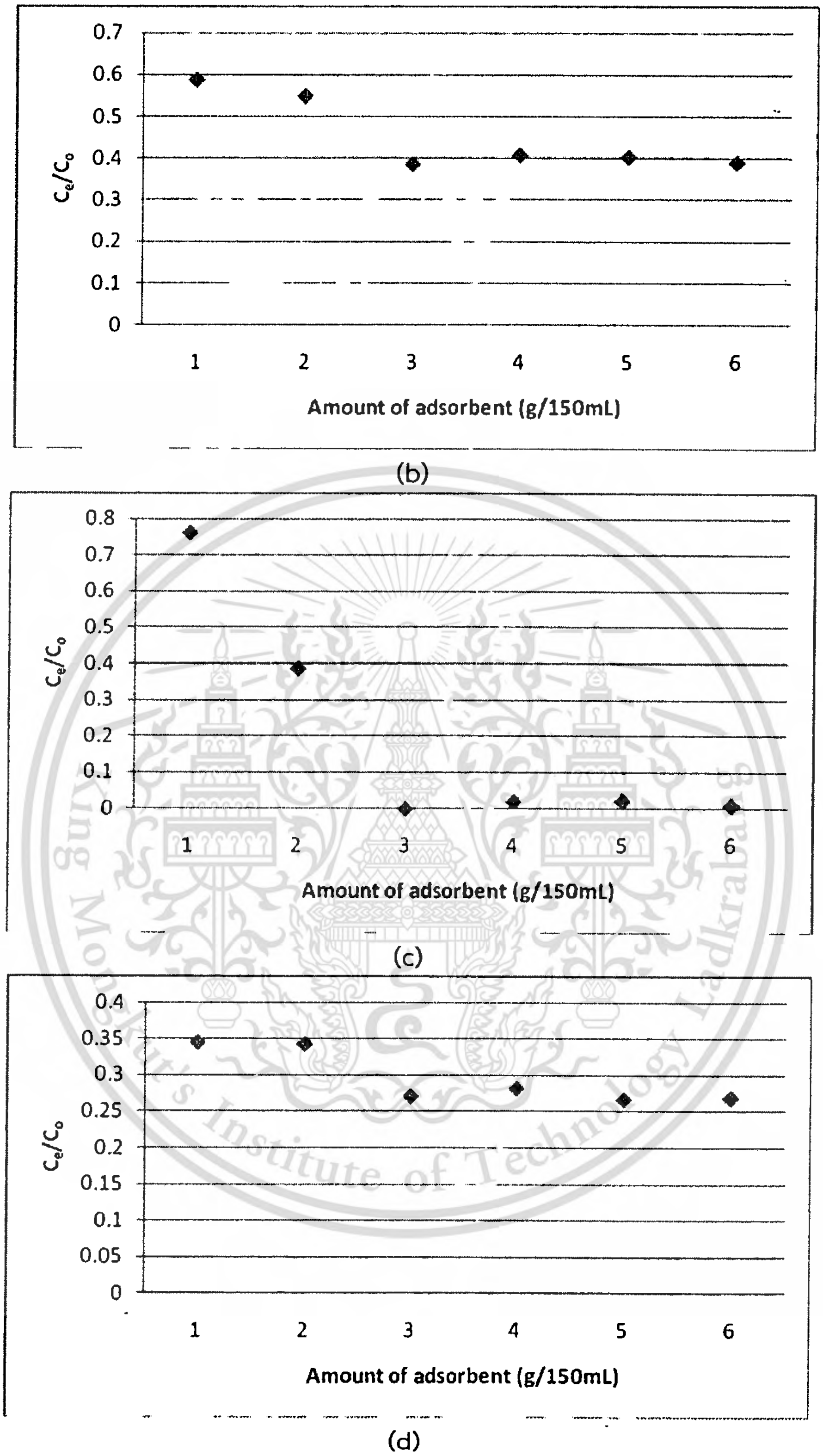


Figure 4.8 Relation between concentration ratio of contaminates before and after adsorption with amount of adsorbent; (a) free fatty acid, (b) soap, (c) free glycerin and (d) total glycerin

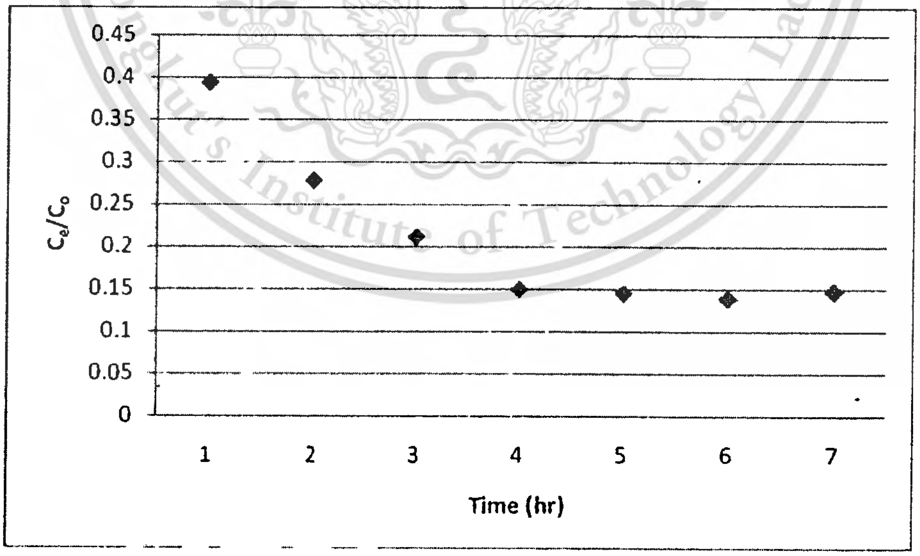
From the study effect on dosage amount of synthesized magnesium silicates (2.04:1 SiO_2/MgO), the optimum amount of adsorbent was 4 grams of adsorbent per 150 grams biodiesel. Therefore, the optimum conditions were used to study equilibrium time of adsorption in next topic.

Table 4.4 Contaminates adsorption efficiency of magnesium silicate at different dosage amount of adsorbent

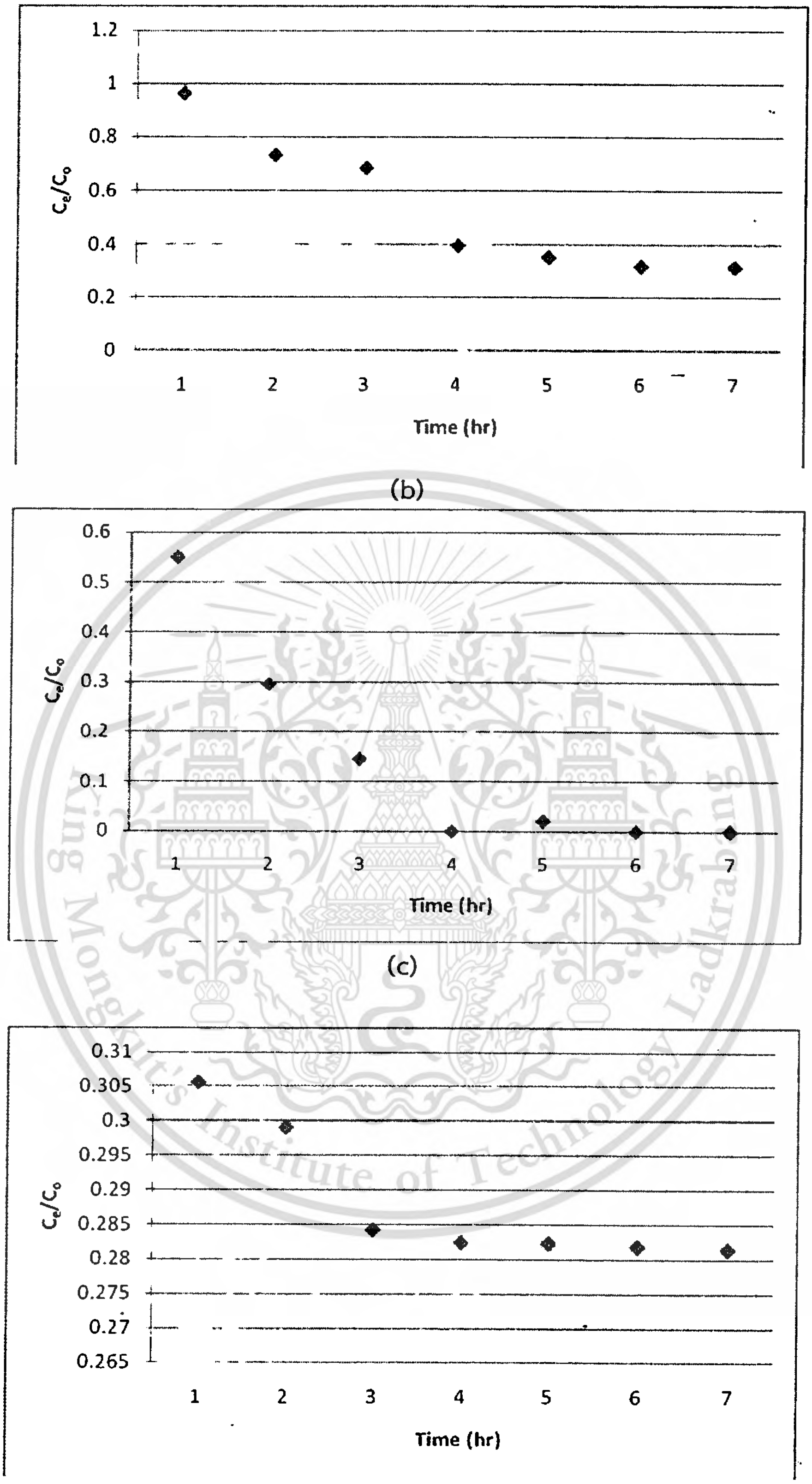
Amount of adsorbent (g)	Efficiency (%)			
	FFA	Soap	Free glycerin	Total glycerin
1	62.15	41.29	23.95	65.49
2	64.07	45.11	61.35	65.73
3	67.96	61.46	100	73.00
4	82.37	59.28	97.97	71.88
5	84.16	59.74	97.77	73.44
6	83.94	61.03	99.12	73.19

4.5 The study of equilibrium time of contaminates adsorption in biodiesel

From the previous study, the optimum conditions for synthesis and adsorption of magnesium in biodiesel were SMA as silica source, 2.04:1 molecular ratio of SiO_2/MgO and 4 grams dosage amount of adsorbent per 150 grams biodiesel. In this topic, these conditions were used to study the equilibrium time of magnesium silicate.



(a)



(b)

(c)

(d)

Figure 4.9 Equilibrium time of contaminates adsorption in biodiesel by synthesized magnesium silicate; (a) free fatty acid, (b) soap, (c) free glycerin and (d) total glycerin

In figure 4.9, the behavior of adsorption were exhibited to study the equilibrium time of adsorption, which free fatty acid, soap and free glycerin reach equilibrium time at 4 hours while total glycerin presents at 3 hours. The efficiency of free fatty acid, soap, free glycerin and total glycerin adsorption at equilibrium time were 85.11%, 60.52%, 100% and 71.59%, respectively. The variation of contaminates amount decrease noticeably in couple of hours at beginning, after that the adsorption reach equilibrium time.

Table 4.5 Contaminates adsorption efficiency of magnesium silicate at different time of adsorption.

Time (hr.)	Efficiency (%)			
	FFA	Soap	Free glycerin	Total glycerin
1	60.70	3.62	44.95	69.43
2	72.29	26.72	70.45	70.09
3	78.91	31.52	85.55	71.59
4	85.11	60.52	100	71.76
5	85.59	64.77	97.97	71.78
6	86.22	68.20	100	71.82
7	85.38	68.48	100	71.86

Therefore, the optimum conditions for free fatty acid, soap, free glycerin and total glycerin adsorption in biodiesel were synthesized magnesium silicate as adsorbent, which derived from crystalline sodium metasilicate from Aldrich company (SMA) and magnesium sulfate (VI) with 3.0:0.5M of Na_2SiO_3: $MgSO_4$ concentration ratios (2.04:1 molecular ratio of SiO_2/MgO), and adsorb the contaminates with 4 grams of synthesized magnesium silicate per 150 grams biodiesel for 4 hours. The capacity of contaminates adsorption with these condition were 49.44 mg/g for free fatty acid, 0.76 mg/g of soap, 2.43 mg/g of free glycerin and 109.43 mg/g of total glycerin.

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

This research aims to study the adsorption of contaminants; free fatty acid, soap, free glycerin and total glycerin, in biodiesel by using magnesium silicate as adsorbent. The method involves precipitation reaction between magnesium sulfate (VI) and four different sources of silica. The four different sources of silica; (I) solution of sodium silicate from Merck Company (SSM), (II) solution of silica was extracted from rice husk ash (RHA), (III) crystalline sodium metasilicate from Rankem (SMR) and (IV) Aldrich Company (SMA) were prepared to provide a reactant. The efficiency of adsorbents in the purification of biodiesel was obtained and compared with commercial magnesium silicate. From the results, magnesium silicate, which was provided by SMA silica source, exhibited highest adsorption capacities of contaminants with 0.76:1 SiO_2/MgO ratio. After that, effect of concentration ratios of synthesized magnesium silicate was studied by using SMA as source of silica which varied in three different concentration ratios of silica and magnesium sulfate(VI) (Na_2SiO_3: $MgSO_4$); 0.5:1.5M, 0.5:0.5M and 3.0:0.5M. The result presented increasing in efficiency of adsorption when silica concentration increased. From the X-ray fluorescence spectrometer (XRF), the result exhibited that synthesized magnesium silicate, which derived from SMA silica source with 3.0:0.5M Na_2SiO_3: $MgSO_4$ concentration ratio, consisted highest silica content; 2.04:1 molecular ratio of SiO_2/MgO. On the other hand, 0.5:1.5M Na_2SiO_3: $MgSO_4$ concentration ratio of magnesium silicate presented 0.36:1 molecular ratio of SiO_2/MgO. For the diffraction patterns from the X-ray diffractometer were shown that crystallinity of magnesium silicate was very weak, suggesting that magnesium silicate were amorphous. And the infrared spectrums of magnesium silicate were studied by Fourier transform infrared spectroscopy (FTIR) technique. It showed the vibration of siloxane bonding; Si-O-Si, hydroxyl stretching band (-OH) and Mg–O stretching vibration which related with XRF result.

The synthesized magnesium silicate, which derived from crystalline sodium metasilicate from Aldrich Company (SMA) and magnesium sulfate (VI) with 2.04:1 molecular ratio of SiO_2/MgO, was used to study effect on dosage amount and equilibrium time of adsorbents. The results presented the optimum conditions of contaminates adsorption, which were 4 grams of synthesized magnesium silicate per 150 grams biodiesel for 4 hours. The highest efficiency of contaminates adsorption with these condition were 49.44 mg/g for free fatty acid, 0.76 mg/g of soap, 2.43 mg/g of free glycerin and 109.43 mg/g of total glycerin.

From behavior of adsorption of free fatty acid, soap free glycerin and total glycerin in biodiesel, the silica content in synthesized magnesium silicate affected on capacity of contaminates adsorption. Due to the hydrophobic part in magnesium silicate; siloxane

$(\equiv\mathrm{Si{-}O{-}Si}\equiv)$ groups, effected on polar structure of contaminates and identically the hydrophilic part of magnesium silicate effected on nonpolar structure of contaminates. And both structure of free fatty acid and soap are partially polar and non-polar; while glycerin presents non- polar structure. Therefore, increasing of silica content was the cause of adsorbed capacity increased. And in physical terms, pore size of magnesium silicate relates to structure size of adsorbate which effect on adsorption efficiency.

5.2 Recommendations

1. The surface modification of magnesium silicate should be studied for increase the adsorbed capacity in biodiesel.
2. The contaminates adsorption should be included methanol.
3. Study adsorption phenomena of pure contaminates to compare each contaminates adsorption phenomena.

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Appendix

Appendix A

Determination of NaO_2 and SiO_2 in solution of Sodium silicate [49,50]

Appendix A

A.1 Determination %W of NaO_2 in solution of sodium silicate

1. Weigh solution of sodium silicate 0.5 g into a 250 mL Erlenmeyer flask.
2. Mix the solution with distilled water approximately 50 mL.
3. Drop methyl red indicator 2-3 drops (the mixture's color will change colorless to yellow).
4. Titrate the mixture with 0.5 M hydrochloric acid.

Calcutation

$$\%NaO_2 = \frac{3.1xV_{HCl}xC_{HCl}}{W_{sol}} \tag{A.1}$$

where V_{HCl} is volume in mL of hydrochloric acid titration solution, C_{HCl} is normality of the hydrochloric acid titration solution (0.5M) and W_{sol} is weight of the solution of sodium silicate in grams.

A.2 Determination %W of SiO_2 in solution of sodium silicate

1. Add Sodium fluoride 2.5 grams into the solution from A.1. The orange color of mixture will change to yellow.
2. Mix the mixture with 30 mL methanol.
3. Titrate the mixture with 0.5 M hydrochloric acid until become pink color.
4. Titrate the mixture with 0.5 M potassium hydroxide until become yellow color.

Calcutation

$$\%SiO_2 = \frac{1.5022x[(V_{HCl}xC_{HCl})-(V_{KOH}xC_{KOH})]}{W_{sol}} \tag{A.2}$$

where V_{HCl} is volume in mL of hydrochloric acid titration solution, C_{HCl} is normality of the hydrochloric acid titration solution (0.5M), V_{KOH} is volume in mL of potassium hydroxide titration solution, C_{KOH} is normality of the potassium hydroxide titration solution (0.5M) and W_{sol} is weight of the solution of sodium silicate in grams.

Appendix B

Raw data of the adsorption in contaminated biodiesel by synthesized magnesium silicate with different silica sources compare with commercial magnesium silicate

Table B.1 Adsorption of free fatty acid in biodiesel using synthesized magnesium silicate which derived from different silica sources compare with commercial magnesium silicate.

Silica sources	Amount (g/50mL)	Weight of sample (g)	Volume of NaOH titration (mL)	FFA(%)	Average FFA(%)	Adsorption efficiency (%)	q_e (mg/g)
Unwash	-	11.23	13.6	3.11	3.08	-	-
		10.59	12.6	3.06			
RHA	1	10.54	2.9	0.73	0.66	78.76	239.74
		9.20	2.1	0.58			
SMA	1	9.26	0.8	0.22	0.25	91.90	287.25
		11.01	1.2	0.28			
SSM	1	10.62	4.6	1.12	1.03	66.61	215.23
		10.33	3.8	0.94			
SMR	1	10.32	9.4	2.32	2.37	23.18	73.83
		10.33	9.7	2.41			
Commercial magnesium silicate	1	11.00	9.1	2.11	2.18	29.34	96.07
		10.23	8.9	2.24			

Table B.2 Adsorption of soap in biodiesel using synthesized magnesium silicate which derived from different silica sources compare with commercial magnesium silicate.

Silica sources	Amount (g/50mL)	Weight of sample (g)	Volume of HCl titration (mL)	Soap (ppm)	Average Soap (ppm)	Adsorption efficiency (%)	q_e (mg/g)
Unwash	-	11.09	1.7	477.96	475.83	-	-
		9.02	1.4	473.70			
RHA	1	10.54	1.1	308.98	318.42	33.08	1.62
		10.10	1.1	327.86			
SMA	1	10.98	0.95	266.14	275.91	42.01	2.137
		10.40	0.97	285.68			
SSM	1	10.39	0.9	272.31	265.09	44.29	2.141
		9.93	0.8	257.87			
SMR	1	10.60	1.5	431.01	427.79	10.10	0.49
		9.74	1.4	424.57			
Commercial magnesium silicate	1	9.76	1.3	395.67	400.39	15.85	0.75
		10.03	1.3	405.11			

Table B.3 Adsorption of free glycerin in biodiesel using synthesized magnesium silicate which derived from different silica sources compare with commercial magnesium silicate.

Silica sources	Amount (g/50mL)	Weight of sample (g)	Volume of NaOH titration (mL)	Free glycerin (%)	Average Free glycerin (%)	Adsorption efficiency (%)	q_e (mg/g)
Unwash	-	35.88	2.3	0.059	0.022	-	-
		36.61	1.7	0.042			
RHA	1	34.92	1.0	0.027	0.005	56.08	9.59
		32.18	0.6	0.017			
SMA	1	33.64	0.2	0.005	0.010	90.78	16.11
		35.95	0.2	0.004			
SSM	1	34.66	0.4	0.012	0.030	79.61	14.08
		34.70	0.4	0.009			
SMR	1	35.04	1.5	0.039	0.029	40.78	7.26
		34.76	0.8	0.022			
Commercial magnesium silicate	1	37.68	1.0	0.024	0.051	41.76	7.93
		36.77	1.4	0.036			

Appendix C

Raw data of the adsorption of contaminates in biodiesel by synthesized magnesium silicate from SMA silica source with different molecular ratios of SiO_2/MgO compare with commercial magnesium silicate

Table C.1 Adsorption of free fatty acid in biodiesel using synthesized magnesium silicate, which derived from SMA, with different molecular ratios of SiO_2/MgO compare with commercial magnesium silicate.

Molecular ratios of SiO_2/MgO	Amount (g/150mL)	Weight of sample (g)	Volume of NaOH titration (mL)	FFA (%)	Average FFA (%)	Adsorption efficiency (%)	q_e (mg/g)
Unwash	-	10.25	7.8	1.94	1.95	-	-
		11.64	8.9	1.96			
0.36 : 1	1	10.75	6.7	1.59	-	18.23	38.24
	2	9.66	5.6	1.48		23.99	22.64
	3	10.40	5.0	1.23		36.94	24.99
0.76 : 1	1	10.42	4.4	1.08	-	44.62	90.76
	2	10.12	4.0	1.01		48.14	47.53
	3	10.51	3.4	0.82		57.57	39.37
2.04 : 1	1	10.68	3.9	0.93	-	52.09	108.54
	2	9.83	3.5	0.91		53.28	51.09
	3	10.44	1.8	0.44		77.39	52.57
Commercial magnesium silicate	1	10.43	4.6	1.13	-	42.16	85.83
	2	10.18	4.2	1.05		45.88	45.58
	3	11.22	2.2	0.50		74.29	54.23

Table C.2 Adsorption of soap in biodiesel using synthesized magnesium silicate, which derived from SMA, with different molecular ratios of SiO_2/MgO compare with commercial magnesium silicate.

Molecular ratios of SiO_2/MgO	Amount (g/150mL)	Weight of sample (g)	Volume of HCl titration (mL)	Soap (ppm)	Average Soap (ppm)	Adsorption efficiency (%)	q_e (mg/g)
Unwash	-	11.33	1.84	495.24	497.55	-	-
		10.67	1.75	499.86			
0.36 : 1	1	11.17	1.8	490.63	-	1.39	0.06
	2	10.46	1.4	407.46		18.11	0.44
	3	11.25	1.4	378.97		23.83	0.37
0.76 : 1	1	10.18	1.5	448.53	-	9.85	0.50
	2	10.99	1.3	360.19		27.61	0.75
	3	11.37	1.0	267.81		46.17	0.87
2.04 : 1	1	9.94	1.0	306.12	-	38.48	1.90
	2	10.03	0.6	182.08		63.41	1.58
	3	10.69	0.4	113.91		77.11	1.37
Commercial magnesium silicate	1	9.16	1.0	332.29	-	33.21	1.85
	2	9.92	0.7	214.73		56.84	1.48
	3	9.40	0.5	161.97		67.45	1.26

Table C.3 Adsorption of free glycerin in biodiesel using synthesized magnesium silicate, which derived from SMA, with different molecular ratios of SiO_2/MgO compare with commercial magnesium silicate.

Molecular ratios of SiO_2/MgO	Amount (g/150mL)	Weight of sample (g)	Volume of NaOH titration (mL)	Free glycerin (%)	Average free glycerin (%)	Adsorption efficiency (%)	q_e (mg/g)
Unwash	-	50.12	1.4	0.026	0.023	-	-
		50.92	1.0	0.020			
0.36 : 1	1	48.97	0.6	0.011	-	51.34	5.83
	2	49.19	0.2	0.003		83.85	4.78
	3	48.31	0.2	0.003		83.56	3.12
0.76 : 1	1	49.42	1.2	0.022	-	3.57	0.41
	2	49.61	0.8	0.015		35.96	2.07
	3	49.62	0	0		100	3.84
2.04 : 1	1	38.26	0.7	0.017	-	27.34	2.43
	2	37.62	0.5	0.012		47.22	2.06
	3	30.90	0	0		100	2.39
Commercial magnesium silicate	1	50.13	0.2	0.003	-	84.16	9.78
	2	50.09	0.1	0.001		92.07	5.35
	3	50.04	0	0		100	3.87

Table C.4 Adsorption of total glycerin in biodiesel using synthesized magnesium silicate, which derived from SMA, with different molecular ratios of SiO_2/MgO compare with commercial magnesium silicate.

Molecular ratios of SiO_2/MgO	Amount (g/150mL)	Weight of sample (g)	Volume of NaOH titration (mL)	Total glycerin (%)	Average total glycerin (%)	Adsorption efficiency (%)	q_e (mg/g)
Unwash	-	50.17	81.1	1.49	1.53	-	-
		51.28	87.4	1.57			
0.36 : 1	1	48.38	20.6	0.39	-	74.37	550.46
	2	45.95	18.2	0.36		76.15	267.65
	3	42.57	16.4	0.35		76.81	166.72
0.76 : 1	1	50.71	21.5	0.39	-	74.47	577.73
	2	50.78	19.75	0.35		76.59	297.48
	3	51.02	20.1	0.36		76.28	198.47
2.04 : 1	1	39.92	24.2	0.56	-	63.50	387.74
	2	41.83	14.7	0.32		78.84	252.24
	3	36.67	10.4	0.26		82.92	155.06
Commercial magnesium silicate	1	51.00	24.2	0.44	-	71.44	557.43
	2	49.22	20.8	0.39		74.56	280.73
	3	49.17	20.8	0.39		74.53	186.87

Appendix D

Raw data of the adsorption of contaminates in biodiesel by 2.04:1 SiO_2/MgO molecular ratios synthesized magnesium silicate from SMA silica source with different dosage amount of adsorbent

Table D.1 Adsorption of free fatty acid in biodiesel using 2.04:1 SiO_2/MgO molecular ratio of synthesized magnesium silicate, which derived from SMA, with different dosage amount of adsorbent.

Dosage amount of adsorbent (g/150mL)	Weight of sample (g)	Volume of NaOH titration (mL)	FFA (%)	Average FFA (%)	Adsorption efficiency (%)	q_e (mg/g)
1	12.74	2.7	0.54	0.74	62.15	142.02
	10.68	3.9	0.93			
2	10.96	2.1	0.49	0.70	64.07	64.98
	9.83	3.5	0.91			
3	13.92	4.4	0.81	0.63	67.96	53.85
	10.44	1.8	0.44			
4	12.39	1.4	0.29	0.34	82.37	49.39
	12.20	1.9	0.40			
5	14.61	1.1	0.19	0.31	84.16	42.76
	11.43	1.9	0.43			
6	14.14	1.6	0.29	0.31	83.94	36.93
	12.91	1.7	0.34			

Table D.2 Adsorption of soap in biodiesel using 2.04:1 SiO_2/MgO molecular ratio of synthesized magnesium silicate, which derived from SMA, with different dosage amount of adsorbent.

Dosage amount of adsorbent (g/150mL)	Weight of sample (g)	Volume of HCl titration (mL)	Soap (ppm)	Average Soap (ppm)	Adsorption efficiency (%)	q_e (mg/g)
1	9.94	1.0	306.12	292.10	41:29	2.15
	10.95	1.0	278.09			
2	9.92	0.7	214.73	273.11	45.11	1.28
	12.86	1.4	331.48			
3	10.03	0.6	182.08	191.74	61.46	1.05
	10.58	0.7	201.39			
4	11.34	0.6	161.02	202.58	59.28	0.83
	11.22	0.9	244.14			
5	12.23	0.9	223.97	200.32	59.74	0.67
	10.34	0.6	176.66			
6	12.90	0.8	188.71	192.88	61.03	0.64
	12.23	0.8	199.05			

Table D.3 Adsorption of free glycerin in biodiesel using 2.04:1 SiO_2/MgO molecular ratio of synthesized magnesium silicate, which derived from SMA, with different dosage amount of adsorbent.

Dosage amount of adsorbent (g/150mL)	Weight of sample (g)	Volume of NaOH titration (mL)	Free glycerin (%)	Average free glycerin (%)	Adsorption efficiency (%)	q_e (mg/g)
1	38.26	0.6	0.014	0.017	23.95	2.41
	48.63	1.1	0.020			
2	37.63	0.5	0.001	0.009	61.34	3.07
	48.60	0.3	0.005			
3	30.90	0	0	0	100	3.01
	47.11	0	0			
4	48.91	0.05	0.001	0	97.97	2.82
	50.29	0	0			
5	44.43	0.05	0.001	0	97.77	2.18
	51.88	0	0			
6	44.88	0.02	0	0	99.12	1.77
	47.61	0	0			

Table D.4 Adsorption of total glycerin in biodiesel using 2.04:1 SiO_2/MgO molecular ratio of synthesized magnesium silicate, which derived from SMA, with different dosage amount of adsorbent.

Dosage amount of adsorbent (g/150mL)	Weight of sample (g)	Volume of NaOH titration (mL)	Total glycerin (%)	Average total glycerin (%)	Adsorption efficiency (%)	q_e (mg/g)
1	42.73	26.3	0.57	0.53	65.49	423.59
	41.83	22.2	0.49			
2	42.74	26.6	0.57	0.52	65.73	207.80
	39.92	20.6	0.48			
3	43.59	19.6	0.41	0.41	73.00	149.39
	36.67	16.4	0.41			
4	41.54	20.7	0.46	0.43	71.88	116.06
	42.89	18.7	0.40			
5	43.05	18.1	0.39	0.41	73.44	98.69
	44.80	20.7	0.43			
6	42.72	19.5	0.42	0.41	73.19	79.84
	42.85	18.6	0.40			

Appendix E

Raw data of the adsorption of contaminates in biodiesel by 2.04:1 SiO_2/MgO molecular ratios synthesized magnesium silicate from SMA silica source and 4g adsorbent per 150g biodiesel ratio with different time (hr)

Table E.1 Adsorption of free fatty acid in biodiesel using 2.04:1 SiO_2/MgO molecular ratio of synthesized magnesium silicate, which derived from SMA, at ratio of 4 g adsorbent per 150g biodiesel with different time (hr)

Time (hour)	Weight of sample (g)	Volume of NaOH titration (mL)	FFA (%)	Average FFA(%)	Adsorption efficiency (%)	q_e (mg/g)
1	11.08	3.4	0.79	0.77	60.71	53.75
	10.96	3.2	0.75			
2	9.67	2	0.53	0.54	72.29	48.47
	10.19	2.2	0.55			
3	12.40	2.1	0.43	0.41	78.92	59.11
	11.83	1.8	0.39			
4	10.61	1.2	0.29	0.29	85.11	49.44
	9.66	1.1	0.29			
5	12.39	1.4	0.29	0.28	85.60	59.96
	12.20	1.3	0.27			
6	10.51	1.1	0.27	0.27	86.22	48.76
	9.48	1.0	0.27			
7	12.01	1.3	0.28	0.28	85.38	54.81
	10.47	1.2	0.29			

Table E.2 Adsorption of soap in biodiesel using 2.04:1 SiO_2/MgO molecular ratio of synthesized magnesium silicate, which derived from SMA, at ratio of 4 g adsorbent per 150g biodiesel with different time (hr)

Time (hour)	Weight of sample (g)	Volume of HCl titration (mL)	Soap (ppm)	Average soap (ppm)	Adsorption efficiency (%)	q_e (mg/g)
1	9.35	1.5	488.31	479.54	3.62	0.04
	10.35	1.6	470.76			
2	10.69	1.1	313.40	364.62	26.72	0.35
	10.25	1.4	415.83			
3	11.74	1.4	363.14	340.74	31.52	0.47
	12.43	1.3	318.35			
4	9.89	0.6	184.64	196.43	60.52	0.76
	10.23	0.7	208.22			
5	11.34	0.7	187.85	175.31	64.77	0.91
	11.22	0.6	162.76			
6	10.10	0.6	180.92	158.20	68.20	0.90
	11.23	0.5	135.49			
7	10.25	0.6	178.17	156.80	68.48	0.92
	11.24	0.5	135.44			

Table E.3 Adsorption of free glycerin in biodiesel using 2.04:1 SiO_2/MgO molecular ratio of synthesized magnesium silicate, which derived from SMA, at ratio of 4 g adsorbent per 150g biodiesel with different time (hr)

Time (hour)	Weight of sample (g)	Volume of NaOH titration (mL)	Free glycerin (%)	Average free glycerin (%)	Adsorption efficiency (%)	q_e (mg/g)
1	38.81	0.4	0.009	0.013	44.95	1.03
	40.19	0.7	0.016			
2	39.20	0.36	0.007	0.006	70.45	1.65
	41.49	0.3	0.006			
3	39.41	0.1	0.002	0.003	85.55	2.02
	42.19	0.2	0.004			
4	44.08	0	0	0	100	2.43
	39.83	0	0			
5	48.91	0.05	0	0	97.97	2.82
	50.29	0	0			
6	40.17	0	0	0	100	2.31
	39.49	0	0			
7	37.68	0	0	0	100	2.26
	40.39	0	0			

Table E.4 Adsorption of total glycerin in biodiesel using 2.04:1 SiO_2/MgO molecular ratio of synthesized magnesium silicate, which derived from SMA, at ratio of 4 g adsorbent per 150g biodiesel with different time (hr)

Time (hour)	Weight of sample (g)	Volume of NaOH titration (mL)	Total glycerin (%)	Average total glycerin (%)	Adsorption efficiency (%)	q_e (mg/g)
1	39.29	19.2	0.45	0.47	69.43	105.60
	40.24	21.2	0.49			
2	38.57	17.8	0.43	0.46	70.09	104.35
	39.28	20.9	0.49			
3	39.71	18.9	0.44	0.43	71.59	107.30
	38.68	18.1	0.43			
4	39.36	18.4	0.43	0.43	71.49	109.42
	40.38	19.0	0.43			
5	43.05	19.8	0.42	0.43	71.77	120.57
	44.80	21.4	0.43			
6	37.36	16.7	0.41	0.43	71.82	119.02
	49.29	24.1	0.45			
7	39.28	19.3	0.45	0.43	71.86	109.48
	40.38	17.9	0.41			

Appendix F

บทความวิจัยที่เผยแพร่

1. Pornrin Jintanavansan and Pornsawan Assawasangrat "Synthesis of Magnesium Silicate adsorbent in Biodiesel" ICEAST 2012 International Conference on Engineering, Applied Sciences and Technology November 21-24, 2012 Bangkok, Thailand

2. Weerawat Clowutimon Pornrin Jintanavansan and Pornsawan Assawasangrat "Adsorption of free fatty acid in biodiesel by magnesium silicate" The 3rd TIChE International Conference, October 17-18, 2013 KhonKaen Thailand

Synthesis of Magnesium Silicate as adsorbent in biodiesel

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Abstract— **This research aims to study the adsorption of contaminants in biodiesel by using magnesium silicate as an adsorbent, which involved by precipitation reaction between magnesium sulfate (VI) and four different sources of silica were prepared to provide a reactant; (I) solution of sodium silicate from Merck Company (SSM), (II) solution of silica was extracted from rice husk ash (RHA), and (III) crystalline sodium metasilicate from Rankem (SMR) and (IV) Aldrich Company (SMA). The efficiency of adsorbents in the purification of biodiesel was obtained and compare with commercial magnesium silicate. The impurities in the biodiesel, including free fatty acid, soap, water and free glycerin. The element analysis was studied by X-ray fluorescence method (XRF). And the FTIR technique was used to obtain infrared spectrum. Magnesium silica from SMA as source of silica exhibited high adsorption capacities of FFA, free glycerin and soap with 0.76:1 SiO_2/MgO ratio.**

Key words: Magnesium Silicate; Adsorption

I. INTRODUCTION

Now, the demand of energy, price of petroleum and environmental concerns about air pollution from gas cars are steadily increasing. Biodiesel is alternative fuel and a renewable fuel that consisting of mono-alkyl esters of long chain of fatty acid derived from vegetable oils or animal fats, including Methyl ester or Ethyl ester and Glycerin with a chemical process called Transesterification [1]. The Methyl ester has contaminants frequently that have affect on the quality of biodiesel. The amount glycerin also affects the quality of biodiesel as well [2], the high concentration of glycerol in biodiesel can be the cause of storage problem because biodiesel with high concentration of glycerol is easy to occurs separation of biodiesel phases. And using of that biodiesel, glycerol might accumulate in the nozzle of the engine [3]. The water content in biodiesel cause corrosion of engine or might react with glycerides got soap and glycerol as by-products [4]. In addition, soap and free fatty acids cause the deterioration of engine components. Therefore, the amount of water and free fatty acids affect to indicate the quality of biodiesel.

The purification of crude biodiesel is usually achieved via two notable techniques; wet and dry washings. Conventionally wet washing is the most employed technique to remove impurities such as soap, catalyst, glycerol and residual alcohol from biodiesel. However, the major disadvantage in the use of water to purify biodiesel is increase in cost and production time [5]. Besides, separation of biodiesel phase from water phase is difficult and produces large amount of wastewater. To avoid, the dry washing technique (magnesium silicate as adsorbent) was used to substitute wet washing to remove biodiesel contaminants.

Magnesium silicate surface consists of partially hydrophobic and partially hydrophilic. The hydrophobic part includes siloxane ($\equiv$Si–O–Si$\equiv$) groups and the hydrophilic portion contains isolated hydroxy groups (–Mg–OH), individual silanol groups ($\equiv$Si–OH) and hydrogen bonds formed due to close vicinity of hydroxy groups linked to neighboring silicon atoms. Surface modification is performed to augment hydrophobicity of silicate surface and, thus, to promote binding of several compounds. The modification takes place by introduction of new organofunctional groups to silicate surface [6].

II. EXPERIMENT METHODS

A. Extraction solution of silica from rice husk ash as silica source.

For preparation, rice husk ash (RHA) was boiled in 3M hydrochloric acid for 30 min, and then washed with distilled water until the washed water was neutral. The RHA was dried at 100°C for 24 hrs. For extraction, 10 g of RHA was boiled with 1M of sodium hydroxide at 70-80°C for 24 hr. Then it was filtered with Whatman filter paper No.42. After that, silica content of silicate solution was measured by titration [7]. And then, the solution of silica was synthesized as Magnesium silicate adsorbent.

B. Synthesis of Magnesium silicate by precipitation method

Four different sources of silica were provided for magnesium silicate synthesis. The concentration ratio of silica and magnesium sulfate (VI) is 0.5M:0.5M. The silica was dropped into the 0.5M of magnesium sulfate (VI) solution with stirrer speed of 200 rpm. at room temperature. Centrifuge was used to separate the precipitate about 2000 rpm and then remove liquid phase by filter. The precipitate was dried at 100°C for 24 hr, then mashed and sieved.

C. Biodiesel

The biodiesel was prepared with the reaction between soybean oil, methanol and using KOH as catalyst. Mix 100 mL of Methanol with 4g of KOH at 30°C. And then, add to warm soybean oil and warm the mixer at 70°C for 75 min. After that, transfer the biodiesel to separation funnel. The biodiesel separated to glycerol phase and biodiesel phase, discard the glycerol phase.

D. Adsorption of contaminates from biodiesel

The ratio of Biodiesel 50g per adsorbent 1 g was used to study the contaminates adsorption The shaker machine was set at 60°C, 200 rpm and 2 hr. After shaking, remove the adsorbent and biodiesel was analyzed the contaminations. For %FFA and soap analysis, titration technique was used to calculate follow these equations:

$$\%FFA = \frac{C_{NaOH} x V_{NaOH} x 25.6}{W_{oil}} \qquad (1)$$

where %FFA is concentration of free fatty acid (%wt), C_{NaOH} is normality of the NaOH titration solution, V_{NaOH} is volume in mL of NaOH titration solution and W_{oil} is weight of the sample of oil in grams.

$$C = \frac{(\%FFA_i - \%FFA_f) x V_{oil} x 1000}{W_{abs} x 100} \qquad (2)$$

where C is adsorption capacities of FFA (mg/g of absorbent), $\%FFA_i$ is concentration of free fatty acid before adsorption, $\%FFA_f$ is concentration of free fatty acid after adsorption, V_{oil} is volume in mL of biodiesel and W_{abs} is weight of the absorbent in grams.

$$S = \frac{V_{HCl} x 0.01 x 304.4 x 10^6}{W_{oil} x 1000} \qquad (3)$$

where S is amount of soap in biodiesel (ppm) and W_{oil} is weight of the sample of oil in grams.

$$\%G_{free} = \frac{V_{NaOH} x C_{NaOH} x 0.0921 x 100}{W_{oil}} \qquad (4)$$

where $\%G_{free}$ is amount of glycerin(g) per 100g of biodiesel, V_{NaOH} is volume titrated of NaOH (mL), C_{NaOH} is normality of NaOH solution and W_{oil} is weight of the sample of oil in grams [8].

For water content was calculated from this equation;

$$W = \frac{(wet\ weight - dry\ weight)}{190.4\ x\ 100} x 10000 \qquad (5)$$

where W is amount of water in biodiesel (ppm), Wet weight is weight of biodiesel before heating and dry weight is weight of biodiesel after heating.

E. Characteristic of Magnesium silicate

Chemical characterization of representative sample was undertaken by X-ray fluorescence spectrophotometer (XRFs) for major element detection. And the FTIR technique was used to obtain infrared spectrum of Magnesium silicate. The spectra were obtained from scanning in the range of 400-4000 cm^{-1}.

III. RESULT AND DISCUSSION

A. Chemical compositions by X-ray fluorescence method

Synthesized magnesium silicate was the fine white powder. Table 1 shows the components of commercial magnesium silicate and magnesium silicate derived from SMA and SMR as source of silica. Obviously, SMR provided magnesium silicate precipitates with lower SiO_2/MgO ratio due to SMR solubility in water limited. When, SMA could be able to prepare the desired SiO_2/MgO molar ratio of magnesium silicate with high SiO_2 content. And the commercial Magnesium silicate was exhibited the highest molar ratio of SiO_2/MgO magnesium silicate.

TABLE I. CHEMICAL COMPOSITIONS OF COMMERCIAL MAGNESIUM SILICATE AND MAGNESIUM SILICATE DEVIVED FROM VARIOUS SOURCE OF SILICA.

Source of silica	% wt			Molecular ratio of SiO_2/MgO
	SiO_2	MgO	Other	
SMR	0.41	96.11	3.48	0.004 : 1
SMA	43.18	56.81	0.01	0.76 : 1
Commercial magnesium silicate	48.00	32.40	19.60	1.48 : 1

B. Infrared spectrum by FT-IR method

The FT-IR spectra of magnesium silicate are shown in Fig. 1-3. These spectra were obtained from scanning in the range of 400-4000 cm^{-1}. The band represented vibration of siloxane bonding; Si-O-Si, in magnesium silicate from commercial magnesium silicate, SMR and SMA were showed at 1034.84, 1129.89 and 1025.18 cm^{-1}, respectively. The hydroxyl stretching band (-OH) shows shoulders between 3300-3450 cm^{-1}.

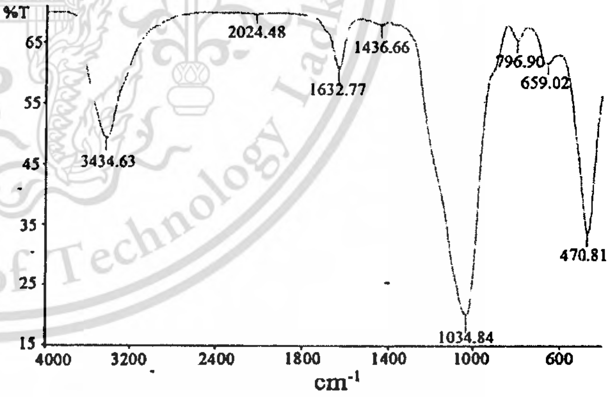

Figure 1. FT-IR spectra of commercial magnesium silicate

Magnesium silicate from commercial magnesium silicate, SMR and SMA were exhibited the bands at 470.81, 451.56 and 446.26 cm^{-1}, due to Mg–O stretching vibration, respectively. The hydroxyl bending of H_2O shows peak between 1630-1635 cm^{-1}.

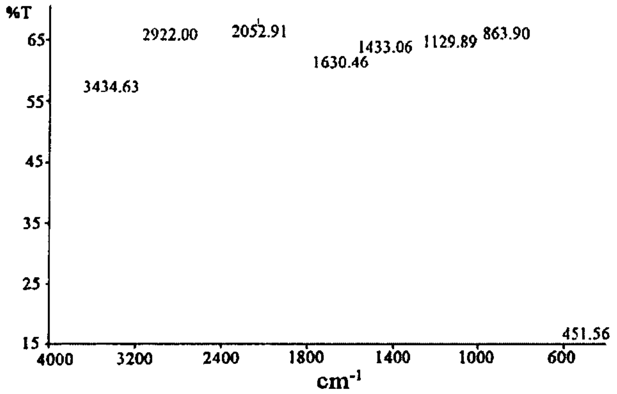

Figure 2. FT-IR spectra of magnesium silicate from SMR as source of silica

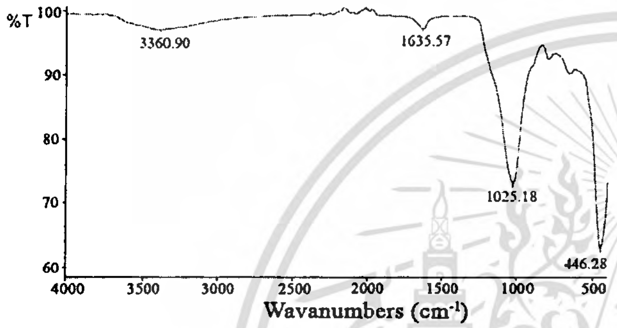

Figure 3. FT-IR spectra of magnesium silicate from SMA as source of silica

From figure 2, the band hardly represented vibration of siloxane bonding; Si-O-Si which related with FTIR result. The band of the synthesized magnesium silicate was much broader and more complex in the spectra. Similar results were observed for vibration of siloxane and Mg-O in commercial magnesium silicate and SMA.

C. Adsorption of free fatty acid in biodiesel

Figure 4 demonstrates comparative efficiency on adsorption of FFA from 50 g of biodiesel using 1 g of magnesium silicate from different source of silica and commercial magnesium silicate. Adsorption capacity of commercial magnesium silicate was 90 mg FFA /g of adsorbent, while magnesium silicate of source of silica from rice husk ash, SMA, SSM and SMR could adsorb 243, 284, 205, 71 mg FFA per gram of adsorbent (respectively). Magnesium silicate of SMA as source of silica had the highest adsorption capacities of FFA per gram of adsorbent.

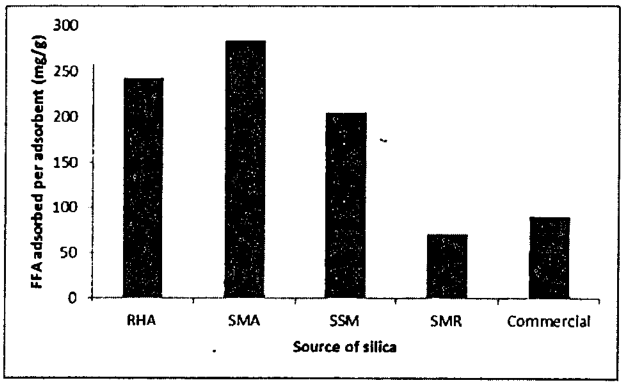

Figure 4. Comparison of efficiency on adsorption of FFA

D. Adsorption of soap in biodiesel

Adsorption capacities of soap per gram of different adsorbents were shows in Figure 5. For the figure, Both of SMA and SSM as source of silicate show similarly high value of soap adsorbed. Magnesium silicate from SSM as absorbent was exhibited highest adsorption capacities of soap 211 ppm per gram adsorbent.

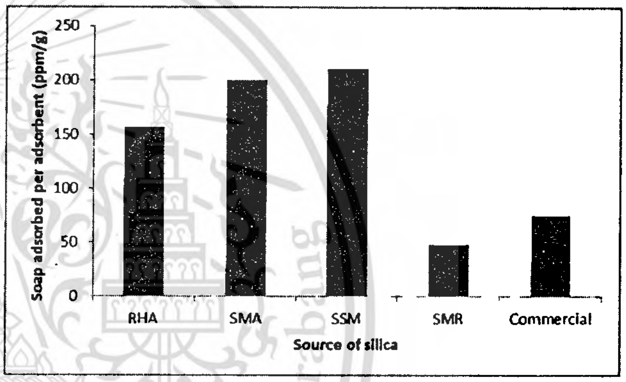

Figure 5. Comparison of efficiency on adsorption of soap

E. Adsorption of water in biodiesel

From figure 6, Magnesium silicate from RHA as source of silica shows the best adsorption capacities of water 0.073 ppm per gram adsorbent.

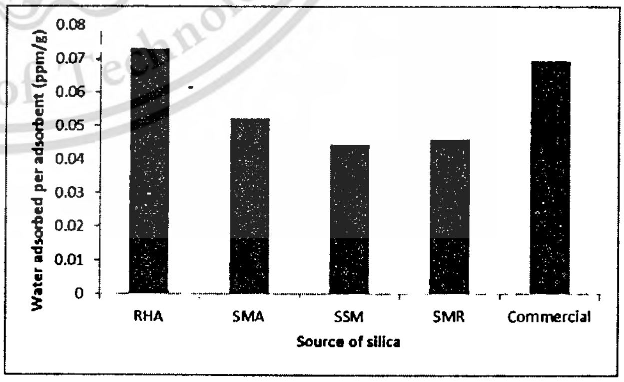

Figure 6. Comparison of efficiency on adsorption of water

F. Adsorption of free glycerin in biodiesel

Figure 7 demonstrates comparative efficiency on adsorption of free glycerin by titration method. It shows that Magnesium silicate from SMA as source of silica can adsorbed free glycerin 463 ppm per gram adsorbent.

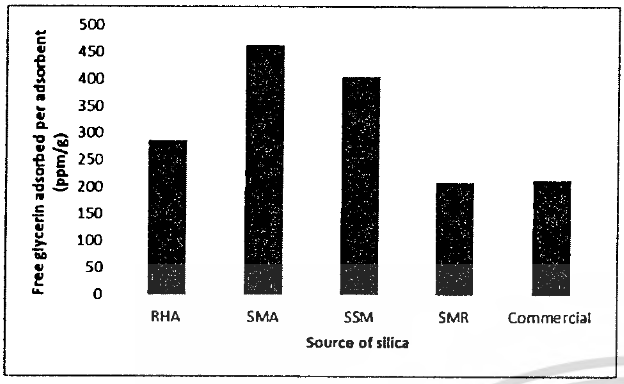

Figure 7. Comparison of efficiency on adsorption of free glycerin

From behavior of adsorption of free fatty acid, soap and free glycerin, magnesium silicate from SMA as source of silica shows higher adsorption capacities which SiO_2/MgO molar ratio of magnesium silicate is 0.76:1. Similar results were observed for soap adsorption of magnesium silicate from SMA and SSM as source of silica. For adsorption of water, magnesium silicate from RHA and commercial presented higher efficiency of adsorption due to hydrophilic part of adsorbent. Consistent with the results of XRF analysis, magnesium silicate from SMA and commercial were exhibited high content of SiO_2/MgO molar ratio which related with FTIR result that clearly represented vibration of siloxane bonding; Si-O-Si. Surface modification is performed to augment hydrophobicity (Si-O-Si) of silicate surface.

IV. CONCLUSION

The adsorption of contaminants in biodiesel was obtained which magnesium silicate was synthesized as an adsorbents. It involved by precipitation reaction between magnesium sulfate (VI) and four different sources of silica were prepared to provide a reactant; SSM, RHA, SMR and SMA. From behavior of adsorption of contamination in biodiesel, magnesium silicate from SMA as source of silica shows higher adsorption capacities which SiO_2/MgO molar ratio of magnesium silicate is 0.76:1.

ACKNOWLEDGMENT

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Adsorption of free fatty acid in biodiesel by magnesium silicate

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***Abstract*— Adsorption of free fatty acid in biodiesel by magnesium silicate was studied. The adsorbent was prepared by precipitation of magnesium sulfate (VI) and sodium metasilicate. Molar ratio of SiO_2: MgO was varied 0.36:1, 0.76:1 and 2.04:1. Adsorption studies were carried out in a batch process with temperature 60 °C. In the circumstance, the adsorption process reached to equilibrium in 4 hours and magnesium silicate with the SiO_2: MgO ratio at 2.04:1 was the most effective adsorbent. The FFA adsorption capacity was 108.54 mg/g. For isotherm determination, the adsorption can be described by Langmuir isotherm better than Fruendlich isotherm.**

Keywords: Adsorption, Magnesium silicate, Biodiesel, Free fatty acid.

I. INTRODUCTION

Nowadays, the demand of energy, price of petroleum and environmental concerns about air pollution from gas cars are steadily increasing. Biodiesel is alternative fuel and a renewable fuel. It presents outstanding characteristics as non-toxicity, absence of sulfur, high energy content and biodegradability. Biodiesel consisting of mono-alkyl esters of long chain of fatty acid derived from vegetable oils of animal fats, including methyl ester of ethyl ester and glycerin with a chemical process called transesterification [1]. Transesterification is a chemical reaction relating triglycerides and alcohol with a catalyst. The methyl ester has contaminants frequently that have effect on the quality of biodiesel. Free fatty is a contaminant. It causes the deterioration of engine components. Therefore, the amount of free fatty acid is one parameter that affected to indicate the quality of biodiesel.

The purification of crude biodiesel is usually achieved via two notable techniques; wet and dry washings. Conventionally wet washing is the most employed technique to remove contaminants from biodiesel. However, the major disadvantages in the use of water to purify biodiesel are emulsion formation, preventing the separation of the esters, allowing the formation of free fatty acids and soaps, increase in cost and production time [2]. To avoid, the dry washing technique (ion exchange resins, magnesium silicate as adsorbent) was introduced to substitute wet process. The use of adsorbents turns the process more rapid and there is not a formation of aqueous residues [3-4]. In this study, adsorption of free fatty acid in biodiesel by precipitation of magnesium silicate was studied to evaluate suitable condition for preparation of magnesium silicate and adsorption process.

II. EXPERIMENTS

Synthesis of magnesium silicate

Sodium silicate solution purchased from Aldrich Company was dropped into magnesium sulfate(VI) solution at room temperature and stirred at speed 200 rpm. Concentration ratio of Na_2SiO_4: $MgSO_4$ was 0.5:0.5, 0.5:1.5 and 3.0: 0.5. Precipitated magnesium silicate was separated from the solution by centrifuge with 2000 rpm for 20 minutes. The solution was filtered and the magnesium silicate was washed by distillated water several times. The product was dried in an oven at 105 °C for 24 hours.

Characterization of magnesium silicate

XRF characterization was applied to study elements that present in magnesium silicate and the study of crystalline structure was characterized by XRD. FR-IT was used to study molecular structure of the materials.

Comparison of adsorptive capacity of synthetic magnesium silicate at different molar ratio

One gram of an adsorbent was added in 150 grams of biodiesel. The mixture was shaken in an incubator shaker at 60 °C with speed 200 rpm 2 hours. The adsorbent was separate by centrifuge at 2000 rpm for 20 minutes. Concentration of free fatty acid in biodiesel was measured by tritate the solution by 0.1 M of sodium hydroxide solution.

Adsorption isotherm study

A known amount of the most effective adsorbent was added in biodiesel. The adsorption process was carried out in the same condition as the previous part. The samples were taken at several times. For isotherm determination, biodiesel and different dosage amounts of adsorbent were carried out in a batch process until the adsorption reached to equilibrium.

III. RESULTS AND DISCUSSION

Characterization of magnesium silicate

Chemical composition of synthetic was analyzed by X-ray fluorescence (XRF). Table 1 exhibited the chemical composition of magnesium silicate which was synthesized by varying Na_2SiO_4: $MgSO_4$ concentration ratio. The molar ratio of SiO_2: MgO in synthetic magnesium silicate was 0.36:1, 0.76:1 and 2.04:1 according to the Na_2SiO_4: $MgSO_4$ concentration ratio of 0.5:1.5, 0.5:0.5 and 3.0:0.5, respectively Na_2SiO_4: $MgSO_4$ concentration ratio of 3.0:0.5 exhibited highest molar ratio of SiO_2: MgO while the concentration ratio of 0.5:1.5 showed lowest molar ratio of SiO_2: MgO. Thus, the molar ratio of synthetic magnesium silicate was in agreement with the used concentration ratio.

TABLE 1. CHEMICAL COMPOSITION OF MAGNESIUM SILICATE BY VAROIUS Na_2SiO_4: $MgSO_4$ CONCENTRATION RATIOS

Na_2SiO_4: $MgSO_4$	% wt			Molar ratio of SiO_2: MgO
	SiO_2	MgO	Other	
0.5:1.5	26.34	72.31	1.35	0.36:1
0.5:0.5	43.18	56.81	0.01	0.76:1
3.0:0.5	52.88	25.85	21.27	2.04:1

The average surface area, pore volume and pore size of magnesium silicate were characterized by BET method. The result is showed in the Table 2. The magesium silicate has surface area between 15-58 m^2/g and average pore size is between 50-105 °A which could describe that magnesium silicate was mesoporous formation. From the results, the 2.04:1 molar ratio of SiO_2: MgO has the biggest pore size diameter, 105 °A, which related to contaminates adsorption.

TABLE 2. AVERAGE SURFACE AREA, PORE VOLUME AND PORE SIZE OF MAGINESIUM SILICATE CHARATERIZED BY BET METHOD

Molar ratio of SiO_2: MgO	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size diameter (°A)
0.36:1	15.1	0.0192	50.88
0.76:1	67.19	0.1098	65.34
2.04:1	57.77	0.1516	105

Crystalline structure of magnesium silicate was characterized by X-ray diffraction technique. The diffraction patterns of magnesium silicate from the X-ray diffractometer were showed in Fig. 1 - Fig. 3. The crystallinity of magnesium silicate was very peak, suggesting that magnesium silicate was amorphous.

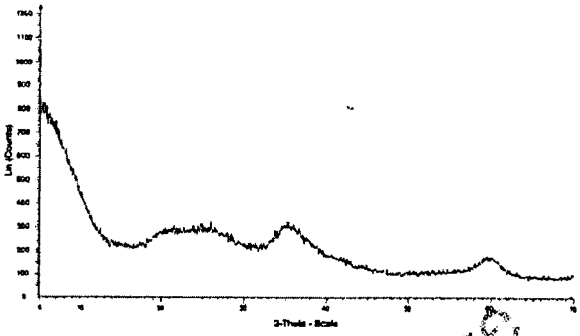

Figure 1. The XRD pattern of magnesium silicate with molar ratio of SiO_2: MgO at 0.36:1

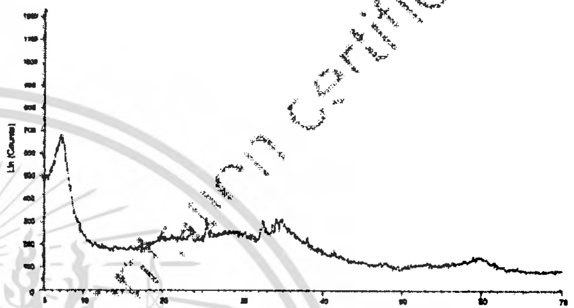

Figure 2. The XRD pattern of magnesium silicate with molar ratio of SiO_2: MgO at 0.76:1

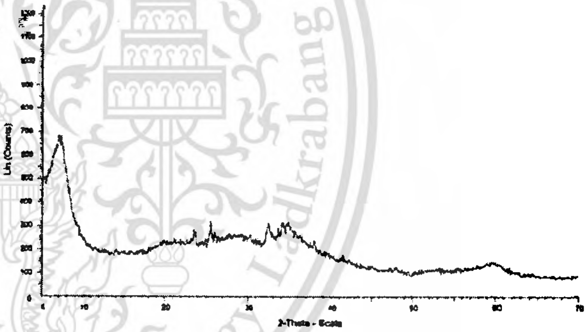

Figure 3. The XRD pattern of magnesium silicate with molar ratio of SiO_2: MgO at 2.04:1

The FT-IR spectra of magnesium silicate which were varied molar ratio of SiO_2 : MgO are shown in Fig. 4 - Fig. 6. The band represented Si-O stretching vibration of magnesium silicate were shown in the range between 950-1100 cm^{-1}. The band at 400- 450 cm^{-1} is attributed to Mg-O stretching vibration and the band at 3200-3800 cm^{-1} are assigned to deformation of hydroxyl strectching (-OH). The bands present at 1400-2000 cm^{-1} are due to the Si-O vibration because of combination and overtones of Si-O [5-7]. Therefore, the infrared analysis indicates the magnesium silicate adsorbents are a material with high content of SiO_2 and MgO.

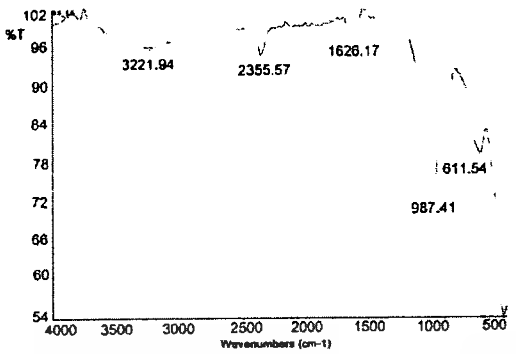

Figure 4. FT-IR spectra of magnesium silicate with the molar ratio of SiO_2/MgO at 0.36:1

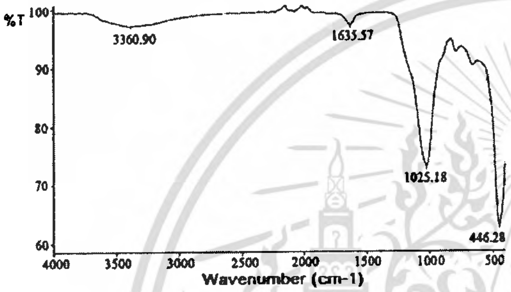

Figure 5. FT-IR spectra of magnesium silicate with the molar ratio of SiO_2/MgO at 0.76:1

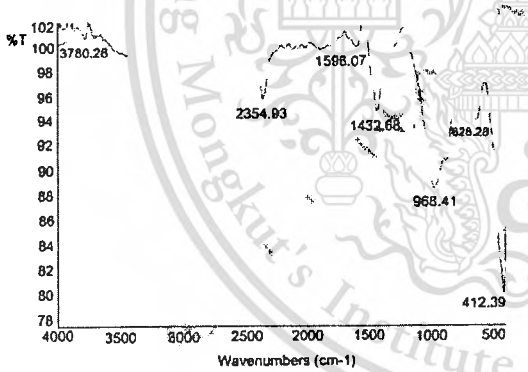

Figure 6. FT-IR spectra of magnesium silicate with the molar ratio of SiO_2/MgO at 2.04:1

Adsorption results

Comparison of adsorption efficiency of free fatty acid of magnesium silicate with different molar ratio was showed in Figure 7. The adsorption efficiency of SiO_2/MgO molar ratios 0.36:1, 0.76:1 and 2.04:1 was 18.23%, 44.62% and 52.09%, respectively. The adsorption capacity of aforementioned ratios was 38.24, 90.76 and 108.54 mg/g. respectively. The magnesium silicate with molar ratio of 2.04:1 has the highest adsorption capacity due to the highest silica content and the biggest pore size diameter, 105 °A, which related to contaminates adsorption.

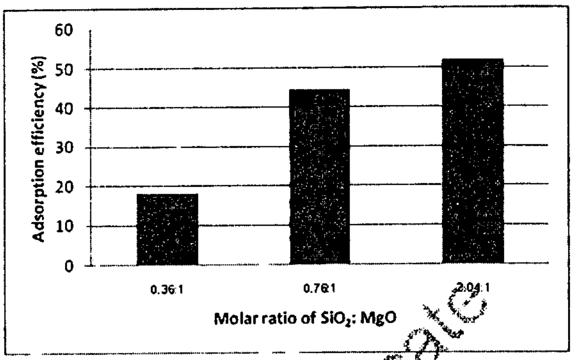

Figure 7. Comparison of adsorption efficiency of free fatty acid from different molar ratio SiO_2: MgO

The adsorption was observed to equilibrium state by the amount of 2.04:1 molar ratio of SiO_2/MgO absorbents were varied at 1, 2, 3, 4, 5 and 6 g. per 150 grams of biodiesel. The study of adsorption was noticed at 60°C for 5 hours. The effect on dosage amount of absorbents were exhibited in Figure 8. It was found that the adsorption of free fatty acid decreased obviously from 1 to 4 g. and then insignificantly changed. The adsorption equilibrium was found at 4 g. adsorbent per 150 g. biodiesel.

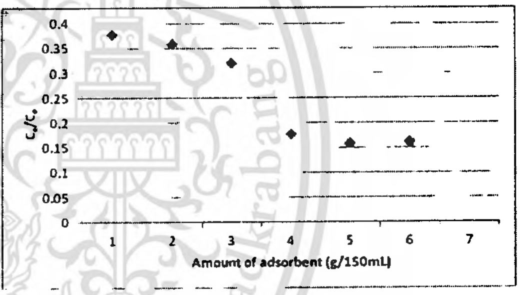

Figure 8. The effect on dosage amount of 2.04:1 molar ratio magnesium silicate

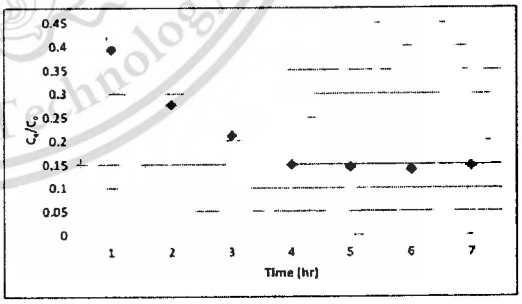

Figure 9. Adsorption isotherm of free fatty acid on magesium silcate with the molar ratio of SiO_2: MgO at 2.04:1

From the previous study, the optimum conditions for synthesis and adsorption of magnesium in biodiesel were 2.04:1 molar ratio of SiO_2/MgO and 4 g. of dosage amount of adsorbent per 150 g. biodiesel. These conditions were used to study the equilibrium time of magnesium silicate. Concentration of free fatty acid in biodiesel at several times was showed in Figure 9. As can seen from the figure, the adsorption of free fatty acid reached to equilibrium in 4 hours and other experiments have same equilibrium time.

Two adsorption isotherms, Langmuir and Fruendlich isotherms, were employed to described the adsorption behavior. The results of the two models are shown in the Table 3.

As can seen from the Table 3, Langmuir isotherm can be applied to describe the adsorption of free fatty acid on magnesium silicate. Thus, free fatty acid adsorption phenomena were monolayer adsorption following Langmuir's assumption. The result agrees with result of Teinkarodjanakul and et.al. [8].

TABLE 3. ADSORPTION ISOTHERMS OF FREE FATTY ACID IN BIODIESEL

Isotherm	Equation	R^2
Langmuir	$q_e = \frac{(625)(0.205)C_e}{1+(0.205)C_e}$	0.8581
Fruendlich	$q_e = 114.37C_e^{0.9631}$	0.8258

IV. CONCLUSIONS

The magnesium silicate was prepared by precipitation of sodium metasilicate solution and magnesium sulfate (VI) solution. A batch adsorption was applied to study adsorption of free fatty acid in biodiesel. Characterization of magnesium silicate found that its structure was amorphous. Comparison of adsorption capacity results, found that magnesium silicate with molar ratio SiO_2: MgO at 2.04:1 has the highest adsorption capacity and its adsorption capacity of FFA was 108.54 mg/g. The adsorption experiments reached to equilibrium in 4 hours. For isotherm, Langmuir isotherm can be applied to described the adsorption process better than Fruendlich isotherm.

ACKNOWLEDGMENT

This research was financially supported by Faculty of Engineering, King Mongkut's Institute Technology of Ladkrabang and National Research Council of Thailand.

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CURRICULUM VITAE

ประวัติส่วนตัว

ชื่อ-สกุล ดร. พรสวรรค์ อัศวแสงรัตน์

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สาขาวิจัยที่มีความชำนาญพิเศษ Catalysis , Environmental Catalysis and Catalytic Reaction Engineering

รางวัลด้านวิชาการ/ด้านวิจัย/งานสร้างสรรค์ (ด้านศิลปะ หรืออื่นๆ) ที่ได้รับ

ปี พ.ศ.	ชื่อรางวัล	สถาบันที่ให้
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ทุนการศึกษาและทุนวิจัยที่เคยได้รับ

ปี พ.ศ.	ทุนการศึกษาและทุนวิจัย	สถาบันที่ให้
2546	การศึกษาเชิงเปรียบเทียบความเสถียรทางผลึกของตัวเร่งปฏิกิริยาซีโอไลต์	สำนักงานกองทุนสนับสนุนการวิจัย
2548	เครื่องสังเคราะห์สารซีโอไลต์	ทุนวิจัยจากเงินรายได้คณะวิศวกรรมศาสตร์
2549	เครื่องจำลองการไหลแบบอุดมคติ	ทุนวิจัยจากเงินรายได้คณะวิศวกรรมศาสตร์
2550	เครื่องเผาอุณหภูมิสูงสำหรับเตรียมถ่านกัมมันต์	ทุนวิจัยจากเงินรายได้คณะวิศวกรรมศาสตร์
2551	การเพอร์แวปเพอเรชันสารละลายเอธานอลเข้มข้นด้วยเมมเบ	ทุนวิจัยจากเงินรายได้คณะวิศวกรรมศาสตร์
2552	การดูดซับกรดไขมันอิสระในน้ำมันปาล์มดิบโดยใช้แมกนีเซียมซิลิเกตที่เตรียมได้จากเถ้าแกลบ	ทุนวิจัยจากเงินรายได้คณะวิศวกรรมศาสตร์
2553	การเตรียมตัวดูดซับซิลิกาจากแกลบ เพื่อใช้ในการดูดซับกรดไขมันอิสระในน้ำมันปาล์มดิบ	ทุนวิจัยจากเงินรายได้คณะวิศวกรรมศาสตร์
2554	การดูดซับแอลฟาโทโคเฟอรอลด้วยตัวดูดซับซิลิกาที่เตรียมจากเถ้าแกลบ	ทุนวิจัยจากเงินรายได้คณะวิศวกรรมศาสตร์
2555	การดูดซับสีย้อมด้วยผลิตภัณฑ์จากแกลบ	ทุนวิจัยจากเงินรายได้คณะวิศวกรรมศาสตร์
2555	การผลิตไบโอดีเซลแบบไม่ล้างน้ำ	งบประมาณแผ่นดิน

ผลงานวิจัย/งานสร้างสรรค์

ผลงานวิจัย/งานสร้างสรรค์ที่ตีพิมพ์เผยแพร่ (ระดับชาติและนานาชาติ)

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