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PURIFICATION OF BIODIESEL BY LIGNITE FLY ASH

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เถ้าลอยลิกไนต์เป็นวัสดุเหลือทิ้งจากโรงงานผลิตไฟฟ้า สามารถใช้เป็นตัวดูดซับทางเลือก ราคาประหยัด สำหรับการทำให้ไบโอดีเซลบริสุทธิ์ร่วมกับการล้างด้วยน้ำ เถ้าลอยลิกไนต์ดิบถูกพิสูจน์เอกลักษณ์โดยอาศัยเทคนิคเอ็กซเรย์ฟลูออเรสเซนต์ กล้องอิเล็กตรอนแบบส่องกราด และวิเคราะห์หาพื้นที่ผิวและรูพรุน ผลการศึกษาพบว่าเถ้าลอยลิกไนต์มีองค์ประกอบของซิลิกาออกไซด์ อะลูมิเนียมออกไซด์ แคลเซียมออกไซด์ และเฟอร์ริกออกไซด์เป็นหลัก ไบโอดีเซลดิบถูกสังเคราะห์จากน้ำมันปาล์ม ผ่านปฏิกิริยาทรานส์เอสเทอริฟิเคชันร่วมกับเมทานอล ด้วยอัตราส่วนโดยโมลของน้ำมันกับเมทานอลเท่ากับ 1:6 และร้อยละ1ของตัวเร่งปฏิกิริยาโซเดียมไฮดรอกไซด์ ทำการศึกษาปัจจัยที่มีผลต่อการดูดซับสิ่งเจือปนในไบโอดีเซล ซึ่งประกอบไปด้วย อนุภาคของเถ้าลอยลิกไนต์ ปริมาณเถ้าลอยลิกไนต์ที่ใช้ และระยะเวลาในการดูดซับ โดยภาวะที่เหมาะสมในการดูดซับสิ่งเจือปน คือ ขนาดของอนุภาคเถ้าลอยลิกไนต์ในช่วง 150-250 ไมครอน ปริมาณของเถ้าลอยลิกไนต์ที่ร้อยละ 3 โดยน้ำหนัก และระยะเวลาในการดูดซับ 60 นาที พฤติกรรมการดูดซับเป็นไปตามไอโซเทอมของฟรุนลิช และจลนศาสตร์การดูดซับสอดคล้องกับสมการแบบสองเทียม เถ้าลอยลิกไนต์สามารถใช้กำจัดสิ่งเจือปนและเมทานอลในไบโอดีเซลได้ และมีประสิทธิภาพเมื่อเปรียบเทียบกับตัวดูดซับทางการค้า ซึ่งประกอบไปด้วย ฟลอริซิล ถ่านกัมมันต์ และซิลิกา นอกจากนี้การใช้เถ้าลอยลิกไนต์เป็นตัวดูดซับ สามารถกำจัดสิ่งเจือปนได้มากกว่าร้อยละ 81 และลดการเกิดน้ำเสียในระบบได้ถึงร้อยละ 80

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A Lignite fly ash is a solid waste from the electricity plant. It was used as an alternative low-cost adsorbent to purify a crude biodiesel combine with water washing. The raw lignite fly ash was characterized by X-ray fluorescent spectrometry, scanning electron microscopy and surface area analysis. The results showed that the lignite fly ash was composted of SiO_2, Al_2O_3, CaO and Fe_2O_3 as major components. A crude biodiesel was synthesized from refined palm oil via transesterification with an oil to methanol mole ratio of 1:6 and 1%wt of sodium hydroxide catalyst. Furthermore, the effect of particle sizes, adsorbent dosage and contact time on the adsorption of impurities in biodiesel was investigated. The suitable conditions in the impurities adsorption were using the lignite fly ash of particle size in the range of 150-250 μm, 3%wt adsorbent and 60 min of contact time. The adsorption behavior at equilibrium could be explained by Freundlich isotherm and the adsorption kinetics followed the pseudo-second order kinetic model. The adsorbent could also be used to remove the impurities and methanol in the biodiesel. The lignite fly ash showed an efficiency comparable to the commercial adsorbents including Florisil, activated carbon and silica. Finally, the use of lignite fly ash could eliminate more than 81% of the impurities and reduce 80% of wastewater generated in the system.

Field of Study:	Petrochemistry and Polymer Science	Student's Signature	....
		Advisor's Signature	....
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LIST OF ABBREVIATIONS

g	gram (s)
^{1}H NMR	proton nuclear magnetic resonance
hr	hour (s)
min	minute (s)
mg	milligram (s)
mL	milliliter (s)
PPM	part per million
M.W.	molecular weight
M	molar
N	normality
°C	degree celsius

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

A global population surpasses in every year and it is the reason of a steady increasing demand of energy. A diesel fuel is produced from fossil sources and the most common source is the petroleum which would run out in the near future. The renewable energy source is a good alternative [1]. The biodiesel is one of popularly used alternative fuels due to its many advantages. The use of biodiesel blended with diesel fuel will decrease the greenhouse gas emission [2-4], because there is more oxygen content in the biodiesel than in the diesel from petroleum, the combustion occurs completely [5]. The absence of sulfur substance in the biodiesel puts an end to the acid rain production which is harmful to plants, aquatic animals and infrastructure. Moreover, the use of biodiesel also helps to increase speeding and power of a diesel engine [6, 7].

The biodiesel is a long-chain alkyl ester produced from several methods [8]. The most popular method to produce biodiesel is the transesterification of triglycerides and alcohol using base catalyst. It gives a higher yield than other methods while performs at a lower pressure and temperature [9]. Sodium hydroxide and potassium hydroxide are catalysts extensively used in the industries due to its large supply in the market and low cost [10, 11]. The raw materials in the production process include vegetable oils, animal fats and used cooking oils. Because different starting raw materials can be used, the biodiesel can be produced in different regions, leading to a reduction in the importation of diesel from foreign country. In Thailand, palm oil is used as a raw material for biodiesel production as palm trees are widely cultivated in the south of the country.

In the production of biodiesel via transesterification, glycerin is obtained as a by-product in a separated layer. The by-products and other impurities (e.g. soaps, residual alcohol) are removed in a purification process. Soap is the main impurity in biodiesel which is hard to eliminate because it forms an emulsion layer between surface of glycerin and alkyl ester layers. The soap is the by-product occurred from saponification and hydrolysis side reaction [12]. The process to eliminate soaps and other impurities contaminated in a crude biodiesel includes wet washing of the crude biodiesel with water but it has some disadvantages including high cost and consumption of large volume of water. Furthermore, a treatment of generated wastewater and drying of the final product are required [13-15]. Other purification processes can be also applied, e.g. ion-exchange, membrane and sorption process [12, 16, 17]. The adsorption is a conventional process where an adsorbent is used to adsorb soap and other impurities in a crude biodiesel. In this research, a fly ash was used as adsorbent in the purification of biodiesel.

The fly ash or fuel ash is a major solid waste from coal combustion in a power plant. It has been successfully used as an admixture in concrete for brick production. Its interesting properties include not only its fine particles but also its chemical composition. Fly ash can be used as an inexpensive adsorbent because it contains high amount of silica [18]. However, the content of silica in fly ash differs, depending on the type of coal and the condition in combustion. Many researches indicated that it could be a good adsorbent for polar molecules [19-28]. Therefore, the application of fly ash as an adsorbent to remove soap and impurities in a crude biodiesel is proposed in this research.

1.2 Objectives

The objectives of this study are listed below.

1. To use the lignite fly ash as an adsorbent to remove the main impurities including soaps, glycerin and residual methanol in biodiesel.

2. To study the adsorption properties and find the suitable conditions for the sorption process.

1.3 Scope of the thesis

The scope of this research is firstly to use the lignite fly ash to remove the impurities in a crude biodiesel in combination with water washing. The obtained lignite fly ash was characterized by X-ray fluorescence spectroscopy (XRF), scanning electron microscopy (SEM) and surface area analysis (Brunauer-Emmett-Teller method, BET). The effect of the particle size, the amount of adsorbent, the remained methanol in biodiesel, the contact time on the adsorption efficiency was studied. The adsorption isotherm and kinetics were also studied. Finally, the quality of treated biodiesel was confirmed by following the quality requirement for biodiesel.

CHAPTER II
THEORY AND LITERATURE REVIEW

2.1 Alternative energy

Alternative energy refers to energy source that substitutes fossil fuels or nuclear energy. Rudolf Diesel who was the inventor of the diesel fueled engine envisioned that a vegetable oil could power a diesel engine when the petroleum was not available. The biodiesel or fatty acid methyl esters (FAME) derived from peanut oil was directly used in a diesel engine. The result evinced that the engine could run without any coal or fuel oil [8]. Biodiesel can be produced from renewable sources, such as vegetable oils, animal fats or waste cooking oil, for use in a diesel engine [9]. The properties of biodiesel are similar to those of petroleum diesel and it is a cleaner-burning alternative fuel.

2.2 Advantages of biodiesel

The biodiesel fuel is an alternative energy which has many advantages. It can be separated in 3 aspects.

2.2.1 Environmental aspects

- It can reduce the greenhouse gas emissions.

- There is no sulfur components in biodiesel which lead to acid rain production and atmospheric contamination.

- It can reduce carbon monoxide and carbon dioxide production which cause air pollution.

- A biodiesel can be made from waste cooking oil and therefore, the use of repeated cooking oil which contains the carcinogens is reduced.

2.2.2 Economic aspect

- It can create jobs and energy markets within country to support the agricultural productivity of agriculturists.
- The importation of petroleum diesel from foreign country and purchasing cost decreased.
- It can add value into an agricultural crop rotation.
- The country can be self-sustaining.

2.2.3 Engine performance

- The lubricating property of the biodiesel can prolong an engine life.
- Because of higher oxygen content in biodiesel, the combustion in engine is more complete.

2.3 Biodiesel production

The production of biodiesel or alkyl ester from vegetable oils and fats can be performed via 3 basic routes; the base catalyzed transesterification of the oil with alcohol, the direct acid catalyzed esterification of the oil with alcohol and the two-step process. The content of free fatty acid in feedstock is the main factor for consideration of the suitable route of biodiesel production [8].

2.3.1. Transesterification with base catalyst

The commonly used route of biodiesel production in industry is homogeneous base catalyzed reaction of a crude oil with methanol because this route is simple. Low pressure and temperature can be applied in the synthesis and it gives high conversion of products [29]. The transesterification with base catalysis reaction is shown in **Figure 2.1**.

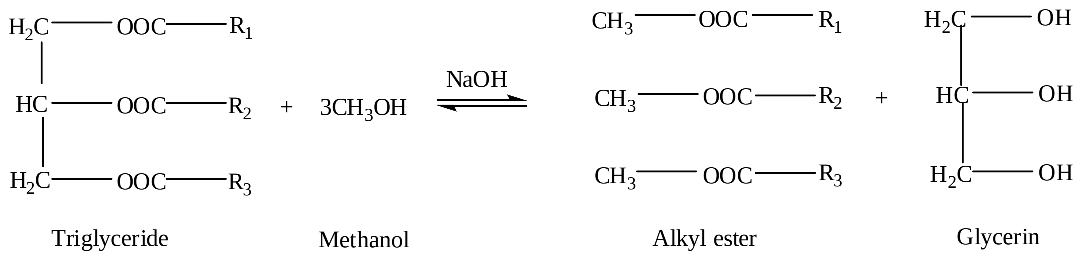
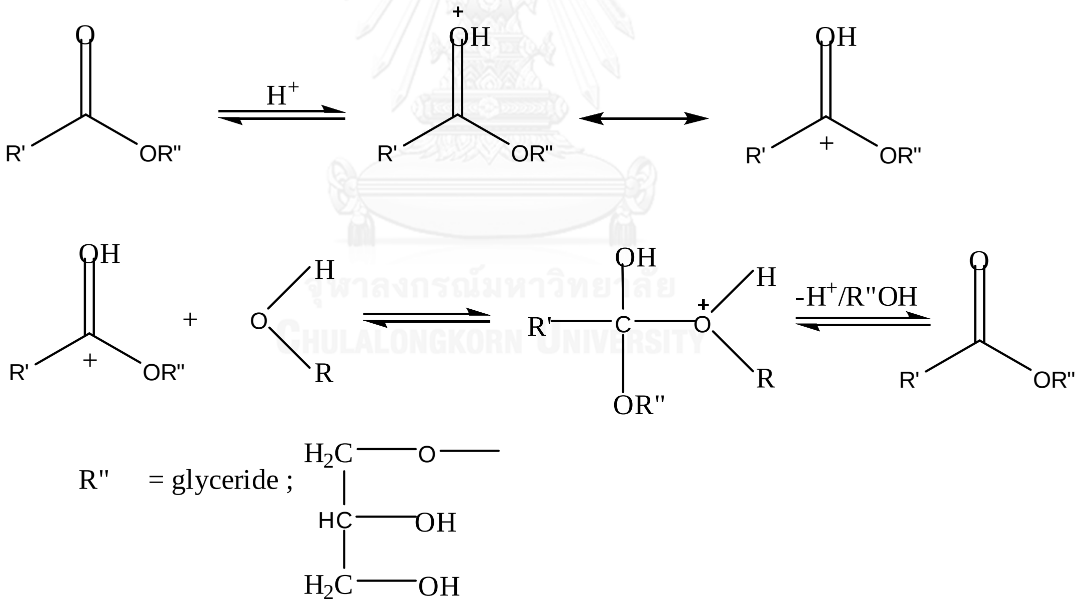


Figure 2.1 Production of biodiesel via transesterification.

2.3.2 Direct acid catalyzed esterification of the oil with alcohol

BrØnsted acid such as sulfonic and sulfuric acid can be a catalyst used in the production of biodiesel via esterification. It gives high yield but the reaction is not reactive. In the operation, high temperature (> 100 °C) and long reaction time (> 3 hr) are required for achieving complete conversion. The chemical reactions are shown in **Figure 2.2**.



R' = carbon chain of fatty acid

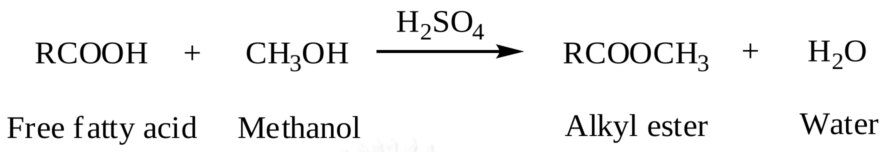
R = alkyl group of the alcohol

Figure 2.2 Production of biodiesel via esterification by acid catalyst [30]

2.3.3 Two-step process

Two-step process is a widely used method in the biodiesel production from crude oil which has high content of free fatty acid. It can be divided into 2 steps.

The first step is called ester formation from reaction of free fatty acid and methanol using acid catalyst (H_2SO_4). The chemical reaction is shown in **Figure 2.3**.



$$RCOOH + CH_3OH \xrightarrow{H_2SO_4} RCOOCH_3 + H_2O$$

Figure 2.3 Esterification by using sulfuric acid catalyst

After the reaction is complete, the acid catalyst dissolved in water layer will be separated and the mixture layer of methyl ester and triglyceride will be undergone through reaction with base catalyst as shown **Figure 2.1** which is the second step.

2.4 Side reaction in biodiesel production

Saponification is the side reaction which cannot be avoided when biodiesel production is produced via transesterification with base catalyst. Soap formations are shown in the **Figure 2.4** below [12].

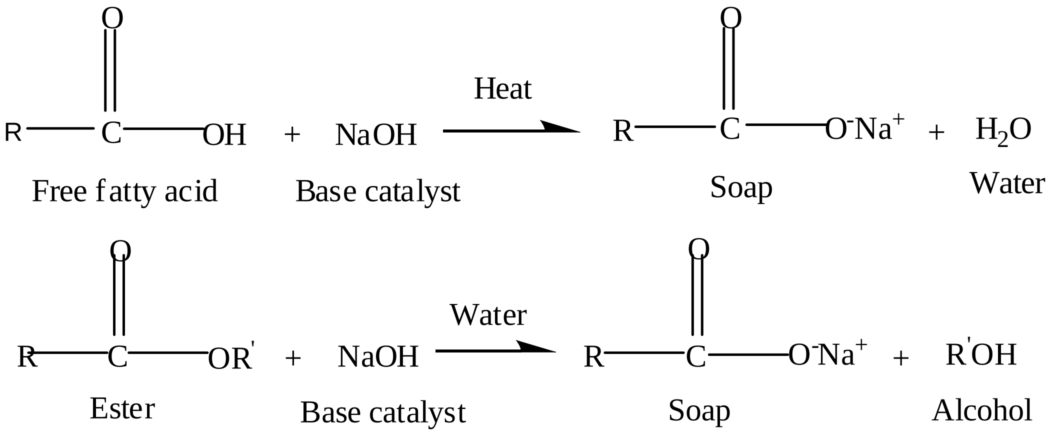


Figure 2.4 Saponification reaction

2.5 Quality requirements

Due to various properties of feedstock and different condition of biodiesel production, a standard quality of biodiesel is set in each country. It ensures that biodiesel has the quality for the use diesel engine. In Thailand, the department of energy business, Ministry of Energy has set the characteristic and quality of biodiesel as summarized in **Table 2.1**.

Table 2.1 Characteristics and standard quality of biodiesel (FAME) in Thailand [31]

Characteristics	Values	Standard method
Methyl ester (%wt)	> 96.5	EN 14103
Density at 15 °C (kg/m^3)	860-900	ASTM D 1298
Viscosity at 40 °C (cSt)	3.5-5.0	ASTM D 445
Flash point (°C)	> 120	ASTM D 93
Sulfur (%wt)	< 0.0010	ASTM D 2622
Carbon Residue, on 10 % distillation residue (%wt)	< 0.30	ASTM D 4530
Cetane number	> 51	ASTM D 613
Sulfated ash content (%wt)	< 0.02	ASTM D 874
Water (%wt)	< 0.050	EN ISO 12937
Total contamination (%wt)	< 0.0024	EN 12662
Copper strip corrosion	< 96.5	ASTM D 130

Oxidation stability at 110 °C (hr.)	> 6	EN 14112
Acid value (mg KOH/g)	< 0.50	ASTM D 664
Iodine value (g Iodine/100 g)	< 120	EN 14111
Linoleic acid methyl ester (%wt)	< 12.0	EN 14103
Methanol (%wt)	< 0.20	EN 14110
Monoglyceride (%wt)	< 0.80	EN 14105
Diglyceride (%wt)	< 0.20	EN 14105
Triglyceride (%wt)	< 0.20	EN 14105
Free glycerin (%wt)	< 0.02	EN 14105
Total glycerin (%wt)	< 0.25	EN 14105
Group I metals (Na+K)	< 5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg)	< 5.0	pr EN 14538
Phosphorus (%wt)	< 0.0010	ASTM D 4951

2.5.1 Effect of impurities in biodiesel [32]

The persistent existence of impurities in biodiesel has a negative effect on engine devices. When impurities contents are higher than the standard quality values, the damage caused by using highly contaminated biodiesel is summarized in **Table 2.2**.

Table 2.2 Effect of impurities in biodiesel

Impurities	**Disadvantages**
Methanol	The engine is corrosive.
Monoglyceride, Diglyceride, Triglyceride	High viscosity, the nozzle cannot diffuse which lead to built-up of grime within engine.
Free glycerin	The precipitation of free glycerin causes the clogging of nozzle.

Total glycerin	At low temperature, total glycerin will precipitate so the nozzle cannot be operated.

2.6 Biodiesel purification

In the production of biodiesel, certain component in feedstock such as monoglyceride, diglyceride and triglyceride from cannot be completely converted to biodiesel and hence they are left as residues in biodiesel. Moreover, glycerin as a by-product is generated after the production is finished. These substances are impurities which must be eliminated from biodiesel before use.

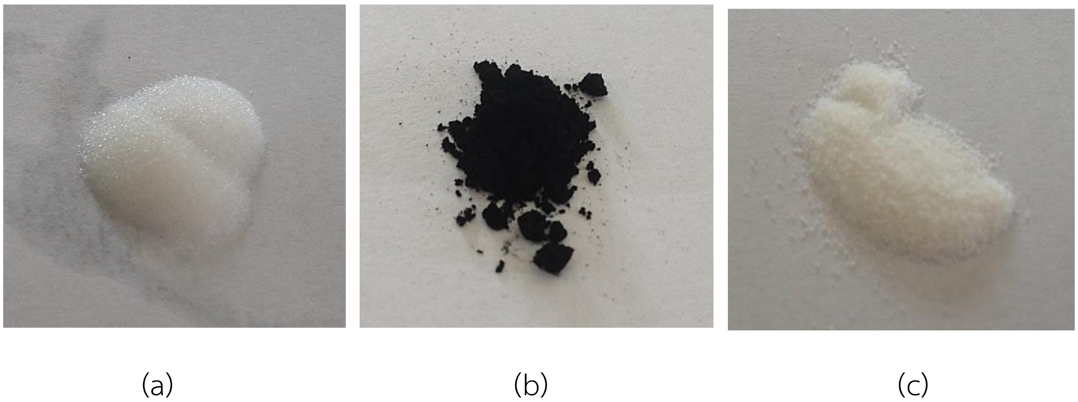
2.6.1 Wet washing

This is a method generally used to remove the impurities in biodiesel e.g. soaps, glycerin and residual methanol. All of polar impurities are removed by extraction into water added to the biodiesel. However, this route has several disadvantages including large volume of water consumption, requirement of treatment of resulting wastewater, loss of energy and time and low biodiesel yields [13-15].

2.6.2 Dry washing

Dry washing is a method used to purify biodiesel without adding water. Dry washing can be separated into many processes, e.g., membrane process, ion-exchange process and adsorption process. It can be coupled to common wet washing to reduce the water consumption in system.

Adsorption process is a simple way to remove impurities in biodiesel. Magnesol or Florisil (magnesium silicate), silica and activated carbon are the commercial adsorbents for biodiesel purification that widely used in industries [12, 16, 17]. The pictures are shown in **Figure 2.5**.



(a) (b) (c)

Figure 2.5 Commercial adsorbents: Magnesol or Florisil (a), activated carbon (b) and silica (c).

2.7 Lignite fly ash

Fly ash or fuel ash is the combustion waste from power plant using coals. Fly ash will be blown via flue, trapped inside silo and removed later. The small ash particles that fly in the air are a cause of pollution. Type of fly ashes can be divided into 2 classes following ASTM C618 (Class F and Class C). Class F is the group of fly ash obtained from anthrasite or bituminus and Class C fly ash is obtained from sub-bituminus or lignite [33]. The color of fly ash varies from tan to gray and black, depending on the amount of unburned carbon in the ash. It was reported in the previous researches that the main chemical composition of fly ash is silica and its use as an adsorbent was also demonstrated [18]. Polar molecules such as basic dyes could be adsorbed on fly ash [19-26].

Normally, the proportion of silica in fly ash depends on temperature, condition of combustion process and type of coals (e.g. peat, lignite, sub-bituminus, bituminus and anthracite).

Maemoh power plant in Thailand burns lignite to generate the electricity. 40,000 Tons of lignite are used in this power plant per day, and 6,000 Tons of lignite fly ashes are generated per a day as waste [32].

2.8 Adsorption

Adsorption is a process where molecules or ions (adsorbate) in gas or liquid phase accumulate on a surface of a solid (adsorbent). It differs from absorption in which a molecule in gas or liquid permeates or is dissolved in a liquid or solid as illustrated in **Figure 2.6**.

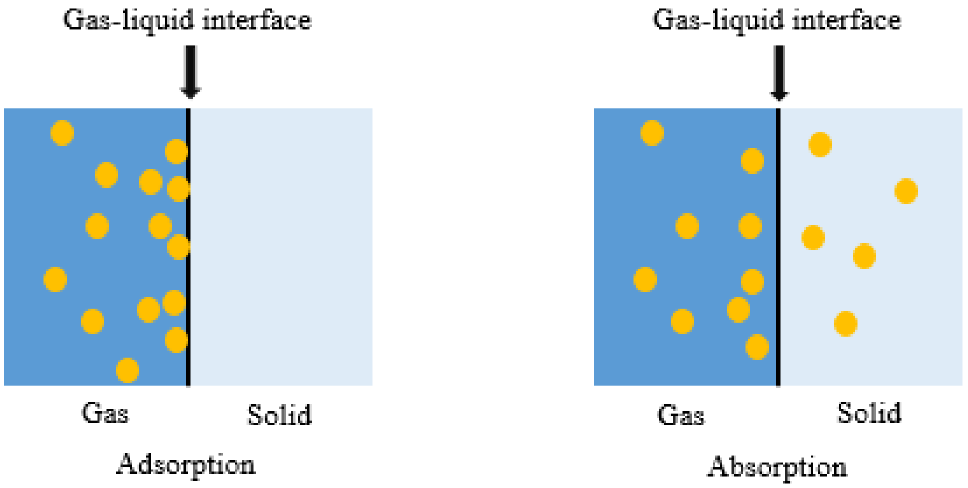


Figure 2.6 The difference between adsorption and absorption

The mechanism of adsorption may be mainly divided into 3 steps as illustrated in **Figure 2.7**.

Step 1: The movement of adsorbates across the mobile phase and cover on the external surface of adsorbent.

Step 2: The adsorbates diffuse into pores of adsorbent.

Step 3: The adsorbates move inside the pore until it is fully loaded. The first layer of adsorbates which cover on the surface inside pores is called monolayer.

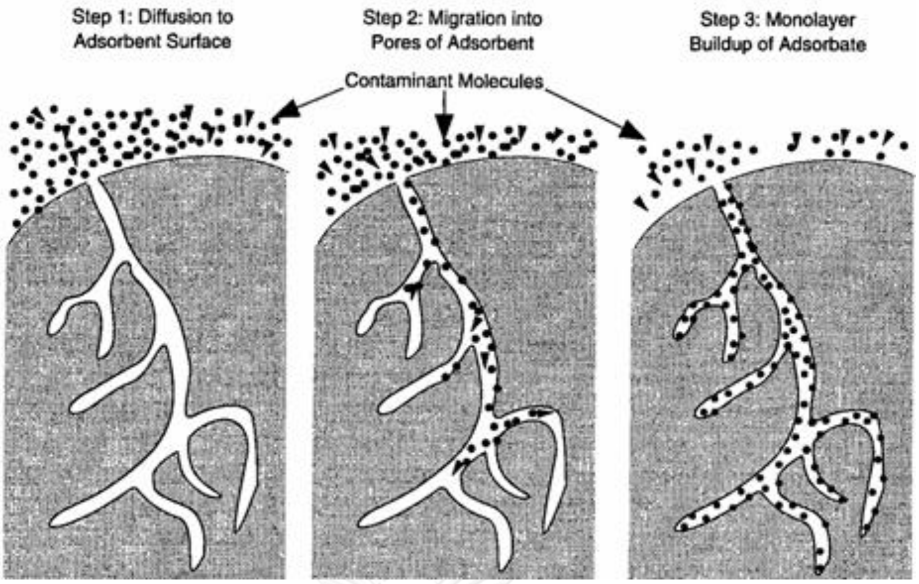


Figure 2.7 The mechanism of adsorption [34]

Adsorption can be divided into 2 types depending on the interaction occurred between adsorbates and adsorbent.

2.8.1 Physical adsorption or physisorption

The interactive force between adsorbates and adsorbent is Van der Waals force. Energy of interaction is very weak. The process, which does not involve any chemical bonding, is achieved quickly at low temperatures. On the other hand, surface coverage is low with temperature increase or pressure decrease.

2.8.2 Chemical adsorption or chemisorption

Chemisorption is a type of adsorption which involves a chemical reaction. The strong interaction between the adsorbate and the substrate surface includes the types of ionic or covalent bonds formation. Only one layer of chemisorbed molecules is formed (monolayer adsorption). The reaction can be slowly reversible or irreversible.

The model of monolayer and multilayer adsorption are shown in **Figure 2.8.**

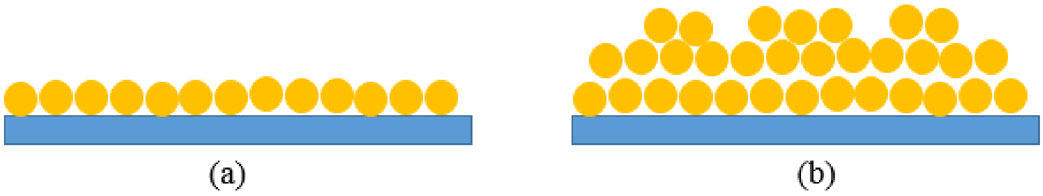


Figure 2.8 Monolayer adsorption (a) and multilayer adsorption (b).

2.8.3 Comparison between physisorption and chemisorption

The difference between physical and chemical adsorption is summarized in **Table 2.3**.

Table 2.3 Comparison between physisorption and chemisorption [35]

	Physisorption	**Chemisorption**
Heat of adsorption (kJ/mol)	20-40 (heat of liquefaction)	>80 (bulk phase chemical reactions)
Rate of adsorption @273 K	Fast	Slow
Uptake temperature	Decrease	Increase
Desorption	Easy-by reducing P or increasing T	Difficult-high T is required to break bonds
Desorbed species	Adsorbate is unchanged	May be different from original adsorptive
Specificity	Non-specific	Very specific
Monolayer coverage	Mono or multilayer	Monolayer

2.8.4 Van der Waal force

Van der Waal force is the attractive or repulsive force between molecules. The force is much weaker than hydrogen bonding. It can be divided into 3 types [36-38].

2.8.4.1 London dispersion force

London dispersion force is the weakest intermolecular force. It is a temporary force between positive nuclei of one molecule attracting the electrons of another molecule.

2.8.4.2 Dipole-dipole force

Dipole-dipole interaction occurs between polar molecules when the interacting molecules contain groups or region of a molecule that are permanently a positive or negative region. It can also be called permanent dipole bond.

2.8.4.3 Ion-dipole force

It is an attractive force between an ion and a neutral molecule that has a molecular dipole. Ion-dipole attractions become stronger as either the charge on the ion increases, or as the magnitude of the dipole of the polar molecule increases.

2.8.5 Influencing factors on adsorption

2.8.5.1 Nature of adsorbent

Surface area of adsorbent is directly related with number of pores. When the adsorbent has large surface area or porous structure, the adsorption capacity possibly increases. Furthermore, pore size of adsorbent is also an important factor which may affect the adsorption. The open pores must be larger than the size of adsorbates so that the adsorbates can move into pores. A good adsorbent should have good chemical and physical stability at the temperature of adsorption.

2.8.5.2 Nature of adsorbate

The lower the solubility of an adsorbate in the solvent, the higher the adsorption strength could be observed [39]. Moreover, the polarity between adsorbate and adsorbent must be compatible in adsorption (like-adsorbs-like) or polar surface prefers polar adsorbate and nonpolar surface prefers nonpolar adsorbate.

2.8.5.3 Experimental conditions

Adsorption is an exothermic process. If the temperature is increased, the rate of reaction increases. Moreover, pH of solution and turbulence in process must also be reasonably suitable.

2.9 Adsorption isotherm

In adsorption process, the adsorbate molecules are adsorbed and accumulated on the surface of adsorbent until the concentration of adsorbates in stationary phase (solid phase) and gas or liquid phase does not change, indicating that the adsorption equilibrium was attained. Adsorption isotherm is the relation between quantity of molecules adsorbed and the concentration in liquid or gas phase at equilibrium observed at constant temperature. The mathematic models which are widely used to describe the adsorption equilibrium are Langmuir and Freundlich models.

2.9.1 Langmuir isotherm

Langmuir isotherm is often used to describe the adsorption corresponding to monolayer coverage. The attractive or repulsive forces between adjacent adsorbate molecules are negligible. The numbers of adsorbates on adsorbents increase continually when the concentration of adsorbates in solution or gas (mobile phase) is increased and finally reached constant values due to the limited number of active sites. Thus, the adsorption capability will depend on the vacancy of active sites on adsorbents and numbers of adsorbates [40, 41]. The equation of Langmuir isotherm is shown in **Equation 2.1** and can be rearrange to linear form as given in **Equation 2.2**;

$$q = \frac{q_{max} b C_e}{(1+bC_e)} \tag{2.1}$$

$$\frac{C_e}{q} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \tag{2.2}$$

where q = the adsorption capacity (mg/g)

q_{max} = the maximum adsorption capacity (mg/g)

C_e = concentration of solution at equilibrium (mg/L)

b = Langmuir adsorption equilibrium constant (L/mg)

Plotting between $\frac{C_e}{q}$ value (y-axis) versus C_e value (x-axis), the slope is $\frac{1}{q_{max}}$ and the intercept is $\frac{1}{bq_{max}}$. Thus, the value of q_{max} and b can be calculated from this linear plot. The example of Langmuir plot is shown in **Figure 2.9**.

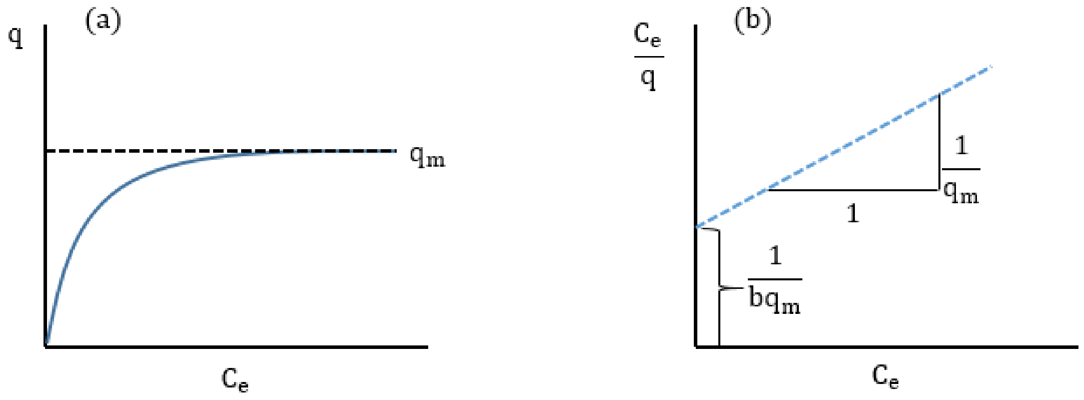


Figure 2.9 Adsorption isotherm of a monolayer coverage on adsorbent (a) and linear plot of Langmuir adsorption isotherm (b).

2.9.2 Freundlich isotherm

Freundlich isotherm is based on a multilayer coverage assumption. The surface of adsorbent may bear different active sites (heterogeneous surface). Freundlich adsorption equation and its linear form are given in **Equation 2.3** and **2.4**, respectively [40, 42];

$$q = K_f C_e^{\frac{1}{n}} \tag{2.3}$$

$$\log q = \log K_f + \frac{1}{n} \log C_e \tag{2.4}$$

where K_f = Freundlich constant related to adsorption capacity of the adsorbent (mg/g)

n = Freundlich constant related to adsorption intensity

Plotting between $\log q$ value (y-axis) versus $\log C_e$ value (x-axis), the slope is $\frac{1}{n}$ and the intercept is $\log K_f$. The example of Freundlich plot is shown in **Figure 2.10.**

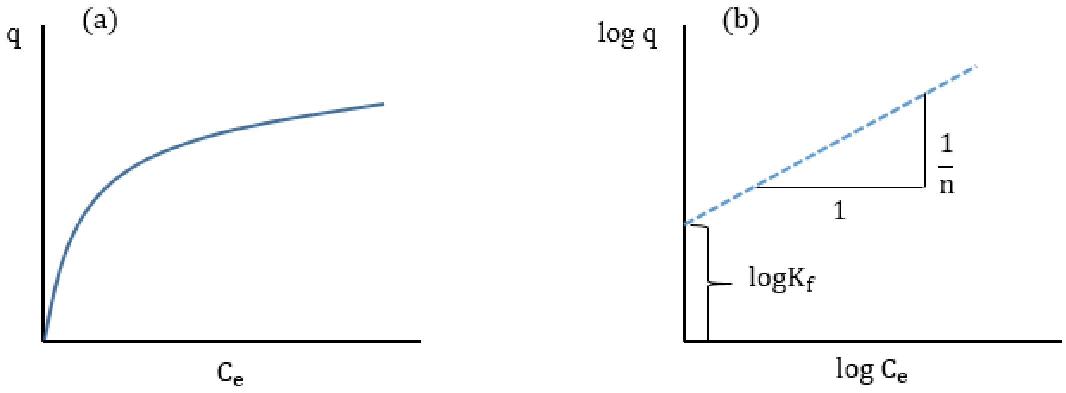


Figure 2.10 The adsorption in a multilayer of surface adsorbent (a) and linear plot of Freundlich adsorption isotherm (b).

2.10 Adsorption kinetics

The reaction rate on adsorption is described by using two well-known kinetic models; pseudo-first order and pseudo-second order model [40].

2.10.1 Pseudo-first order model

The pseudo-first order rate of adsorption is written in **Equation 2.5**;

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.5}$$

where k_1 = pseudo-first order rate constant

q_e = the amounts adsorbed at equilibrium (mg/g)

q_t = the amounts adsorbed at time (mg/g)

The integrated rate law, after applying the initial condition q_t=0 to q_t at t=0 to t, the linear equation is obtained as **Equation 2.6**.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2.6}$$

Plotting between $\log(q_e - q_t)$ versus t gives a linear line for first order kinetic, the slope is $\frac{-k_1}{2.303}$, and the intercept is $\log q_e$. The example of pseudo-first order plot is shown in **Figure 2.11**.

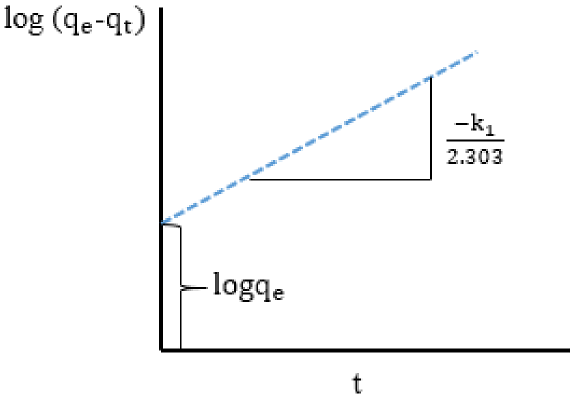


Figure 2.11 Pseudo-first order kinetics plot

2.10.2 Pseudo-second order model

The pseudo-second order rate of adsorption is shown in **Equation 2.7**;

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.7}$$

where k_2 = pseudo-second order rate constant

q_e = the amounts adsorbed at equilibrium (mg/g)

q_t = the amounts adsorbed at time (mg/g)

The integrated rate law, after applying the initial condition t=0 to t and q_t=0 to q_t, is given in **Equation 2.8** and **2.9**.

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{2.8}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2.9}$$

Plotting between $\frac{t}{q_t}$ versus t gives a linear line for second order kinetic with the slope of $\frac{1}{q_e}$ and the intercept of $\frac{1}{k_2 q_e^2}$. The example of pseudo-second order plot is shown in **Figure 2.12**.

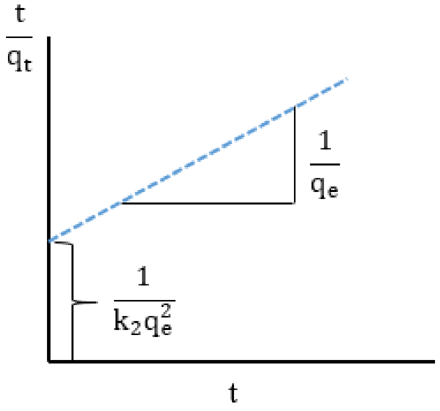


Figure 2.12 Second order kinetics plot

The reaction rate of impurity adsorption in biodiesel can be explained by adopting these two models to fit experimental data. R^2 value (approaches to one) and comparison between q_e calculation and q_e experiment guarantee that the model fits the data well.

2.11 Literature review

A number of researches reported about the alternative processes for biodiesel purification without water washing route. Adsorption is an alternative route and convenient method for purification of biodiesel. Various adsorbents have been proposed for this purpose and the use of low cost adsorbent derived from waste material is an interesting approach. Fly ash is an interesting adsorbent regarding its adsorption performance, efficiency and capacity for polar impurity removal.

2.11.1 Purification of biodiesel

Berrios et al. [17] demonstrated that wet washing is not the proper method to purify biodiesel because it has many disadvantages including large amount of water consumption. The results from applying wet washing, ion exchange resins and magnesium silicate as an adsorbent were compared in term of glycerol and soap removal efficiency. All processes could eliminate glycerol and soap content. To avoid the saturation of adsorbent, the removal of methanol from biodiesel prior to adsorption is essence in the process of magnesium silicate.

Karabesko et al. [43] proposed the use of bioethanol instead of methanol to produce biodiesel because it is more environmental friendly and generated from renewable sources. Rapeseed oil ethyl ester (REE) was produced via transesterification with 1:6 oil:bioethanol molar ratio and 1.5 %wt of KOH. Magnesol and o-phosphoric acid (o-HPO_3) aqueous solution were used to purify crude REE. Total contamination including glycerol, methanol, water, soaps and other impurities could be eliminated better by using Magnesol when compared with o-HPO_3 aqueous solution method. Moreover, the quality of REE treated by Magnesol meets the standard values according to EN 14214 specification standard and this purification method is simpler than wet washing.

Saleh et al. [44] studied the ability of polyacrylonitrile (PAN) membrane to reduce free glycerol content in fatty acid methyl ester (FAME) produced from canola oil and the quality of treated FAME met the standard specifications according to ASTM D6751 and EN14214. The operation was performed at 25 °C under pressure of 552 kPa. The extent of glycerol separation depends on the content of water, methanol and soap in FAME. This technology consumes only 2 g of water per L of FAME which is much lower than the conventional washing (10 L).

Atadashi et al. [45] compared the methods of biodiesel refining (i.e. wet washing, dry washing process using Magnesol and ion exchange resins and membrane). Membrane purification gave the good results in term of biodiesel yield and quality. The value of glycerol in treated biodiesel is 0.013 %wt which is below standard specifications of biodiesel (ASTM D6751 and EN14214). Its advantages are not only less energy consuming but also almost zero wastewater generation.

Wall et al. [16] investigated the performance of ion exchange resins (gel and macroporous resins) and their efficiency. All mechanisms include filtration, physical adsorption; an ion exchange and glycerin/soap interaction appeared to be responsible for the removal of impurities in biodiesel. The results show that soap levels can be reduced from 1,200 ppm to below 50 ppm for about 550 bed volumes (BV) and glycerin levels could be reduced from 0.08% to below 0.02% for about 200 BV.

Braz et al. [46] compared the efficiency of two adsorbent types (Magnesol and silica) and two ion exchange resins (Amberlite BD10 DRY and Purolite PD206) in biodiesel purification. The adsorption process was performed at 65 °C. Residual potassium, alcohol, water and soaps were measured in treated biodiesel. Magnesol and silica gave better results for removing soap, free and bonded glycerol and potassium. One weight percent of Magnesol and two weight percent of silica could reduce impurities to the following values; acid value of 0.17 mg KOH/g, K of 1 mg/kg, soap of 61 ppm, methanol of 0.22% and free glycerol of 0.03%. Moreover, the inorganic matrices Magnesol and silica could successfully reduce 500 mg of water per kilogram of biodiesel.

Leeruang et al. [47] purified crude biodiesel by using activated low-silica bentonite on sorption process. This research studied the effect of the concentration of H2SO4 in bentonite activation, the time of activation, the size of bentonite particles and the amount of bentonite. The conditions in bentonite activation were 0.1 M of H2SO4 in DI water at 100 °C for 1 hr. The activated low-silica bentonite (120-200 mesh) of 5 %wt gave 47% soap removal and fitted to Freundlich isotherm. The surface area, chemical composition and structure of the activated low-silica bentonite were characterized by BET, XRF and FTIR, respectively. After activated by H2SO4, the surface area was increased from 47.557 to 56.866 m2/g.

Fadhil et al. [48] prepared an activated carbon as adsorbent from spent tea waste. A crude methyl ester from base catalyst production was transferred to a chromatography column packed with a bed of activated carbon (5 cm bed height, 2 g) with a flow rate of 15 drop/min. Silica gel was also used in the same approach. The results were compared to that of water washing method. The yield and the biodiesel quality obtained by using activated carbon method were higher than other two processes. The adsorbent could be regenerated and reused without efficiency loss.

Saengprachum et al. [49] investigated the use of adsorbents (i.e. activated carbon and extracted silica from rice husk ash (RHA)) for biodiesel purification. An activated carbon was produced from treating RHA with $ZnCl_2$ in weight ratios of 1:0.25, 1:1 or 1:2 (RHA: $ZnCl_2$) and the carbonization was performed at 700 °C. An extracted silica was obtained by combusting RHA at 700 °C and further treating the product with 2.5 N NaOH. The extracted silica gave better results of biodiesel purification than the activated carbon under optimum conditions (i.e. 5%wt of adsorbent, 150 rpm of agitation, 50 °C, 10 min of adsorption time). The percent of glycerin removal was 84.8 % and 75-80% for a regenerated adsorbent. A biodiesel treated by the extracted silica was clearer than the one treated by $ZnCl_2$-activated carbon and Langmuir model can explain the adsorption equilibrium in this adsorption process.

2.12.2 Use of fly ash adsorbent

Lin et al. [50] suggested that fly ash was a low cost adsorbent for removal of dyes from aqueous solution with high efficiency. Fly ash treated with H_2SO_4 acid has higher surface area and shows better percent of adsorption. The adsorption data could be fitted by Freundlich isotherm and adsorption kinetics followed pseudo-second order model. In term of thermodynamic, the enthalpy (ΔH^0) value was positive (5.63 kJ/mol) indicating that it was endothermic process.

Yadla et al. [51] used fly ash to remove lead (II) ions from aqueous solution. Effect of various factors, denoted as treatment time, initial pH and adsorbent size, were investigated in adsorption process. Percentage of removal increased when increased pH and pH 6 was proposed as its optimum point for maximum removal. Lead (II) ions adsorption reached to equilibrium within 1 hr and kinetic adsorption data fitted well to pseudo-first order model.

Akgerman et al. [18] studied the adsorption of phenolic compounds on fly ash. Fly ash from Texas Municipal Power Agency (TMPA) was used to adsorb phenol, 3-chlorophenol and 2,4-dichlorophenol from water. For the highest concentrations used, the observed capacities of fly ash were 67, 20 and 22 mg/g for phenol, 3-chlorophenol and 2,4-dichlorophenol adsorption, respectively. Phenol exhibited higher affinity on fly ash than others.

Wang et al. [52] inspected the characteristics of coal fly ash. Physical and chemical properties of coal fly ash wastes obtained from different boilers under varying combustion condition of power plant in Western Australia were investigated by using N_2 adsorption, XRD, SEM and pH-titration. They were used to adsorb methylene blue (MB) and humic acid (HA) in aqueous solutions due to their high surface area and pore volume. The capacity of coal fly ashes in MB and HA adsorption were 7 and 10 mg/g, respectively.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1 Chemicals and materials

1. Refined palm oil (palm olein)
2. Sodium hydroxide: analytical grade; ACS
3. Methanol: analytical grade; Merck
4. Isopropyl alcohol: commercial grade; Merck
5. Bromophenol blue: analytical grade; Carlo Erba
6. Phenol red: analytical grade; Carlo Erba
7. Hydrochloric acid: analytical grade; Merck
8. p-Naphtholbenzein: analytical grade; Carlo Erba
9. Toluene: analytical grade; Merck
10. Lignite fly ash: commercial grade; Maemoh, Lampang
11. Silica alumina: commercial grade; Merck
12. Activated carbon: commercial grade; Merck
13. Florisil (Magnesol, Magnesium silicate): standard; Sigma-Aldrich

3.1.2 Equipments

1. X-ray fluorescence spectrometer (XRF); PW 2400 Philips
2. Scanning electron microscope (SEM); JSM-5410LV JEOL
3. Surface area analyzer (Autosorb version 1.19)
4. Gas Chromatography; Agilent 7890A
5. Rotary evaporator; Buchi
6. Nuclear magnetic resonance spectrometer (H^1-NMR); Varian Mercury XL 400 MHz

3.2 Characterization of lignite fly ash

Lignite fly ash collected from Maemoh power plant was obtained from ORC PREMEIR Co., Ltd and characterized by XRF, SEM and surface area analyzer. The chemical composition and the morphology of lignite fly ash were observed with XRF and SEM. Surface area, pore volume and pore diameter were determined from data of N_2 adsorption measured by a surface analyzer and BET method.

3.3 Synthesis of biodiesel from refined palm oil

Refined palm oil (100 g) was weighted into a round bottom flask equipped with condenser adapted to sand bath with thermometer. After the refined palm oil was heated, 11.44, 22.88, 34.32 or 45.76 g of methanol was weighted and used to dissolve sodium hydroxide catalyst (1% wt of sodium hydroxide per 100 g of refined palm oil) and this base catalyst solution was added into a round bottom flask (mole ratio of oil: methanol was 1:6, 1:9 or 1:12). Each mixture was refluxed at 65°C for 90 min. Then, the mixture was transferred to a separatory funnel and let stand for 30 min to separate the glycerin layer. The biodiesel layer was further washed with warm DI water until the bottom aqueous layer was clear. Trace water in the upper layer or methyl ester layer was removed by sodium sulfate before NMR testing. The percent of ester content in biodiesel can be calculated following **Equation 3.1**.;

$$\%\ \text{Ester content} = \left(\frac{2\mathrm{I}_{\mathrm{CH_3}}}{3\mathrm{I}_{\mathrm{CH_2}}}\right) \times 100 \tag{3.1}$$

where $\mathrm{I}_{\mathrm{CH_3}}$ = integrated value of CH_3 in H^1-NMR spectrum

$\mathrm{I}_{\mathrm{CH_2}}$ = integrated value of CH_2 in H^1-NMR spectrum

3.4 Purification of crude biodiesel

According to the results obtained in previous experiments, biodiesel was synthesized as follows. A portion of 800 g of refined palm oil was weighted into a 1000 ml round bottom flask equipped with condenser adapted to a sand bath with a thermometer. After the reactor was heated to 65°C, a solution of sodium hydroxide (8 g) in 183 g of methanol was slowly added into the reactor under continuous stirring for 90 min. The oil:methanol ratio was 1:6. The glycerin layer was separated after the reaction was completed. The crude biodiesel was further used for purification process.

3.4.1 Purification of crude biodiesel by gravitational precipitation method

Biodiesel was synthesized as described previously. The mixture of biodiesel and glycerin was separated into 2 portions. The first portion was transferred to a separatory funnel and let stand for 5, 10, 15, 30, 60, 180 or 360 min. The other portion was treated with 3%wt of Lignite fly ash with particle size of 150-250 μm. The universal titration method was used to determine the content of impurity in biodiesel.

3.4.2 Purification of crude biodiesel by using lignite fly ash

The lignite fly ashes were weighted into the crude biodiesel. The mixtures were shaken by a shaker for a specific period of time. After that, the lignite fly ashes were filtered. The amount of soap and other impurities in the crude biodiesel was determined by the universal titration method.

- Effect of particle sizes of lignite fly ash

The raw lignite fly ash was separated by particle size using sieve shaker for 30 min. The range of sizes was from 425-850 μm, 250-425 μm, 150-250 μm and less than 150 μm. A portion of 30 g of crude biodiesel was added into each bottle containing lignite fly ashes of each particle size and the solid concentration was 3%wt. The bottles were shaken for 6 hr. After adsorption finished, lignite fly ash was filtered out by nylon filter. The content of impurities in the biodiesel samples was determined by the universal titration method.

- Effect of methanol in biodiesel on the removal efficiency

The crude biodiesel was separated into 2 portions. The first portion was heated to remove methanol by using rotary evaporator at 50 °C, while the second portion was used as obtained. Lignite fly ash with particle size of 150-250 μm was weighted into each portions of crude biodiesel to obtain 3%wt of solid. The adsorption was performed with different contact times. The universal titration method was used to determine the content of impurity in biodiesel.

- Effect of contact time and adsorption kinetics

The crude biodiesel containing methanol was subjected to the sorption process with 3%wt of lignite fly ash with particle size of 150-250 μm. The adsorption was performed for different shaking times including 5, 10, 15, 30, 60, 180 and 360 min. After the adsorption, lignite fly ash was filtered out by nylon filter. The universal titration method was used to determine the content of impurity in biodiesel. The results were fitted to pseudo-first order and pseudo-second order kinetics models.

- Effect of adsorbent dosage

A portion of 30 g crude biodiesel was weighted into each bottle containing fly ash of different weight to obtain solid dose of 1, 2, 3, 4 and 5 %wt of lignite fly ash. The lignite fly ash used in the process had particle size in a range of 150-250 μm. This adsorption process was carried out for 360 min. Then, lignite fly ash was filtered out by nylon filter. The content of impurities in the biodiesel samples was determined by the universal titration method.

- Adsorption isotherm

Adsorption isotherm describes the interaction between soap molecules as impurities on the adsorbent surface at equilibrium. According to the experiment, 30 g of crude biodiesel containing various concentrations of impurities in the range of 9,974 to 20,063 ppm was added in each bottle with 3%wt of lignite fly ash with particle size of 150-250 μm and shaken for 60 min. After the adsorption finished, the adsorption results were fitted to Langmuir and Freundlich isotherm models.

3.4.3 Purification of crude biodiesel using commercial adsorbents

Silica, activated carbon and Florisil as commercial adsorbents were weighted into each bottle containing crude biodiesel with methanol. 3%wt of adsorbent was used in the adsorption for 60 min. After the adsorption finished, the commercial adsorbents were filtered out by nylon filter. The content of impurities in the biodiesel samples was determined by the universal titration method.

3.4.4 Purification of crude biodiesel by water washing

After the biodiesel production finished, the crude biodiesel layer was separated from the glycerin layer. Warm water was used in this process to eliminate the impurities in crude biodiesel. This washing step was repeated until the aqueous layer was clear. The obtained biodiesel product should have a pH value close to 7. It can be approximately achieved when the pH value of water runoff was close to 7. The content of impurities before and after water washing were checked by the universal titration method.

3.5 Biodiesel analysis

3.5.1 Determination of soap and unreacted catalyst by the universal titration method (AOCS Method Cc 17-79) [53]

At the first step, 5 g of crude biodiesel sample was dissolved in 100 ml of isopropanol in an Erlenmeyer flask with 2 ml of 1% phenol red as indicator. The solution was titrated with 0.01 M HCl solution until the color of solution changed from red to yellow. The volume of titrant in the first step is referred as “A”. In the second step, 1 ml of 0.04% bromophenol blue indicator was dropped in the solution and titration was further performed with the same titrant until the color of solution changed from blue to yellow. The volume of titrant in the second step is referred as “B”. The amount of unreacted catalyst and soap as impurity in biodiesel was calculated by using **Equation 3.2** and **3.3** below.

In the first step, the amount of unreacted catalyst in biodiesel can be calculated by using **Equation 3.2**;

$$\text{g of catalyst/g of sample} = \frac{\text{A}\times 0.01\times 40.0}{\text{W}} \tag{3.2}$$

where A = volume of HCl used in the first step (L)

W = weight of biodiesel sample (g)

0.01 = concentration of HCl (mol/L)

40.0 = molecular weight of sodium hydroxide (g/mol)

In the second step, the amount of soap impurity in biodiesel can be calculated by using **Equation 3.3**;

$$\text{Soap level (ppm)} = \frac{\text{B}\times 0.01\times 304.4}{\text{W}} \times \frac{10^3\ \text{mg}}{1\times 10^{-3}\ \text{kg}} \tag{3.3}$$

where B = volume of HCl used in the second step (L)

W = weight of biodiesel sample (g)

0.01 = concentration of HCl (mol/L)

304.4 = average molecular weight of sodium oleate (g/mol)

3.5.2 Determination of free and total glycerin content, mono-, di- and tri-glyceride (EN 14105).

Gas chromatography is the technique used to determine biodiesel quality including quantity of free and total glycerin, mono-, di- and tri-glyceride in biodiesel. The European standard for biodiesel (EN 14105) set the limit of free and total glycerin to 0.02 and 0.25 %wt, respectively. Mono-, di- and triglyceride content should not exceed 0.7, 0.2 and 0.2 %wt, respectively.

3.5.3 Determination of the biodiesel properties

The physical properties of biodiesel were tested according to the universal method. The viscosity at 40 °C (mm^2/s), %free fatty acid and acid value (mg KOH/g) were tested according to ASTM D445, ASTM D5555 and ASTM D974 method, respectively.

- Viscosity (ASTM D445)

According to the experiment, 7 ml of biodiesel was added into the viscometer tube before being immersed into water bath. The operation was performed at 40 °C. Time was recorded when biodiesel flow from initial point to final point within viscometer tube. The viscosity can be calculated by using **Equation 3.4**;

$$\mathrm{Viscosity} = \mathrm{C} \times \mathrm{t} \tag{3.4}$$

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

t = measured flow time from initial point to final point (s)

- Free fatty acid

According to the experiment, 1 g of refined palm oil was weighted into an erlenmeyer flask followed by 75 ml of ethanol. Then, 2 ml of 1% phenopthalein was dropped into the mixture. The mixture was titrated with 0.25 N NaOH solution until the color changed from pale yellow to pale pink. The volume of titrant (ml) can be used to calculate the percent of free fatty acid by following **Equation 3.5**;

$$\%\mathrm{FFA} = \frac{\mathrm{Volume\ of\ NaOH\ (ml)} \times \mathrm{N} \times 256}{\mathrm{W}} \times 100 \tag{3.5}$$

where W = weight of refined palm oil (g)

N = normality of NaOH (mol/1000 ml)

256 = average molecular weight of palmitric acid (g/mol)

- Acid value

The solvent was prepared by using 250 ml of toluene mixed with 247.5 ml of isopropanol and 2.5 ml of DI water. To prepare indicator solution, 0.5 g of p-naphtholbenzein was dissolved in 100 ml of the prepared solvent. Then, 2 g of biodiesel was weighted into an erlenmeyer flask followed by 25 ml of the solvent and 0.125 ml of indicator solution. The mixture was titrated with 0.01 N KOH solution until the solution color changed from orange to green at the end point. The volume of titrant (ml) was used to calculate acid value in biodiesel by following **Equation 3.6**;

$$\text{Acid value (mg KOH/g)} = \frac{\text{Volume of titrant (ml)} \times \text{N} \times 56.1 \times 10^{3}\,\text{mg}}{\text{W}} \qquad (3.6)$$

where W = weight of biodiesel (g)

N = normality of KOH (mol/1000 ml)

56.1 = average molecular weight of KOH (g/mol)

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Preparation of crude biodiesel by transesterification of refined palm oil (palm olein)

A biodiesel from refined palm oil was synthesized via transesterification with a mole ratio of oil to methanol of 1:6. Thin layer chromatography (TLC) which is a simple method was used to pre-check the conversion of triglyceride (from refined palm oil) to methyl ester. On basic principle of TLC, the different position of spots on paper indicates that the substances on paper are different.

The result is shown in **Figure 4.1**. The position of methyl ester and triglyceride on TLC plate was different and methyl ester could migrate further than did triglyceride. The TLC results confirm that triglyceride was completely converted to methyl ester under the chosen synthesis condition.

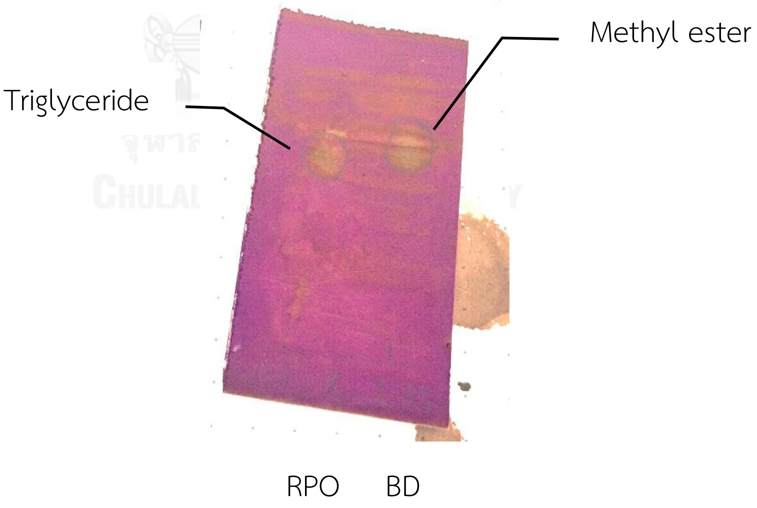


Figure 4.1 TLC of biodiesel synthesized via base-catalyzed transesterification; RPO: Refined palm oil, BD: Biodiesel, mobile phase: hexane, ethyl acetate, acetic acid (90:10:1 v/v)

4.2 Characterization of adsorbent

The raw lignite fly ash used in this research was obtained from electricity plant. It is a brown-grey powder consisting of fine-grained particles and its picture is shown in **Figure 4.2**. To observe the size distribution, 500 g of raw lignite fly ash was sieved by a sieve shaker through several sizes of sieve plates for 30 min. The obtained results are shown in Table 4.1. Most of lignite fly ash had particles size in the range of 150-250 μm, followed by fly ash of the size of less than 150 μm. It was further characterized by different techniques.

Figure 4.2 Lignite fly ash

Table 4.1 The amount of raw lignite fly ash of each size range

Size of particle (μm)	% w/w
< 150	28.37
150-250	66.82
250-425	3.76
425-850	0.42
> 850	0.02
Loss	0.62

4.2.1 Composition analysis

An X-ray fluorescence spectrometer (XRF) is used for identifying elemental composition of raw lignite fly ash from Maemoh power plant, Lampang. The major components of fly ash observed by XRF are shown in **Table 4.2**.

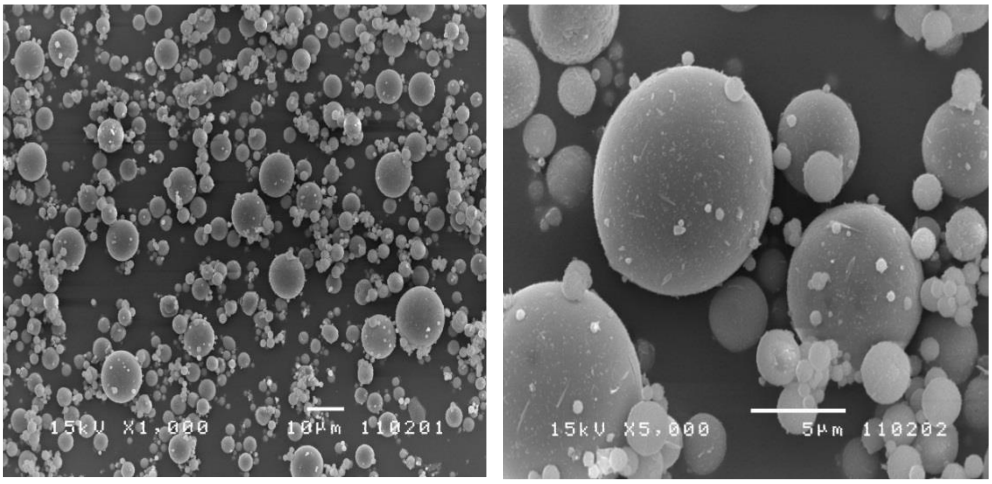
Table 4.2 X-ray fluorescence spectrometric results of lignite fly ash characterization

Chemical composition	% w/w
SiO_2	37.10
Al_2O_3	20.40
CaO	17.20
Fe_2O_3	11.20
SO_3	4.15
K_2O	2.47
MgO	2.08
Na_2O	1.54

The XRF results reveal that the lignite fly ash contained high content of Si, Al, Ca and Fe. They are probably in their oxide forms. Silica, alumina and iron oxide are the components which can adsorb the hydrophilic molecules and they are commonly and widely used adsorbents [54].

4.2.2 Morphology

A scanning electron microscope was used to observe the external surface or morphology of materials. The SEM images of fly ash are shown in **Figure 4.3**.



(a) (b)

Figure 4.3 SEM images of lignite fly ash at (a) ×1000 and (b) ×5000 magnification

The SEM images show that particles of lignite fly ash are in spherical shape of various sizes. The size of particle depends on the condition of burning in electricity plant. Some particles agglomerate and their surface are slightly rough.

4.2.3 Surface analysis

The data of N_2 adsorption by the lignite fly ash of different particle sizes were collected from a surface area analyzer. Using the results of N_2 adsorption, the BET method was adopted in this study to determine the surface area, total pore volume and average pore size diameter of the lignite fly ash. The adsorption isotherms plotted between relative pressure (P/P_0) and volume (cc/g) are shown in **Figure 4.4, Figure 4.5 and Figure 4.6**.

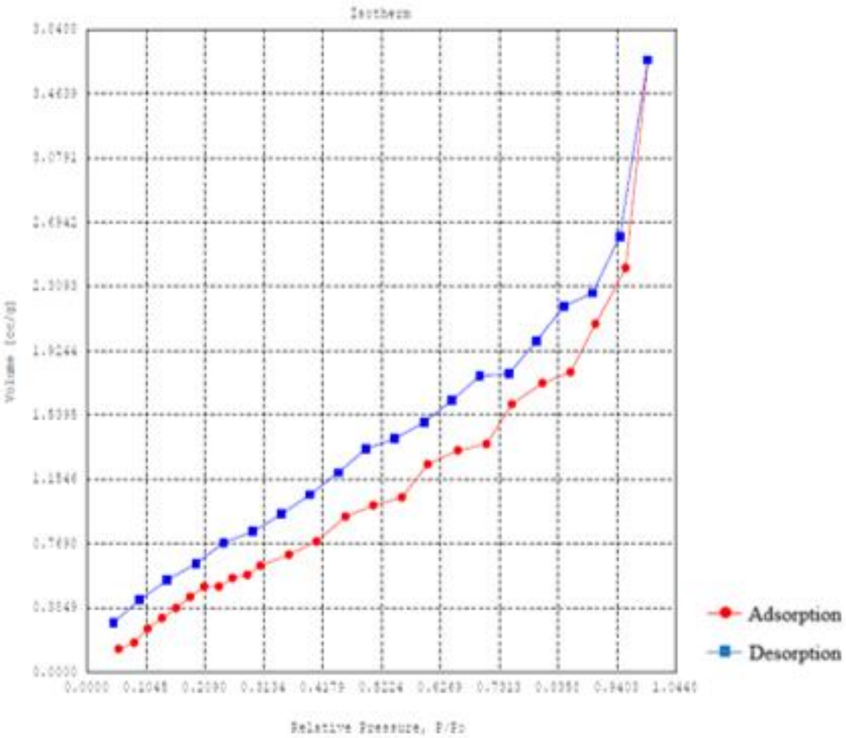


Figure 4.4 Isotherm of N_2 adsorption by the lignite fly ash having particle size less than 150 μm.

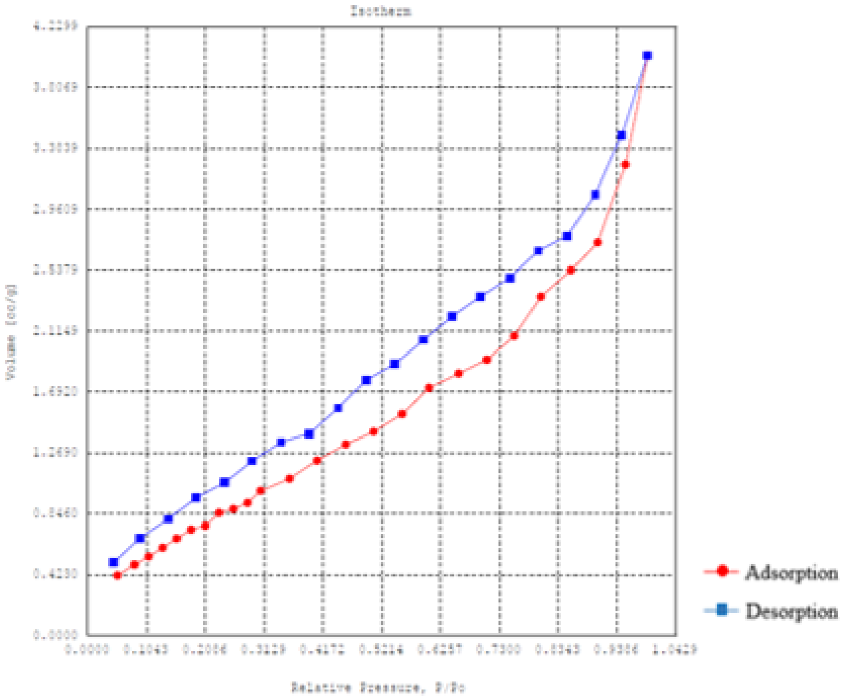


Figure 4.5 Isotherm of N_2 adsorption by the lignite fly ash having particle size in the range of 150-250 μm.

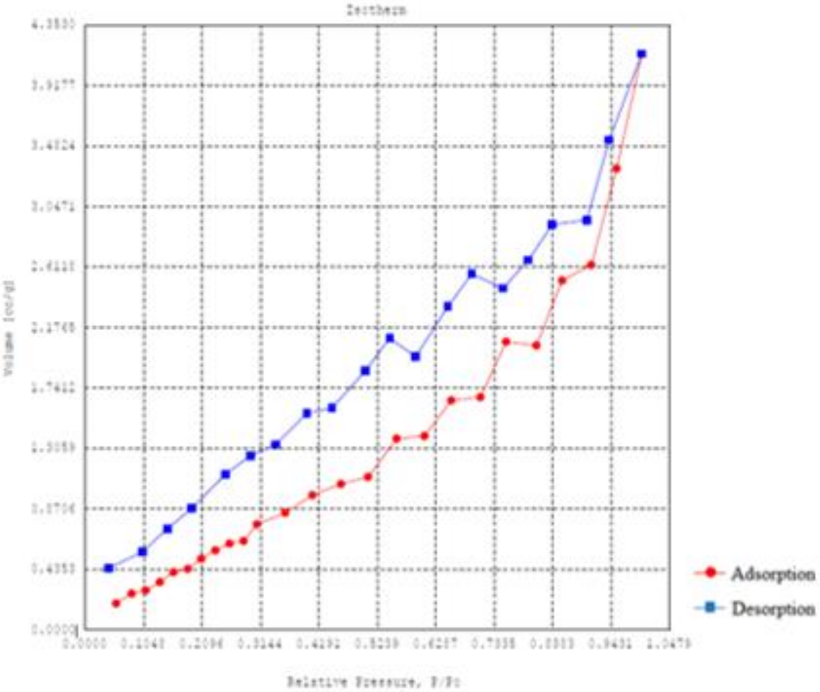


Figure 4.6 Isotherm of N_2 adsorption by the lignite fly ash having particle size in the range of 250-425 μm.

These adsorption isotherms are quite similar to type III for gas adsorption, commonly associated with both non-porous and microporous adsorbents [55, 56]. The obtained value of surface area (S_{BET}), total pore volume (V_p) and average pore size diameter (d_p) calculated by the BET method are summarized in **Table 4.3**. From the results of BET technique, the surface area of lignite fly ash is not as high as microporous materials; therefore, it indicates that the lignite fly ash might be categorized as a non-porous adsorbent.

Table 4.3 Surface physical properties calculated by BET method

Lignite fly ash size (μm)	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size diameter (nm)
<150	4.663	0.0057	4.864
150-250	3.418	0.0062	7.292
250-425	2.911	0.0064	8.812

From **Table 4.3**, it shows that the smallest particle size of lignite fly ash (<150 μm) had the lowest total pore volume and average diameter but exhibited the highest surface area. However, from the results in **Table 4.1**, it was found that the lignite fly ash having particle size in range of 150-250 μm are present as the large majority of particles when compared with particles of other size. Thus, the lignite fly ash of this size will be used in further experiments.

4.3 Synthesis of biodiesel and variation of oil to methanol ratio

When the biodiesel is synthesized by using different quantities of alcohol, the content of ester will be different. In this study, to find a condition for the biodiesel synthesis from palm oil via base-catalyzed transesterification, various ratios of oil and methanol were used. The content of ester in the obtained biodiesel was determined and the results are presented in **Table 4.4**.

Table 4.4 Ester contents in biodiesel synthesized by using different quantity of methanol

Ratio of oil: methanol	% Ester content
1:6	95
1:9	99
1:12	100

According to the results observed, when the mole ratio of oil to methanol of 1:6, 1:9 and 1:12 were used, the ester content of 95% and higher was observed in the obtained biodiesel. The mole ratio of 1:6 was selected for biodiesel synthesis in the further study.

4.4 Purification of crude biodiesel

The impurities in biodiesel investigated in this work consisted of soap molecules as the major component and some trace of methanol. The content of impurities was monitored under influence of different parameters of purification as follows.

4.4.1 Comparison of purification of crude biodiesel by gravitational precipitation and adsorption by fly ash

Normally, after the production of biodiesel is completed, the biodiesel will be let stand for 1-2 days before undergoing the purification process by water washing [57]. In this experiment, the biodiesel was synthesized and let stand to allow the separation of impurities by the gravitational precipitation and the level of impurities was monitored as a function of time. The amount of impurities decreased as the biodiesel was let stand for a long period of time as shown in **Figure 4.7.** The gravitational precipitation also had impacts on impurities separation. The biodiesel of the same initial impurity content was treated with 3%wt of lignite fly ash at different contact times ranging from 5-360 min. It was found that the impurities content in the biodiesel was removed by the adsorption by lignite fly ash better than by the gravitational precipitation method at shorter treatment period.

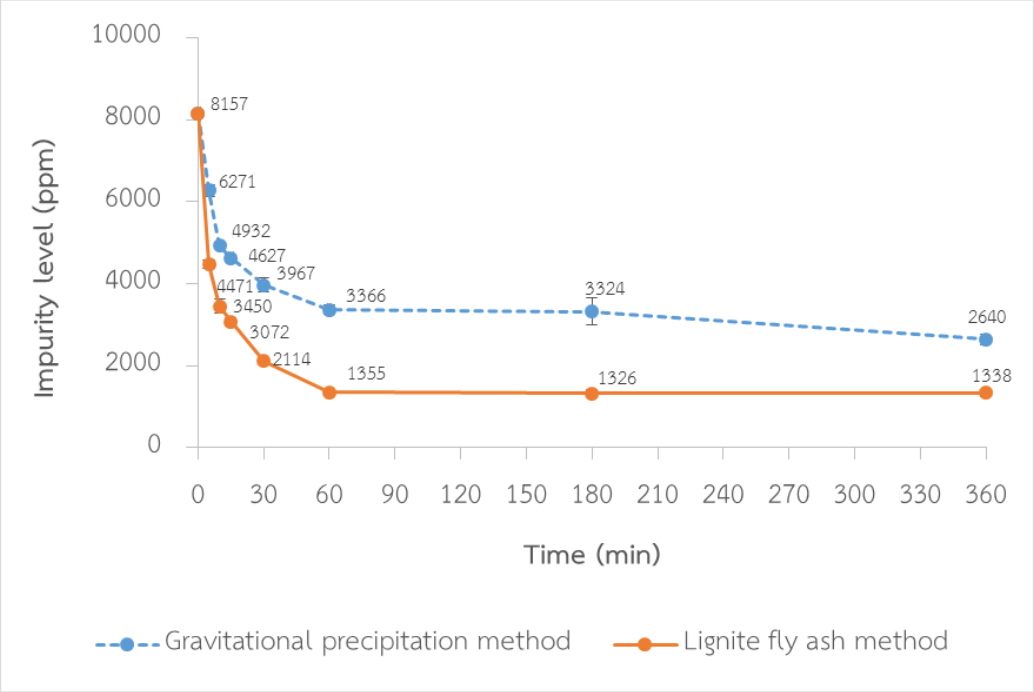


Figure 4.7 The effect of gravitational precipitation and adsorption by the lignite fly ash on the content of impurities in biodiesel as function of time.

4.4.2 Purification of crude biodiesel by using lignite fly ash

The effects of certain parameters were investigated to find suitable condition of biodiesel purification by the lignite fly ash. The efficiency in impurities adsorption will be presented in term of a percent removal which is calculated by using **Equation 4.1**;

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \qquad (4.1)$$

where C_i = initial concentration of impurities (mg/L)

C_f = final concentration of impurities (mg/L)

- Effect of particle sizes of lignite fly ash

The raw lignite fly ash was separated by size using a sieve shaker for 30 min before being used in this experiment. A crude biodiesel containing 8,909 ppm impurity was treated by the lignite fly ash of several particle sizes range from less than 150 to 850 μm. The adsorption process was operated at room temperature for 360 min shaking time. The dosage of lignite fly ash in the process was 3%wt. The results are shown in **Figure 4.8**. The removal of impurities by the gravitational separation was also observed and compared.

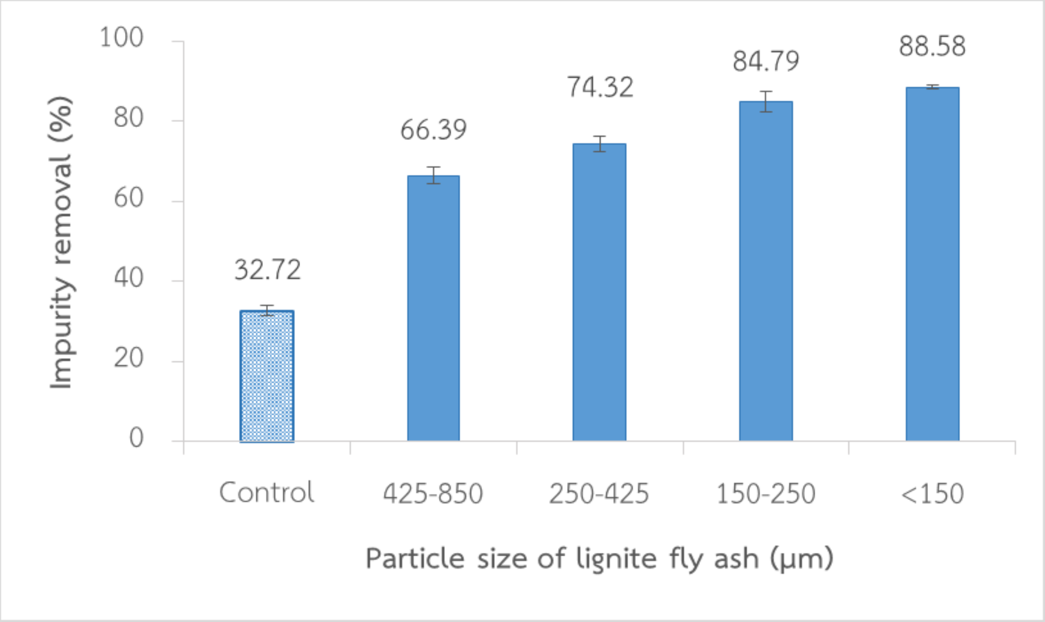


Figure 4.8 Effect of particle size on impurity removal efficiency compared to the gravitational precipitation (control).

Comparing the results of biodiesel purification by the adsorbent and the gravitational precipitation, the lignite fly ash with particle size smaller than 150 μm gave the highest percentage of impurity removal (88.58%). The results indicated that the smaller the particle size is, the better the adsorption efficiency could be achieved. It is because small particles have large surface area and they can be thoroughly dispersed in the biodiesel. On the other hand, it was difficult to filter the small particles out of the treated biodiesel and the solid separation took a long time. Moreover, the majority of lignite fly ash had particle size in the range of 150-250 μm and these particles could also remove the impurities with a high efficiency (84.79%). Therefore, the fly ash with particle size in the range of 150-250 μm was chosen for the further study.

- Effect of methanol in biodiesel on the removal efficiency

The remaining methanol in biodiesel is one of the impurities that must be eliminated because it causes engine corrosion. The quality requirement (EN 14110) indicates that the biodiesel should not contain methanol more than 0.20 %wt. In general, methanol can be evaporated from biodiesel at temperature above 64.7 °C but the process involved is unnecessarily complicated and costly. Regarding the chemical composition of the lignite fly ash, it may have a strong affinity for polar molecules including methanol. To avoid wasting time on solvent removal process, the use of the lignite fly ash may be a simple alternative to remove both methanol and all the polar impurities from a crude biodiesel.

In this study, a biodiesel containing 18,115 ppm impurities was separated into two portions. The first portion was heated to remove methanol with a rotary evaporator. During this experiment, some impurities dissolved in methanol were also removed and the biodiesel eventually contained 8,214 ppm impurities. The second portion was used directly as prepared without methanol elimination step. The lignite fly ash (3%wt) was added into each portion and the adsorption was carried out. The percent of impurity removal was observed at different time of adsorption (5-60 min) and the results are presented in **Figure 4.9**.

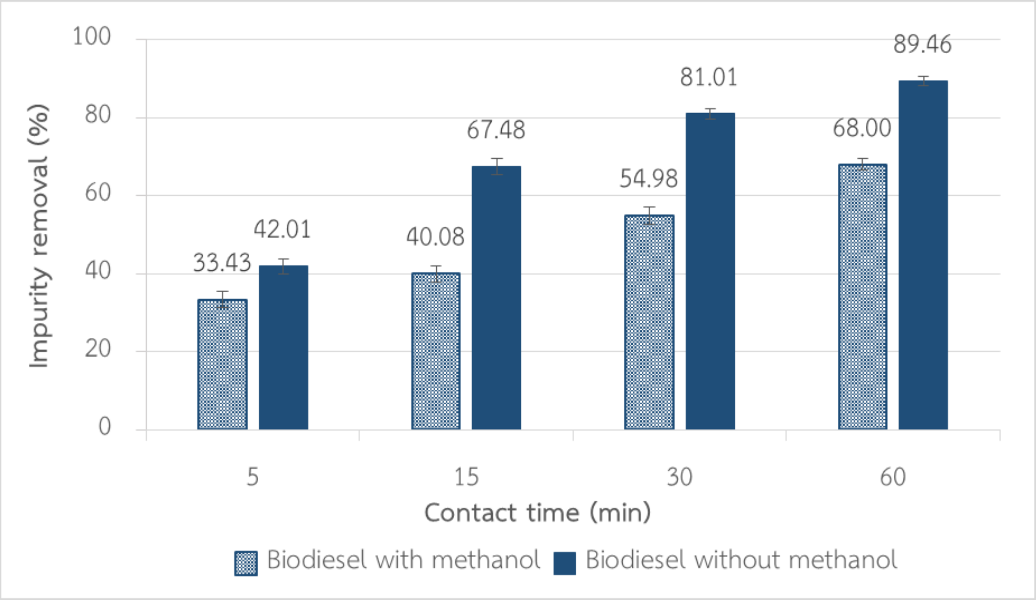


Figure 4.9 Effect of methanol in biodiesel on the removal efficiency

From the results in **Figure 4.9**, the percent of impurity removal from crude biodiesel containing methanol was lower than the one without methanol after adsorption by the lignite fly ash. However, to eliminate methanol from a crude biodiesel, it requires evaporation process and it is a waste of time and costly. This research recommends the use of the lignite fly ash adsorbent with a crude biodiesel containing methanol residue.

- Effect of contact time

This experiment was performed in order to find a suitable time of adsorption for the studied system. A crude biodiesel with 8,157 ppm of impurity was treated with 3%wt of lignite fly ash at various shaking times ranging from 5 to 360 min and the results are presented in **Figure 4.10**.

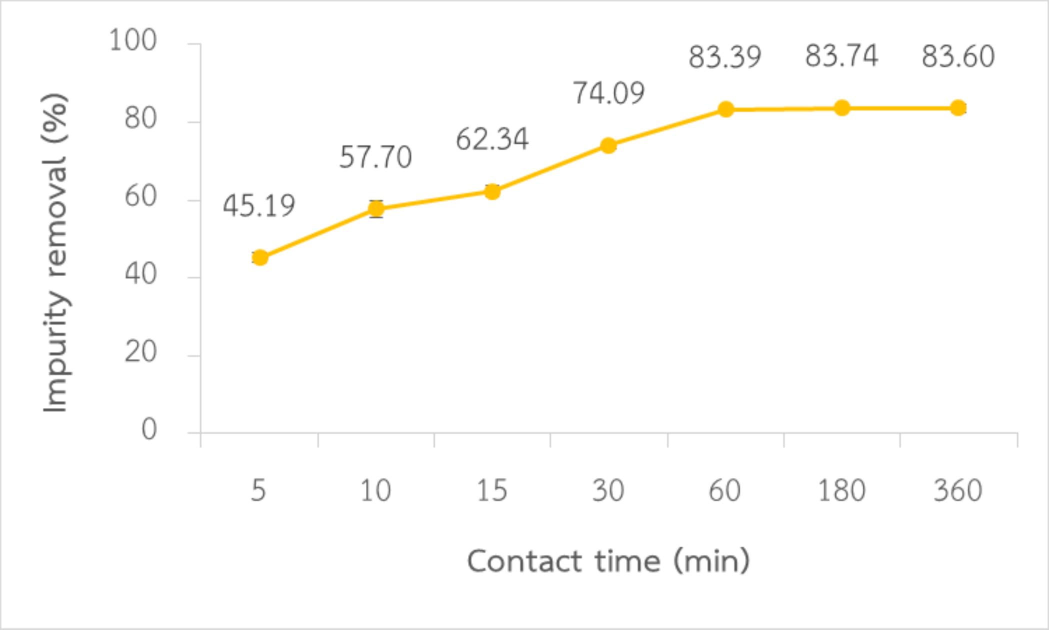


Figure 4.10 Effect of contact time on the impurity removal efficiency

The adsorption in the studied process occurred rapidly at the beginning and reached the equilibrium within 60 min. Despite not having porous structure, the fly ash exhibited a fast adsorption which was probably attributed to the small particle size of the adsorbents and hence, the large surface per volume for impurity adsorption.

- Effect of adsorbent dosage

The several dosages of lignite fly ash were added into a biodiesel containing 8,036 ppm of impurity and methanol. The sorption process was operated for 360 min, compared to the gravitational precipitation. The results of this experiment are shown in **Figure 4.11**.

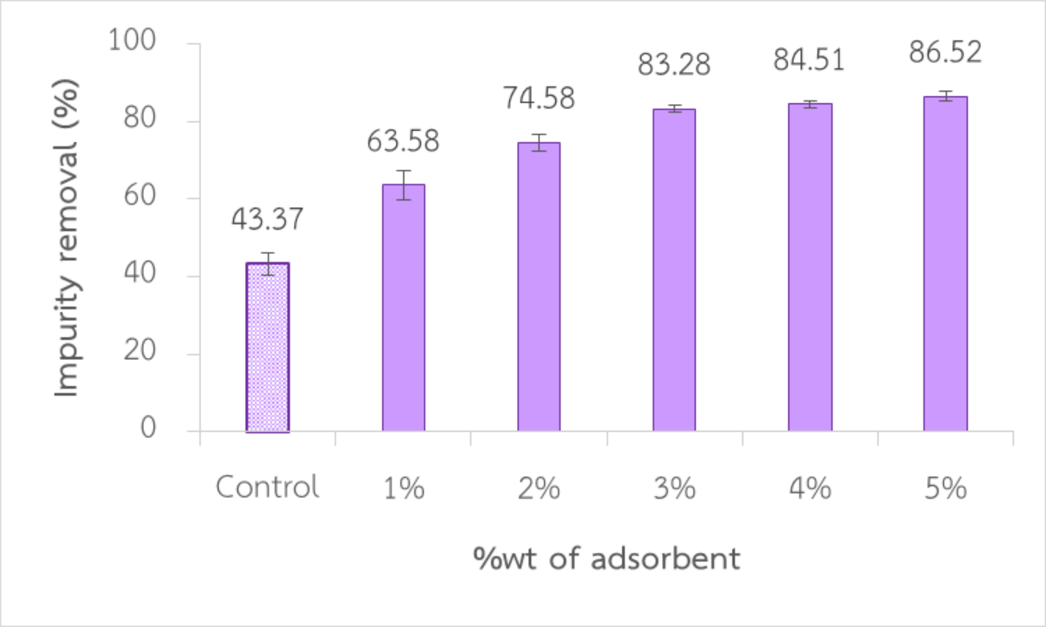


Figure 4.11 Effect of adsorbent dosage on the impurity removal efficiency compared to the gravitational precipitation (control)

In **Figure 4.11**, the efficiency in impurity removal by the gravitational precipitation was the least, compared to the use of adsorbent. When increased the dosage of adsorbent, the removal efficiency constantly increased and eventually reached relatively constant values despite of a further increase of dosage. According to this experiment, a dosage of 4%wt or 5%wt of fly ash did not give remarkably higher efficiency in impurity removal than a dosage of 3%wt. To avoid wastage, the appropriate dosage for this purification system was 3%wt which could remove 83% of impurity in this experiment.

4.4.3 Purification of crude biodiesel by commercial adsorbents

The commercial adsorbents such as Florisil or Magnesol, activated carbon and silica were used to purify a biodiesel containing 8,148 ppm of impurities and their efficiencies were compared to those of lignite fly ash and the gravitational precipitation. The results are shown in **Figure 4.12** and the properties of commercial adsorbents are shown in **Table 4.5**.

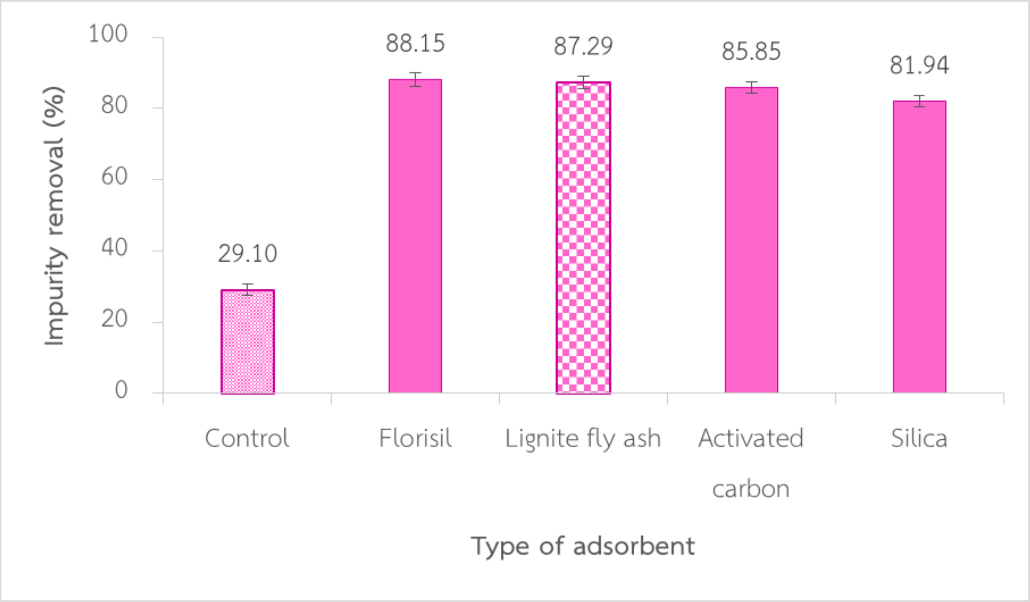


Figure 4.12 Efficiency in impurity removal by commercial adsorbents, lignite fly ash and the gravitational precipitation (control).

Table 4.5 The properties of commercial adsorbents

Adsorbent	Surface area (m^2/g)
Florisil or Magnesol	289
Activated carbon	500
Silica	800

It was found that 29% of impurities precipitated within 60 min without adsorbent, while the use of adsorbents exhibited much higher efficiency. The lignite fly ash and the commercial adsorbents could remove higher than 81% of impurity from the biodiesel. When comparing the results of lignite fly ash with each adsorbent by -tests, it was found that the efficiency of lignite fly ash was not significantly different from that of Florisil or Magnesol and activated carbon at 95% confidence interval. On the other hand, the lignite fly ash showed a significantly higher efficiency than silica. Although the surface area of lignite fly ash (3.418 m^2/g) was much less than those of commercial adsorbents, the fly ash showed a high efficiency in impurities removal, revealing a high affinity of impurities toward lignite fly ash. These results indicates that the lignite fly ash can replace these commercial adsorbents in biodiesel purification.

4.4.4 Comparison of water consumption between wet washing and lignite fly ash combined with wet washing

One hundred grams of biodiesel containing 8,148 ppm of impurities was purified with the water washing method and with the fly ash combined with water washing. To remove the impurities, for 100 g of biodiesel, 2,500 mL of DI water was consumed. Otherwise, to purify biodiesel previously treated with 3%wt of lignite fly ash, it required 500 mL of DI water. This experiment demonstrates that the purification of biodiesel by the lignite fly ash combined with water washing can reduce 80% of water consumption. The result is shown in **Figure 4.13**.

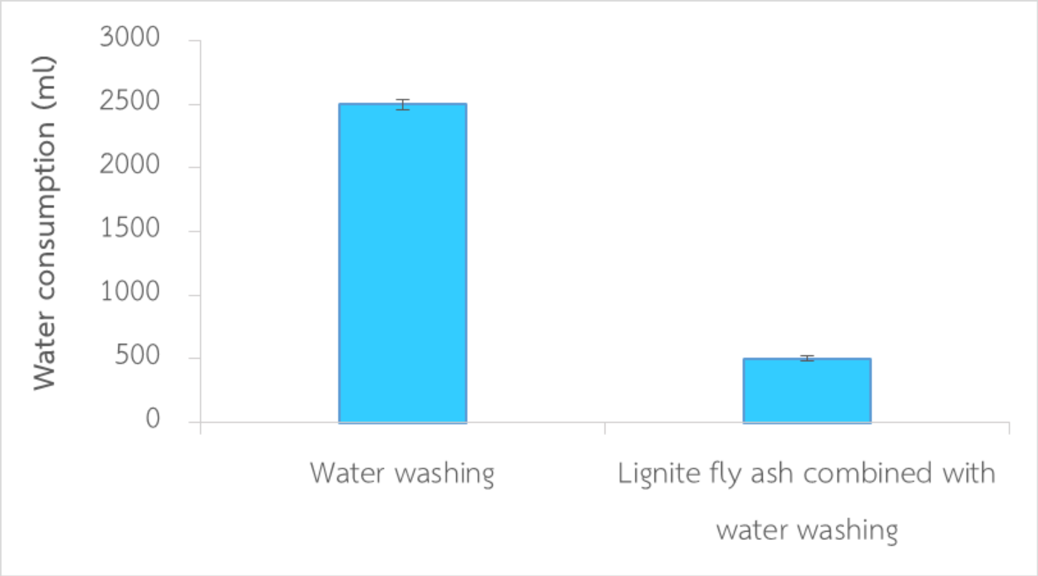


Figure 4.13 Water consumption for biodiesel purification by water washing and adsorption by lignite fly ash combined with water washing method.

4.5 Adsorption isotherms

The adsorption behavior of impurities on the lignite fly ash can be explained by an adsorption isotherm which is presented in **Figure 4.14**. It demonstrates the relationship between the amount of impurities covered on lignite fly ash and the remaining impurity concentration in biodiesel at equilibrium at a constant temperature.

In this experiment, the amount of lignite fly ash was fixed at 3%wt while the content of impurities in biodiesel was varied and the adsorption was performed under a chosen contact time (60 min) at room temperature.

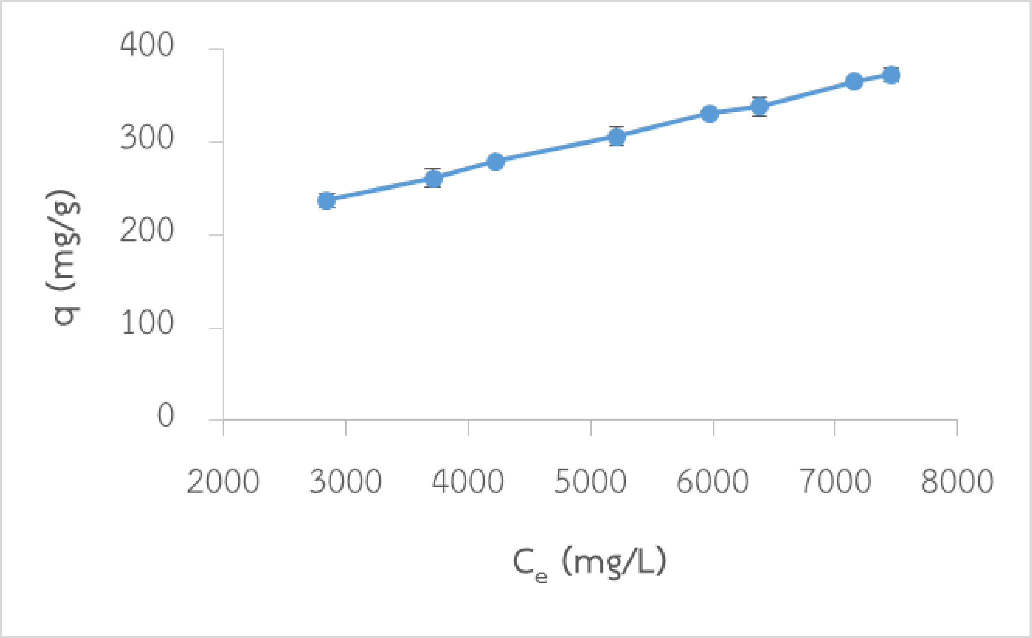


Figure 4.14 Adsorption isotherm of impurity adsorption by the lignite fly ash (time = 60 min and adsorbent dose = 0.9 g)

Langmuir isotherm is a model with assumption that a monolayer adsorption of adsorbates occurred on an adsorbent surface and adsorbate molecules do not interact with each other. The adsorption could occur via specific reaction between adsorbate molecules and active sites on adsorbent surface or chemisorption. The linear equation of Langmuir adsorption isotherm is shown in **Equation 4.2**. On the other hand, Freundlich isotherm was developed from Langmuir model with an assumption of multilayer adsorption. The interaction between adsorbate and adsorbent is weak or physisorption. The linear equation of Freundlich adsorption isotherm is shown in **Equation 4.3**.

$$\frac{C_e}{q} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad (4.2)$$

$$\log q = \log K_f + \frac{1}{n}\log C_e \quad (4.3)$$

Langmuir and Freundlich adsorption isotherm were plotted using experimental data as shown in **Figure 4.15** and **Figure 4.16**, respectively.

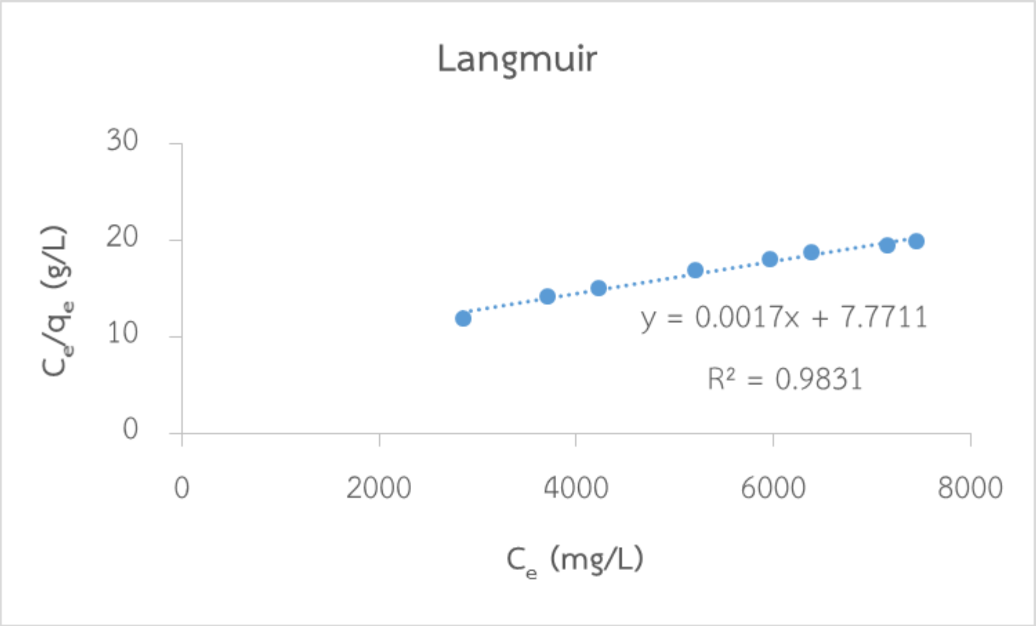


Figure 4.15 Langmuir plot of impurity adsorption by the lignite fly ash.

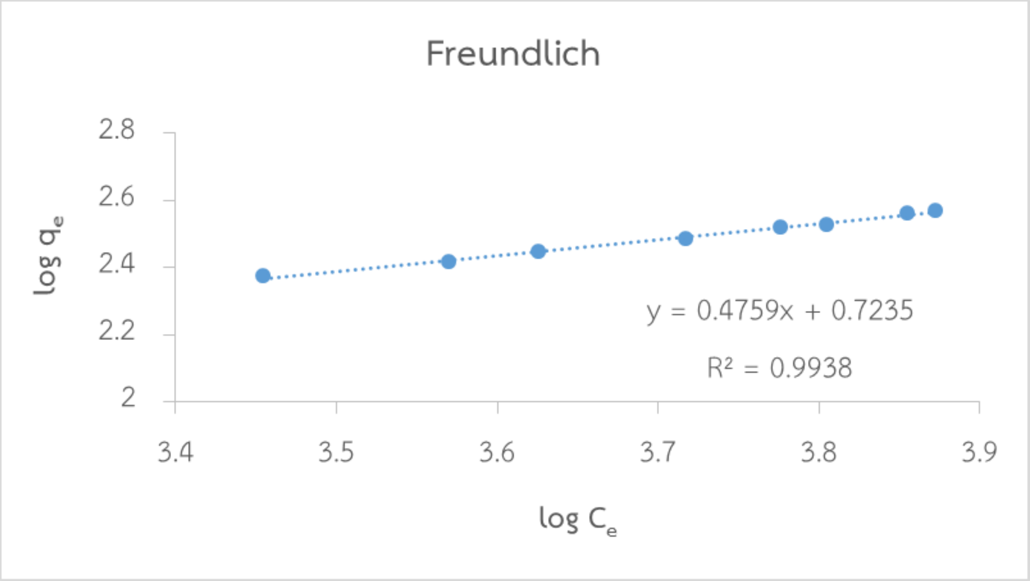


Figure 4.16 Freundlich plot of impurity adsorption by the lignite fly ash.

Considering the correlation coefficient (R^2) for linear regression in **Figure 4.15** and **Figure 4.16**, the linear relationship are observed in both Langmuir and Freundlich plots; however, Freundlich model seems to fit to adsorption data (R^2=0.9938) better than Langmuir model (R^2=0.9831). The Langmuir constants including the maximum adsorption capacity (q_m) and Langmuir constant related to the free energy of adsorption (b) are calculated and summarized in **Table 4.6**. The maximum adsorption capacity of impurities calculated from equation ($q_{m,cal}$) was 588.2 mg/g while the maximum adsorption capacity observed in the experiment ($q_{m,exp}$) was 373.2 mg/g. These results are not in agreement, indicating that the adsorption data did not fit well to Langmuir isotherm. Furthermore, Freundlich constant (K_f) and adsorption intensity (n) were calculated and presented in **Table 4.7**. For n=1, the partition between the two phases is independent of the concentration. If value of $\frac{1}{n}$ is below one, it indicates a normal adsorption while $\frac{1}{n}$ above one indicates a cooperative adsorption [58-60].

Table 4.6 Parameters of the Langmuir isotherm for adsorption of the impurities

Model	Equation	R^2	$q_{m(exp)}$ (mg/g)	$q_{m(cal)}$ (mg/g)	b (L/mg)
Langmuir	y = 0.0017x + 7.7711	0.9831	373.2	588.2	0.0002

Table 4.7 Parameters of the Freundlich isotherm for adsorption of the impurities

Model	Equation	R^2	K_f(mg/g)	n
Freundlich	y = 0.4759x + 0.7235	0.9938	5.29	2.10

Base on the assumption of Freundlich model, the adsorption of impurities in biodiesel on lignite fly ash occurred through weak and non-specific interaction. The adsorption could occur between the positive region of impurities (soap, methanol and glycerin) and the negative region of oxide surface of lignite fly ash. The intermolecular force between them was likely to be Van der Waals presumably in type of dipole-dipole interaction.

4.6 Adsorption kinetics of impurities

Two different adsorption kinetics models were applied to describe the experiment data i.e. pseudo-first order and pseudo-second order as presented in **Equation 4.4** and **Equation 4.5**, respectively. This parameter can be used to predict a time for purification of biodiesel in industrial plant.

$$\log\ (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{4.4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4.5}$$

Three weight percent of lignite fly ash was used to adsorb 8157.17 ppm of impurity in a crude biodiesel with different adsorption time (5-360 min) at room temperature. The amount of impurities adsorbed by the lignite fly ash as function of time is shown in **Figure 4.17**. The adsorption of impurities by the fly ash occurred relatively fast and reached adsorption equilibrium within 60 min of contact time. The experimental data was used to construct kinetics plot by following pseudo-first order and pseudo-second order kinetics model as shown in **Figure 4.18** and **Figure 4.19**, respectively.

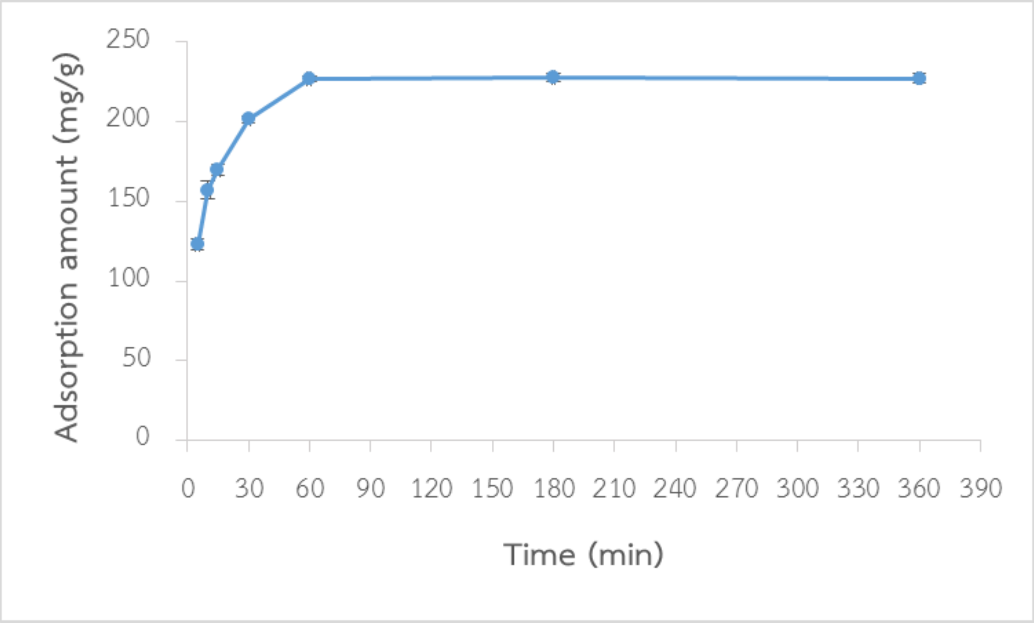


Figure 4.17 Effect of contact time on adsorption of impurities by the lignite fly ash.

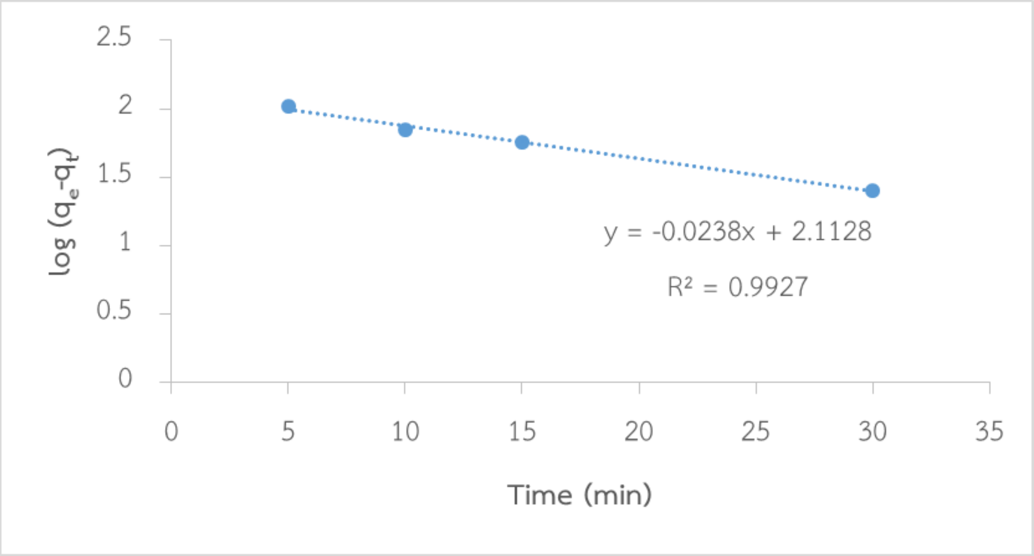


Figure 4.18 Pseudo-first order kinetics plot of impurity adsorption by the lignite fly ash.

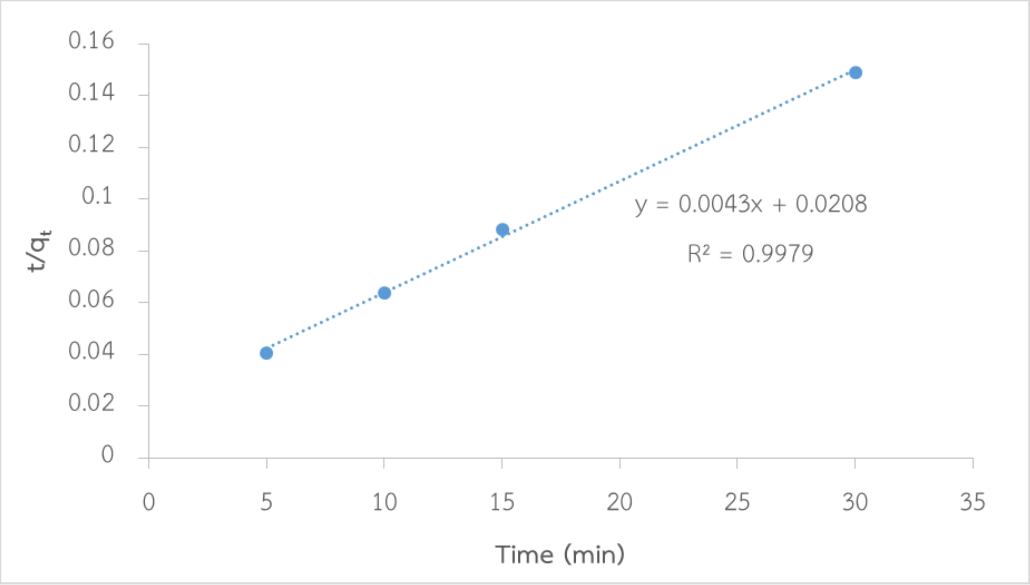


Figure 4.19 Pseudo-second order kinetics plot of impurity adsorption by the lignite fly ash

The value of correlation coefficient (R^2) from **Figure 4.18** and **Figure 4.19** indicated that the adsorption data fit well to both pseudo-first order (R^2=0.9927) and pseudo-second order (R^2=0.9979) model. However, when calculated the kinetics parameters from the linear equations obtained as summarized in **Table 4.8** and

Table 4.9, there is a large difference between the equilibrium adsorption capacity observed in the experiment ($q_{e,exp}$) and obtained by calculation ($q_{e,cal}$) using pseudo-first order model. It indicates a poor fit of the pseudo-first order to the experimental data. On the other hand, the value ($q_{e,cal}$) obtained by using the pseudo-second order equation agrees well with the experimental value.

Table 4.8 Pseudo-first order kinetics constant for adsorption of impurities by the lignite fly ash

Model	Equation	R^2	k_1 (min^{-1})	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)
Pseudo-first order	y = -0.0238x + 2.1128	0.9927	0.0548	226.74	129.66

Table 4.9 Pseudo-second order kinetics constant for adsorption of impurities by the lignite fly ash

Model	Equation	R^2	k_2 (min^{-1})	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)
Pseudo-second order	y = 0.0043x + 0.0208	0.9979	0.0009	226.74	232.56

4.7 Quality of biodiesel after purification

The quality of biodiesel treated by water washing and by the lignite fly ash combined with water washing was evaluated by determining the level of glycerin, mono-, di- and triglycerides by GC chromatography following the methodology of EN 14105. The results are summarized in **Table 4.10**. The content of glycerin, mono-, di- and triglycerides in biodiesel treated by the lignite fly ash combined with water washing are slightly higher than those observed in biodiesel treated by water washing. However, the quality of these treated biodiesels is acceptable in respect to the regulations of the ministry of energy.

Table 4.10 The quantitative results for glycerin, mono-, di- and triglycerides in treated biodiesel analyzed by GC chromatography

Substances	**Biodiesel treated by water washing**	**Biodiesel treated by Lignite fly ash combined with water washing**	**Specification (%wt)**
Monoglyceride	0.596	0.668	0.70
Diglyceride	0.121	0.126	0.20
Triglyceride	0.028	0.047	0.20
Free glycerin	0.016	0.017	0.02
Total glycerin	0.189	0.211	0.25

Finally, the other quality parameters including the acid value and the viscosity of biodiesel purified by the lignite fly ash combined with water washing were determined as shown in **Table 4.11**. The results indicate that the quality of biodiesel after treatment could be improved to meet the international biodiesel standard specifications.

Table 4.11 Comparison of treated biodiesel by lignite fly ash combined with water washing and international biodiesel standard specifications

Items	**Value**	**Specification**	**Standard**
Acid value	0.31 mg KOH/g	< 0.5 mg KOH/g	ASTM D664
Viscosity at 40 °C	3.96 cSt	3.5-5 cSt	ASTM D445

It should be mentioned that the quality of feedstock dictates the method of its production and the quality of the final biodiesel. Therefore, the content of free fatty acid should be determined. In this study, the refined crude palm oil as feedstock contained 1.92% free fatty acid. This value did not exceed 3% and therefore, the biodiesel can be synthesized via alkali transesterification using this refined crude palm oil.

CHAPTER V
CONCLUSION

5.1 Conclusion

A raw lignite fly ash as a waste from electricity plant (Maemoh, Lampang, Thailand) was demonstrated in this research that it can be used as an adsorbent in purification of biodiesel. The physical and chemical properties of the lignite fly ash was investigated by X-ray fluorescence spectroscopy (XRF), scanning electron microscopy (SEM) and surface area analysis (Brunauer-Emmett-Teller analyzer, BET). The results from these techniques showed that its properties are suitable to the adsorption of soap as a main impurity in crude biodiesel.

The adsorptive properties of the lignite fly ash can be changed depending on the particle size, the presence of methanol in crude biodiesel, the amount of adsorbent and the contact time. A crude biodiesel was synthesized via transesterification by using base catalyst process at 1:6 mole ratio of oil to methanol; then it was purified by using the lignite fly ash. The suitable conditions for adsorption of the impurities by the lignite fly ash were the use of lignite fly ash with the particle size in the range of 150-250 μm, 3%wt of adsorbent and 60 min of contact time. The results showed that more than 81% of impurities was eliminated from a crude biodiesel and the residual methanol could also be removed along with other impurities by the lignite fly ash. The equilibrium of impurities adsorption on lignite fly ash could be described by Freundlich model that the adsorption was likely to be a physical adsorption. The adsorption kinetics is found to follow a pseudo-second order kinetic model. The quality of the biodiesel purified by the lignite fly ash combined with water washing was evaluated according to EN 14105 test method. The results indicated that the content of impurities including all glycerin (total and free glycerin) and glyceride contents (mono-, di- and triglycerides) was lower than the upper limit of biodiesel quality standards. These results confirmed that the adsorption by the lignite fly ash combined with water washing has high efficiency in removing impurities in a crude biodiesel.

5.2 Suggestions

The lignite fly ash can be modified to have properties of an adsorbent for hydrophilic molecules adsorption. Using acid such as sulfuric acid may activate or increase surface area of the fly ash.

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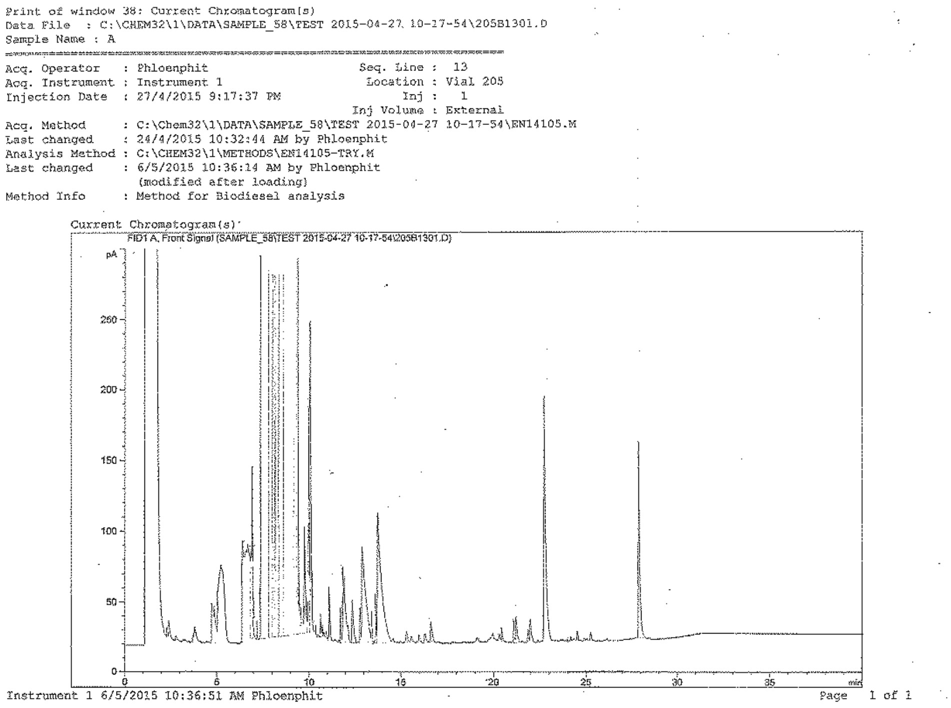
APPENDICES

APPENDIX A

GC CHROMATOGRAM OF BIODIESEL



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Acq. Instrument : Instrument 1                     Location : Vial 205
Injection Date  : 27/4/2015 9:17:37 PM                  Inj :   1
                                                Inj Volume : External
Acq. Method     : C:\Chem32\1\DATA\SAMPLE_58\TEST 2015-04-27 10-17-54\EN14105.M
Last changed    : 24/4/2015 10:32:44 AM by Phloenphit
Analysis Method : C:\CHEM32\1\METHODS\EN14105-TRY.M
Last changed    : 6/5/2015 10:36:14 AM by Phloenphit
                  (modified after loading)
Method Info     : Method for Biodiesel analysis

        Current Chromatogram(s)
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Instrument 1 6/5/2015 10:36:51 AM Phloenphit                              Page    1 of 1
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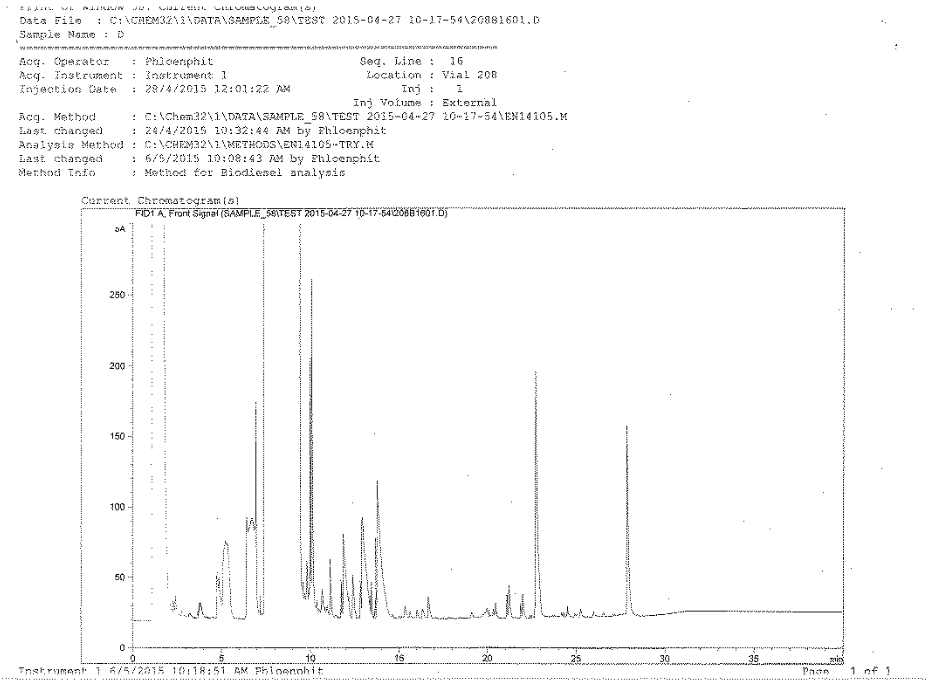
Figure A1 GC chromatogram of biodiesel treated with water washing



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Acq. Instrument : Instrument 1                     Location : Vial 208
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                                                Inj Volume : External
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Method Info     : Method for Biodiesel analysis

        Current Chromatogram(s)
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Figure A2 GC chromatogram of biodiesel that treated by lignite fly ash combined with water washing

APPENDIX B

^{1}H-NMR CHROMATOGRAM OF BIODIESEL

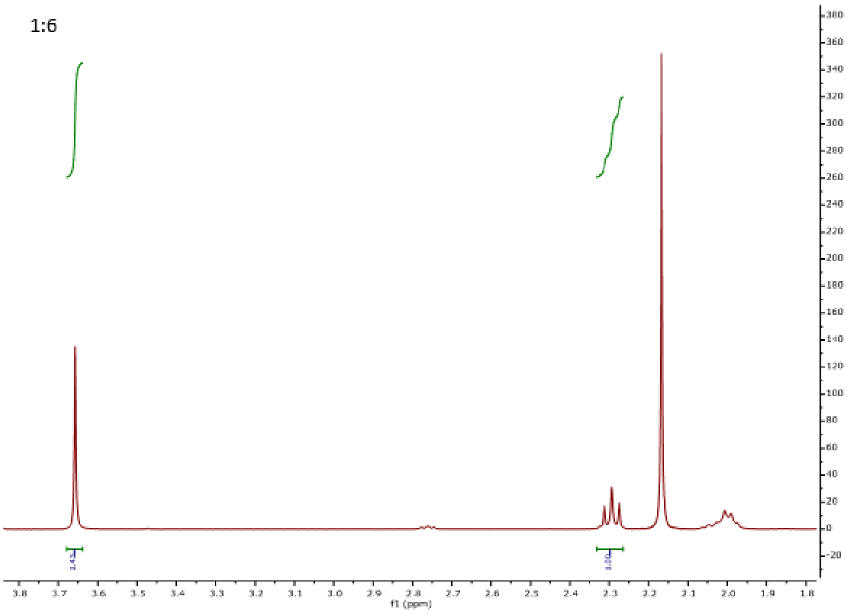

Figure B1 ^{1}H-NMR chromatogram of biodiesel in mole ratio of oil:methanol (1:6)

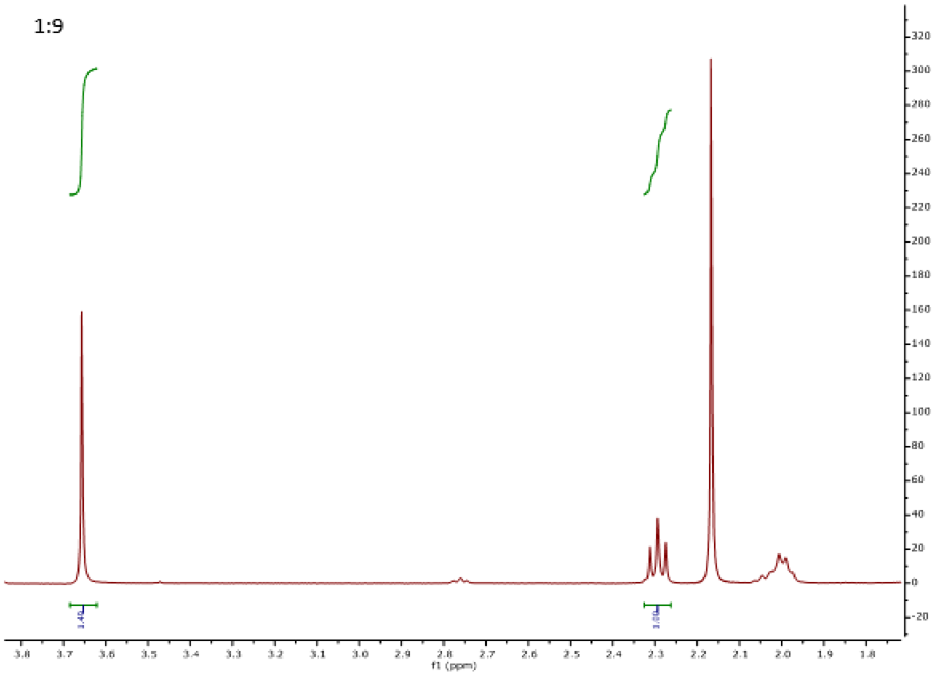

Figure B2 ^{1}H-NMR chromatogram of biodiesel in mole ratio of oil:methanol (1:9)

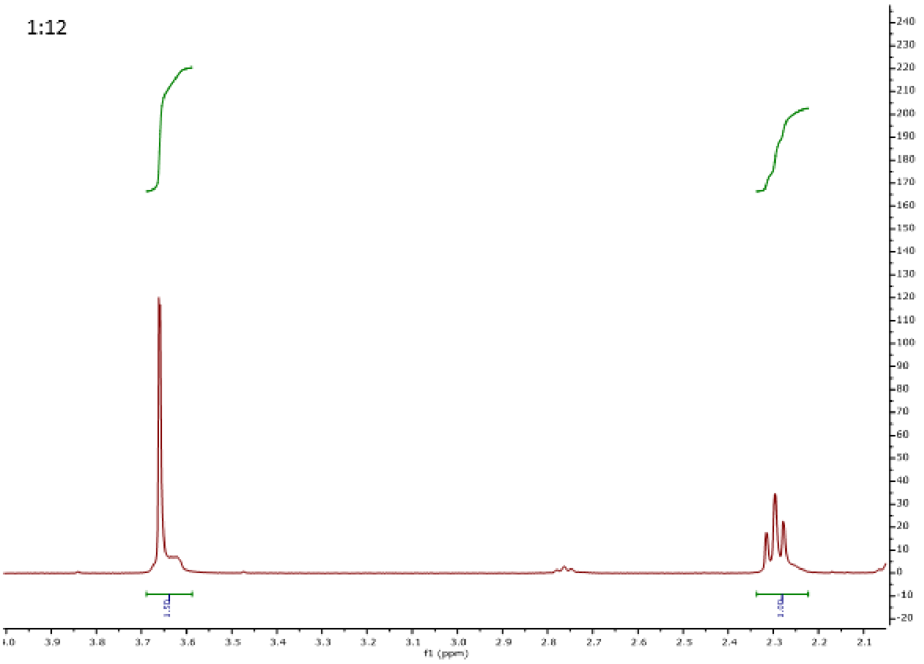

Figure B3 ^{1}H-NMR chromatogram of biodiesel in mole ratio of oil:methanol (1:12)

VITA

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