



THE STUDY ON THE PREPARATION OF DOLOMITE-IMPREGNATED ON DIATOMITE FOR
THE USE AS THE CATALYSTS IN BIODIESEL PRODUCTION



A Thesis Submitted in Partial Fulfillment of the Requirements

for Master of Engineering CHEMICAL ENGINEERING

Department of CHEMICAL ENGINEERING

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THE STUDY ON THE PREPARATION OF DOLOMITE-IMPREGNATED ON
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By
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MR. Wuttichai PLIANSUWAN : The Study on the Preparation of Dolomite-impregnated on Diatomite for the Use as the Catalysts in Biodiesel Production Thesis advisor : Sunthon Piticharoenphun, Ph.D.

This work studied the synthesis of dolomite-doped onto diatomite for the use as the catalyst in transesterification reaction for biodiesel production. Dolomite composed of CaMgCO_3 as the main compound. After dolomite was calcined at 800°C , CaO and MgO were obtained. Therefore, calcined dolomite which contained CaO can be used as the catalyst in transesterification reaction for biodiesel production. However, calcined dolomite cannot be reused several times due to leaching. Therefore, this work aimed to improve the properties of dolomite by doping dolomite onto diatomite. Diatomite which contained SiO_2 as the main compound provided high porosity and high surface area. Hence, diatomite was suitable to be used as the supporter.

The results showed that 40 %wt. dolomite-doped onto diatomite provided high %FAME of 92.38%. Then, Box-Behnken method used for the experimental design was used to find the suitable conditions for the reaction. It found that the suitable conditions for the reaction were as follows; methanol to oil molar ratio of 15.18:1, catalyst loading of 7.06%, reaction time of 3.33 hours (or 199 minutes). From the experiment, this condition offered the highest %FAME of 94.56% which differentiated to the predicted value only 1.35% (predicted value = 95.84%). In addition, it presented that reaction time strongly influence the reaction. For the study on the effect of co-solvent in the reaction, acetone was used. It showed that the use of 10 %wt. acetone as the co-solvent can improve the efficiency of the reaction. %FAME obtained from the use of 10 %wt. acetone reached to 97.12%. Acetone helped to enhance the solubility between methanol and palm oil, resulting to the increase of %FAME.



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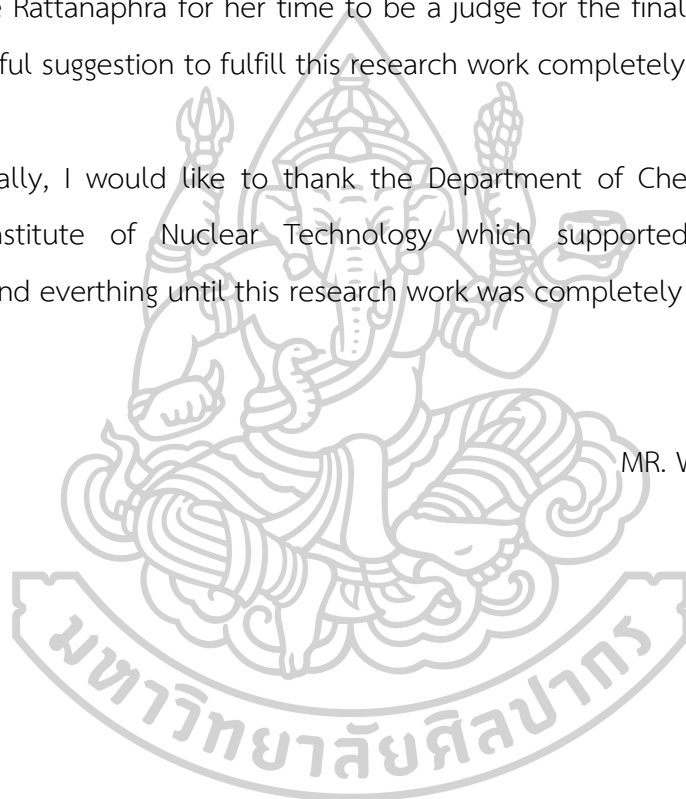
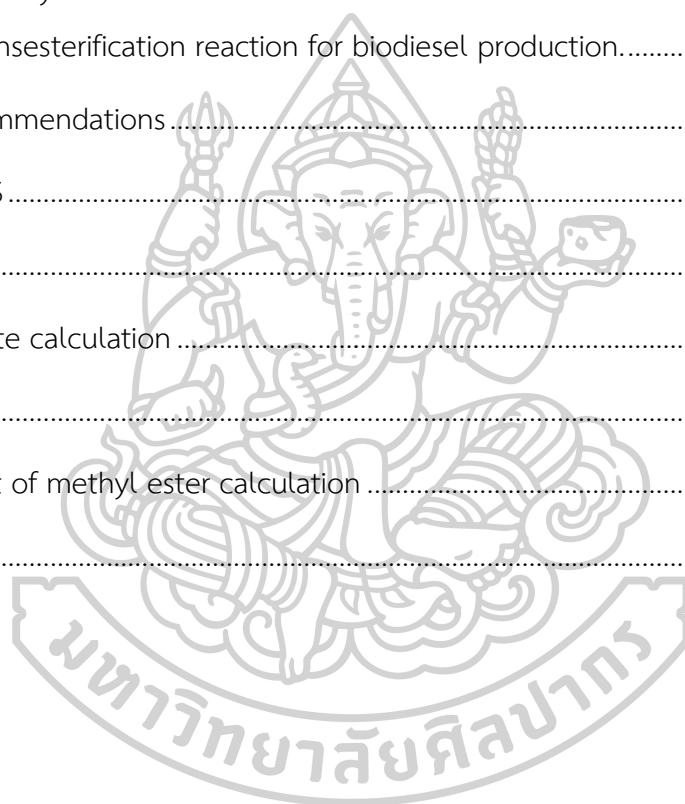


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Chapter 1 Introduction

This chapter mentioned about the background and the importance of this research about biodiesel production and transesterification reaction. The benefit of dolomite and diatomite used as the catalysts in transesterification for biodiesel production was also explained, including the use of co-solvent for the reduction of biodiesel cost production.

1.1 Biodiesel

From the current situation, several types of energy are very important for human life and economic development. Especially, the energy demand from many industrial sectors, including transportation, considerably increased every year. In the past, energy from fossil sources, such as crude oil, natural gas and coal, was still adequate for the demand. However, the energy from fossil sources which is unsustainable cannot provide adequate amount of energy in the future. In addition, the use of fossil energy creates some environmental problems. The combustion of fossil oil emits sulfur dioxide (SO_2), carbon monoxide (CO) and carbon dioxide (CO_2), including PM2.5 dust. As a result, the problems of global warming, environmental pollution, human health and catastrophe are not able to be avoided [1-3]. Therefore, the use of fossil energy significantly brings serious problems for human and environment at the present and in the future.

As mentioned above, it is very important to study about alternative energy sources for the use in the future. One type of alternative energy, which can effectively replace fossil energy, is biodiesel [4]. Biodiesel is the product from transesterification reaction, using vegetable oil, animal fat and waste cooking oil as the raw materials. These sources are abundant. In addition, waste oil can be reused. Thus, the use of biodiesel is sustainable. Moreover, biodiesel is environment friendly since it emits less amount of toxic gas, preventing global warming problem. Biodiesel also provides more heating values than fossil source [1, 5]. Therefore, the

governments in many countries support the use of biodiesel as alternative energy to reduce the use of fossil energy.

Transesterification reaction is normally used to produce biodiesel as the reaction is simple and it provides more efficiency for biodiesel production. Several sources of raw material, such as vegetable oil and animal fat, can be used to react with methanol in the presence of catalyst. In the industry, the homogeneous catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) are mostly used because they offers more activity in catalysis. However, this type of catalyst is mixed with the product. Therefore, the separation process is needed to purify the products. In addition, the use of homogeneous catalyst generates the large amount of wastewater from the biodiesel production process, leading to environmental problem and high production cost. This research aims to study the use of heterogeneous catalyst because the separation process of catalyst is easily performed because of different phases [6]. In addition, the heterogeneous catalyst showed high efficiency in transesterification reaction. Calcium oxide and zinc oxide are often used as the heterogeneous catalyst in transesterification. They can provide more 90% FAME.

1.2 Dolomite

Dolomite is a type of stone found in the nature, containing carbonate compound in the composition. Dolomite is generally found in Thailand. Its chemical formula is calcium magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$). Its composition composed of 30.4% CaO, 21.7% MgO. Normally, the ratio of CaCO_3 to MgCO_3 is 1:1 [7]. The crystal structure of dolomite is hexagonal. The crystal structure of this ore is normally found in rhombic shape. The surface of crystal is curved and sometimes it looks like saddle shape. Some crystal structure can be slightly observed as rough grains or condensed small grains which are stiff (glass-like). Some crystals are shining, similar to pearl spar. The normal color is white or cream. Dolomite provides several benefits for cement industry and agriculture. Furthermore, dolomite is cheap [8]. After the calcination at

high temperature, the compositions of dolomite were changed into oxide form which can be used as the catalyst in transesterification reaction for biodiesel production. The oxide compounds showed high basicity, low cost, less toxicity and environmental friendly property [7]. Therefore, dolomite is suitable for the use as the catalyst in biodiesel production.

1.3 Diatomite

Diatomite or diatomaceous earth is from the fossilized remains of diatom (a type of hard-shelled protist). Diatomite is light and porous (like chalk). It is also inert for reaction and low heat conductive. It can be used to polish metal vessel because diatomite contains fine-sized silica [9]. Therefore, diatomite is sedimentary rock which composes of silica. It is soft, found in the form of white fine dust in the nature. The particle sizes is sometimes less than 1 micron or more than 1 mm. The particle size of 10-200 micron is mostly found. Chemical compositions contain 80-90% silica, 2-4% alumina (mostly found in clay mineral) and 0.5-2% ferrous oxide. Diatomite is often used in the industry. It is used as the absorber as diatomite has high porosity. Therefore, some researcher used diatomite as the support due to its high porosity and surface area. Moreover, diatomite is stable for heat-resistance. Furthermore, diatomite is cheap and abundant in the nature [10]. This research used diatomite to be the support of dolomite for the use as the catalyst to improve biodiesel production and add more value to diatomite.

1.4 Co-solvent

Biodiesel production mostly uses transesterification reaction which needs to use the catalyst to reduce the reaction time and decrease the reaction temperature. Although, the catalysts were used, the large amount of energy was still consumed in the commercial scale production. Therefore, this research is interested in the use of co-solvent, in order to improve reaction conditions. Co-solvent is the solution which is used to dissolve the solutes for more homogeneous solution. In addition, it helps

to dissolve polar solution with non-polar solution. In the dissolution principle, the solution can be well dissolved with another solution when they both are polar or non-polar (like dissolve like). Therefore, co-solvent was expected to help the dissolution between oil (non-polar) and methanol (polar) in transesterification reaction. This research chose acetone as the co-solvent because acetone has relative polarity value between those of oil and methanol. Thus, acetone could be able to improve the dissolution of oil and methanol which affect to the efficiency of transesterification reaction for biodiesel production [11]. Normally, there are 3 phases which are oil, methanol and solid catalyst in the reaction. After the addition of co-solvent, the phases of oil and methanol is able to become one phase due to adequate dissolution, leading to 2 phases in the reaction. This can decrease the reaction time and reduce the reaction temperature [12]. As a result, the cost of biodiesel production can be decreased.

From mentioned above, this work aims to study the use dolomite which is doped onto diatomite (supporter) to be used as the catalyst for biodiesel production. The amount of catalysts, molar ratio of methanol to oil, reaction time and the use of co-solvent were investigated, in order to improve transesterification reaction, reduce the energy consumption and also increase the efficiency of biodiesel production in the future.

1.5 Objectives of research

1.5.1 To study the effect of catalyst preparation for transesterification reaction.

1.5.2 To study the suitable conditions for transesterification reaction, using dolomite-doped onto diatomite as the catalyst.

1.6 Scope of research

1.6.1 To use calcination temperatures of 800, 850 and 900 °C in catalyst preparation

1.6.2 To use 20, 30, 40 and 50 %wt. dolomite to be doped onto diatomite, using calcination temperature of 800 °C.

1.6.3 To use 3, 6 and 9 %wt. catalyst (dolomite-doped onto diatomite) in transesterification reaction.

1.6.4 To use methanol to oil molar ratios of 9:1, 15:1 and 21:1 in transesterification reaction.

1.6.5 To use reaction times of 120, 180 and 240 minutes

1.6.6 To reuse the catalyst (dolomite-doped onto diatomite)

1.6.7 To use acetone as the co-solvent at 0, 5, 10, 15, 20 %wt.

1.6.8 To use acetone as the co-solvent and use temperature reactions at 45, 55, 65 and 75 °C

1.7 Expected benefits and outcomes

1.7.1 To obtain the suitable calcination temperature in catalyst preparation for transesterification reaction

1.7.2 To obtain the suitable amount of dolomite which was doped onto diatomite for transesterification reaction

1.7.3 To obtain the suitable amount of catalyst (dolomite-doped onto diatomite) in transesterification reaction.

1.7.4 To know about the effect of co-solvent (acetone) and obtain the suitable amount of acetone in transesterification reaction



Chapter 2 Literature Review

2.1 The properties of dolomites

Ngamcharussrivichai C. et al. (2010) [7] studied about the biodiesel production using dolomites as the catalyst. Dolomites was obtained from Dolomite Company (Thailand) Limited, Suratthani, Thailand. The main component of dolomites was cuttlebones from squids. From X-ray fluorescence, CaO and MgO content were 40.65 and 31.20% , respectively, including Fe_2O_3 of 298 ppm and SrO of 198 ppm. As a result, dolomites have CaO and MgO as the main components. Therefore, dolomites are suitable and potential to be used as the catalyst in the biodiesel production.

2.2 The use of dolomites as the catalyst in biodiesel production

Ngamcharussrivichai C. et al. (2010) [7] studied about transesterification reaction for biodiesel production from crude oil for palm nuts and methanol as raw materials. Calcium oxide from natural sources, such as limestone calcite, cuttlebone, dolomite, hydroxyapatite and dicalcium phosphate, were used as the catalysts. The temperature of reaction of 60 °C with the pressure of 1 atm were used in the reaction. This work was interested in the use of dolomite as it contains the large amount of calcium carbonate and magnesium carbonate as the main components. After calcination of dolomite, CaO as the active sites can be obtained. It was found that the great amount of CaO was obtained from calcination temperature of 800 °C. In the reaction, 6% catalyst (by weight of oil), ratio of methanol to oil of 30 and 3 hours of reaction were used, obtaining 98% methyl ester. In addition, the catalyst can be reused effectively. The properties of biodiesel obtained from this work were in the standard values.

Ilgen Q. (2011) [13] studied about the use of dolomite as the catalyst in transesterification reaction using canola oil and methanol. The several factors, such as calcination temperature, the amount of catalyst, methanol/oil ratio and reaction

time were investigated. It was found that the suitable conditions were 850 °C of calcination temperature, 6 :1 of methanol-canola oil ratio and 3% catalyst. The 91.78% FAME was obtained after 3 hours of reaction.

Correia L.M. et al. (2015) [14] studied the use dolomite as the heterogeneous catalyst for biodiesel production. Dolomite provides high content of calcium carbonate and magnesium carbonate. After the calcination, CaO and MgO were obtained, which were active sites for the use to catalyse transesterification reaction. Canola and sunflower oil was used as raw materials, in order to react with methanol. It was found that canola oil offered more efficiency of biodiesel production than sunflower oil. The conversion of 98.81% from canola oil was obtained, while the conversion from sunflower oil was 96.52%.

Murguia-Ortiz D. et al. (2021) [15] investigated about the use of Na-CaO/MgO as the catalyst. This work used sodium nitrate which was doped on Mexican dolomite using calcination temperature of 900 °C, in order to obtain CaO/MgO and Na-CaO/MgO. After transesterification reaction using canola oil, methanol and these catalysts, the highest conversion of 95.4% was obtained.

Niu S. et al. (2020) [16] studied the reusability of dolomites for catalysis. It has been known that only few batches of reaction can be obtained from the use of dolomites as CaO in the dolomites were leached out from dolomites during the reaction. Therefore, cerium oxide was used as the support doped with CaO to prevent the leaching of CaO. There were 3 methods used for doping which were wet impregnation, direct wet impregnation and solid mixing. As a result, wet impregnation method provided the highest yield of biodiesel at 97.21%, using Ce:Ca molar ratio of 0.6, 0.05 %wt. catalyst, methanol to oil molar ratio of 15:1, reaction temperature of 65 °C and 2 hours of reaction time. In addition, the catalyst can be used for 5 times of reaction with the yield of 88.63%. The reusability of this catalyst can be achieved because the strength of the bonds between CaO and CeO₂ was strong, leading to less leaching of CaO.

Jindaporn W. et al. (2018) [17] used the dolomite as the catalyst for transesterification reaction of biodiesel production. The results showed that dolomites, which were calcined, provided CaO and MgO as the active site to catalyze transesterification reaction of triglyceride and methanol for biodiesel production. However, there were no reports to consider the effect of pure MgO, CaO, dolomite and mixed MgO-CaO, using the same portion of Mg and Ca as found in dolomite for biodiesel production. Therefore, this work carried out the experiments to find the effect of metal oxide from these catalysts mentioned above for transesterification reaction. As a result, MgO offered low activity while dolomites provided the highest activity for biodiesel production. The highest FAME yield using dolomite was 99%. It implied that dolomites showed good potential to be used as the catalyst for transesterification reaction of biodiesel production.

Shajaratun Nur Z.A. et al. (2014) [8] investigated the increase of efficiency of Malaysian natural dolomite used as the catalyst in transesterification reaction for biodiesel production. The results showed that the use of SnO₂ doped on dolomite can provide the conversion of 99.98% in transesterification reaction, using methanol to oil molar ratio of 15:1 and 4 hours of reaction time. This might be that the doping of SnO₂ on dolomite can increase the basicity of the dolomite. Therefore, it provided higher activity in catalysis than those of normal dolomites.

Zhao S. et al. (2019) [18] studied the use of La-dolomite as the catalyst in transesterification reaction for biodiesel production. The lanthanum to dolomite ratio of 1:1 was used under the calcination temperature of 800 °C. After that, the transesterification reaction was carried out using 7 %wt. catalysts, methanol to oil molar ratio of 18:1, reaction temperature of 65 °C and reaction time of 180 minutes. It showed that 98.7% yield was obtained and the catalysts can be reused for 5 times with more than 89.1% yield. Thus, La-dolomite provided good activity in transesterification reaction for biodiesel production.

2.3 The use of diatomite as the support of the catalyst for biodiesel production

Rabie A.M. et al (2019) [1] studied the use of diatomite supported CaO/MgO as the catalyst in transesterification reaction for biodiesel production. The waste cooking oil which was cheap was used as raw material, in order to increase its value. The diatomite was chosen to be used as the support because diatomite provided high surface area and large pores. These properties of diatomite were suitable for the use as the support of CaO/MgO to increase catalysis activity in transesterification reaction. It was found that 96.47% conversion can be achieved, using 6 %wt. catalyst, methanol to oil molar ratio of 15:1, reaction temperature of 90 °C and reaction time of 120 minutes.

Shan R. et al. (2017) [19] used the diatomite as the support of CaO to prepare the catalyst for biodiesel production. The results showed that 30% wt. diatomite used can provide the highest activity in transesterification reaction for biodiesel production. The 92.4% biodiesel yield can be obtained as the catalyst offered the highest basicity. In addition, the reusability of catalysts reached to 10 times because doped CaO onto diatomite built the strong bond of Ca-O-Si which prevented the leaching of CaO during the reaction.

Modiba E. et al. (2015) [20] used KOH doped onto diatomite as the catalyst in transesterification reaction for biodiesel production. The experimental design was performed using the method of Response Surface Methodology based on a Central Composite. This aimed to find the optimum condition of reaction. The results showed that the suitable conditions were 5 %wt. catalyst, methanol to oil molar ratio of 30:1, reaction temperature of 75 °C and reaction time of 4 hours. In addition, K_2O was observed in diatomite as the active sites to catalyze transesterification reaction for biodiesel production.

2.4 The use of co-solvent in transesterification reaction for biodiesel production

Laskar I.B. et al. (2020) [11] studied the use of CaO as the heterogeneous catalyst and the use of acetone as the co-solvent, in order to catalyze the transesterification reaction between soybean and methanol under reaction temperature at room temperature. The results demonstrated that 98% biodiesel yield was achieved using 20 %wt. co-solvent (compared to weight of oil), 3 %wt. catalyst, methanol to oil molar ratio of 6:1 and reaction time of 2 hours. The reusability of catalyst reached to 11 times. It implied that the use of co-solvent with heterogeneous catalyst provided similar activity which was compared to the use of homogeneous catalyst.

Chumaung N. et al. (2017) [21] studied the use of Tetrahydrofuran (THF) as the co-solvent with the use of calcium methoxide ($\text{Ca}(\text{OCH}_3)_2$) as the catalyst in the transesterification reaction for biodiesel production. The waste cooking oil was used as raw material. In addition, the experimental design was performed using the method of Response Surface Methodology (RSM), in order to fine the optimum conditions of reaction. The results showed that the highest conversion of 99.43% was obtained, using 2.83 %wt. catalyst, methanol to oil molar ratio of 11.6:1, reaction time of 100.14 minutes and 8.65 %v/v. THF/methanol. From the result, it implied that the use of co-solvent can reduced the amount of catalyst, methanol to oil molar ratio and reaction time. In addition, THF was environmental friendly compound which can be sustainably used for biodiesel production.

Singh V. et al. (2017) [12] used $\text{Ca}_2\text{Al}_2\text{O}_5$ as the catalyst, waste vegetable oil and methanol for biodiesel production. Acetone was also used as the co-solvent in the reaction. The results demonstrated that 97.98% conversion was obtained, using 1.2 %wt. catalyst, methanol to oil molar ratio of 6:1, reaction temperature of 55 °C, reaction time of 25 minutes and 20 %wt. acetone (co-solvent). Furthermore, the reusability of catalyst was more than 8 times with >75% conversion.

Chapter 3 Theory

This chapter explained the definition and importance of biodiesel and biodiesel production process in the present, including the details of dolomite and diatomite used as the catalyst for transesterification reaction. The preparation of catalysts, the use of co-solvent and its application, and experimental design using Box-Behnken were also mentioned.

3.1 Biodiesel

Thailand is a developing country which need the large amount of energy consumption to develop the country. One of important energy sources is fossil energy which is the main energy source of the world [22]. Therefore, the great deal of fossil energy has been imported, leading to trade deficit. Thus, it is important for Thailand to find alternative energy which is sustainable and this energy can be produced within the country for solving these problems.

Biodiesel is a clean energy which is often used in several countries as it is a renewable energy which can be simply produced [23]. In Thailand, the main raw materials for biodiesel production are palm oil which is abundant. Therefore, biodiesel is the important alternative energy to replace diesel from fossil source imported from other countries. In addition, the use of biodiesel in the Thailand can reduce trade deficit and can increase the value of agricultural raw material. As a result, biodiesel provides the safety of energy consumption and economics to be able to sustainably develop Thailand.

Biodiesel is produced from vegetable oil or animal fact using transesterification reaction. Triglycerides in the oil are transformed into methyl ester (biodiesel) which can be used in diesel engine directly or mixed with diesel from fossil source. Normally, more than 7 %v/v. mixture ratio is used. The mixtures of biodiesel and diesel were named following different ratios. For example, B20 was

named as it contains 20% biodiesel and 80% diesel. However, biodiesel and diesel have different structure, leading to different properties. The properties of biodiesel and diesel can be showed in Table 3.1.

Table 3.1 The properties of biodiesel and diesel

Properties	Biodiesel	Diesel
Content of sulfur from combustion, leading to acid rain	No sulfur, preventing acid rain	Contain sulfur, leading to acid rain
Exhaust which generates small dust particle and black smoke	Contain oxygen and aromatic compounds of 10-12%, generating little amount of dust and black smoke	Contain oxygen and aromatic compounds of 20-40%, generating high amount of dust and black smoke
Ignition of machine	High flash point, slow ignition	Low flash point, fast ignition
Storage duration	Short duration for storage, due to double bonds in vegetable oil which lead to oxidation reaction	Long duration for storage, due to single bonds in diesel
Corrosion of machine	Low corrosion	High corrosion

3.2 Transesterification reaction [24]

Transesterification reaction is the reaction between vegetable oil or animal fat and alcohol to transform oil structure from triglyceride into mono-alkyl ester compounds (biodiesel) and glycerol as by-product, as seen in Figure 3.1

From the reaction as seen in Figure 3.1, one mole of triglyceride completely reacts with three moles of alcohol. However, this reaction is reversible. Therefore, the excess alcohol is needed in the practical way to drive the equilibrium to the right side, obtaining high yield of product.

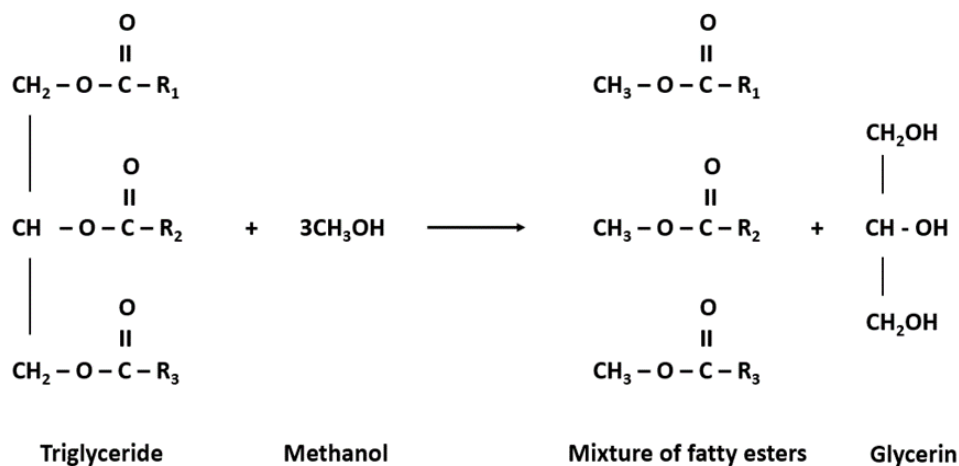


Figure 3.1 Transesterification reaction.

Alcohol used for biodiesel production has small size of molecules, such as methanol, ethanol, propanol and butanol. Methanol is mostly used as its small size of molecule can easily reacts with triglyceride, resulting to fast reaction and it is also cheap. Transesterification reaction can happen in atmosphere pressure and the temperature range from room temperature to boiling point of alcohol under the presence of catalysts. The catalysts used in the reaction can be acids, bases and enzymes. Normally, bases are mostly used as the catalyst for biodiesel production because the reaction rate is fast and less corrosion in the reactor is observed. Although the use of enzyme as the catalyst provides high purity of methyl ester, longer reaction time cannot be avoided, compared to the use of acids and bases.

3.3 The use of catalysts in transesterification reaction

3.3.1 The use of bases as the catalyst [25-27]

The use of bases as the catalyst in transesterification reaction, such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide (NaOCH₃), can catalyze the reaction faster than that of acids. NaOH is mostly used because it is cheap. In addition, glycerol which is by-product from reaction is desired by the

factory. The reaction mechanism from the use of base catalysts is carried out from the reaction between bases and alcohol, generating alkoxides (1st step). Then, alkoxides are used as nucleophile to react to carbonyl group of triglyceride, changing into tetrahedral intermediate (the slowest reaction, 2nd step). Tetrahedral intermediate will rearrange electron structure, obtaining the anions of alkyl ester and triglyceride (3rd step). The last step, triglyceride anions move protons from the catalyst, changing into diglyceride, monoglyceride and glycerol (4th step).

The limitation of the use of base catalyst is that the vegetable oil used as the catalyst have to contain free fatty acids less than 1% to prevent the formation of soap from saponification reaction between base catalysts and free fatty acids. In addition, soap has properties of emulsifier which interrupt the separation between methyl ester and glycerol. Then, the large amount of water is used to wash the product, resulting to low yield. Therefore, high content of free fatty acid in the raw material, such as waste cooking oil and animal fat, need the removal process to eliminate the free fatty acid before the reaction.

3.3.2 The use of acids as the catalyst [28, 29]

The use of acids as the catalyst can catalyze the reaction slower than that of base catalyst. The reaction temperature is also higher than 100 °C and the reaction time is longer than 3 hours for complete reaction. However, the use of acid catalyst, such as sulfuric (H_2SO_4), phosphoric (H_3PO_4) and hydrochloric (HCl), can be used although vegetable oil contains a lot of free fatty acids or water. For the 1st step for the mechanism of transesterification reaction using acid catalyst, carbonyl of ester is protonated, changing into carbocation. The 2nd step is that alcohol reacts with carbocation, getting tetrahedral intermediate. For the 3rd step, the rearrangement of structure happen, obtaining methyl ester and diglycerides.

3.3.3 The use of enzymes as the catalyst [30, 31]

The enzyme which is often used to catalyze transesterification reaction is lipase enzyme. There are several types of lipase from different microorganism species. Different types of lipases showed different activities. For example, extracellular lipase is not suitable to catalyze the reaction between triglycerides and methanol because methanol can denature the protein of enzyme. However, the use of alcohol which has the larger number of carbon provides higher yield of product. As mentioned before, the use of enzyme is limited in several ways. Therefore, the use of enzyme is rarely used.

3.4 The preparation of heterogeneous catalyst

There are several methods used for heterogeneous catalyst preparation. Only 3 methods are often applied which were impregnation, co-precipitation and kneading. These methods often use the support which were impregnated by the catalyst. After the preparation, it is necessary for the catalysts to be washed using water to remove contaminants. Then, the catalysts are baked to be dry at 80-300 °C. The last step, the catalysts are calcined with oxidation or reduction condition, in order to change the structure into oxide form which is suitable for reaction.

3.4.1 Impregnation [32]

Before the use of impregnation method, the support need to be considered as how many catalysts the support can adsorb. The adsorption can be carried out using the mixing between catalyst ions of catalyst such as metal ion (liquid phase) and the support (solid phase). After that, the mixture is stirred and then the mixture is kept for a specific duration to allow the adsorption of catalyst on the support. Next, the catalyst is calcined in the furnace.

3.4.2 Co-precipitation [33]

For the preparation of catalyst using co-precipitation, the solution, which contains dissolved catalyst and support, is added with an agent, in order to precipitate the dissolved catalyst and support. The catalyst-impregnated on supports are filtered, washed with water and then calcined.

3.4.3 Kneading [34]

For the kneading method, the catalyst in the solution is precipitated. The support in the form of powder or hydrogel is added to the precipitates of catalyst. In addition, the binders can be added such as water. The mixture is then mixed using ball mill for good mixing.

3.5 Dolomite [7]

Dolomite is a mineral, composing of carbonate compound. The main components of dolomite are calcium and magnesium. Its chemical formula is $\text{CaMg}(\text{CO}_3)_2$ or $\text{CaO} \cdot \text{MgO} \cdot (\text{CO}_2)_2$. The contents of calcium oxide and magnesium oxide in dolomite are varied from different sources located in several areas. There are some trace metals in dolomite, such as iron, manganese, cobalt, lead and zinc. The crystal of dolomite is rhombohedral. Its shape is similar to rock salt of sodium chloride. The powder of dolomite can be aggregated into a big lump.

3.5.1 The properties of dolomite

1. Chemical property

- Base : after dissolved in water, pH is about 9.0-10.71
- Can react with HCl, generating bubbles

2. Physical property

- Color of surface : white, yellow, pink, grey-brown
- Hexagonal or rhombohedral crystal structure with curved surface
- The strength in Mhos scale standard = 3.5-4
- Specific density of 2.82-2.95

3.6 Diatomite [19]

Diatomite is often known as diatomaceous earth or known as orange soil or light soil as its color is orange and its weight is light. Diatomite is a type of sedimentary rock with very light weight. It composes of fossilized remains of single-celled aquatic algae, called diatoms. After the large number of dead cell of diatoms have been aggregated, sedimentary rocks of diatomite are obtained. The sedimentary rocks are porous and similar to chalk. The rock is white or yellow-brown. The porosity of the rock is quite high at more than 70%. Diatomite is not dissolved in most types of chemicals. In addition, diatomite is badly heat conductive. The source of diatomite is often found at some lakes. The layers of diatomite were found to alternate with the layers of clay, covered with the layer of laterite at the top. In Thailand, the source of diatomite was found at Lampang province (Kohka, Maeta, Subprab and Muang districts). The application of diatomite is used as filter media in several industries such as city water, sugar, liquor, oil and solvent productions. In addition, diatomite can be used as a filler in some industries. For example, diatomite help to add more dense and smooth to the paper. Moreover, diatomite is used in plastic, synthetic rubber and painting industries. As diatomite provides badly heat conductivity, it is used as the composition of heat insulator. It is also used as the mixture or carrier in DDT and insecticide productions.

3.7 Co-Solvent [35]

Co-solvent is the chemical which can dissolve the solute in the form of solid, liquid or gas, becoming well-mixed solution. The solvent which is regularly known for

the use in daily life is water. For the definition of organic solvent, it is the organic compounds which contain carbon in the composition. Normally, the solvent has low boiling point but it is easily evaporated. Therefore, the separation of solvent can be carried out using normal distillation process. The solvent should not react with the solute. Thus, the solvent should be chemically inert. Normally, the solvent is clear (no color). Most solvent has their own specific odor. The concentration of solution is defined as the amount of solute which is dissolved in the specific volume of solvent. The solubility is the maximum amount of solute which can be dissolved in the specific volume of solvent at certain temperature and pressure. Several organic solvents which are often used have different relative polarity as seen in Table 3.2.

Table 3.2 The properties of organic solvents

Solvent	Formula	Boiling point (°C)	Relative polarity
acetone	C ₃ H ₆ O	56.2	0.355
acetonitrile	C ₂ H ₃ N	81.6	0.46
acetyl acetone	C ₅ H ₈ O ₂	140.4	0.571
2-aminoethanol	C ₂ H ₇ NO	170.9	0.651
aniline	C ₆ H ₇ N	184.4	0.42
anisole	C ₇ H ₈ O	153.7	0.198
benzene	C ₆ H ₆	80.1	0.111
benzonitrile	C ₇ H ₅ N	205	0.333
benzyl alcohol	C ₇ H ₈ O	205.4	0.608
1-butanol	C ₄ H ₁₀ O	117.6	0.586
2-butanol	C ₄ H ₁₀ O	99.5	0.506
i-butanol	C ₄ H ₁₀ O	107.9	0.552
2-butanone	C ₄ H ₈ O	79.6	0.327
t-butyl alcohol	C ₄ H ₁₀ O	82.2	0.389
carbon disulfide	CS ₂	46.3	0.065
carbon tetrachloride	CCl ₄	76.7	0.052
chlorobenzene	C ₆ H ₅ Cl	132	0.188

Solvent	Formula	Boiling point (°C)	Relative polarity
chloroform	CHCl ₃	61.2	0.259
cyclohexane	C ₆ H ₁₂	80.7	0.006
cyclohexanol	C ₆ H ₁₂ O	161.1	0.509
cyclohexanone	C ₆ H ₁₀ O	155.6	0.281
di-n-butylphthalate	C ₁₆ H ₂₂ O ₄	340	0.272
1,1-dichloroethane	C ₂ H ₄ Cl ₂	57.3	0.269
diethylene glycol	C ₄ H ₁₀ O ₃	245	0.713
diglyme	C ₆ H ₁₄ O ₃	162	0.244
dimethoxyethane (glyme)	C ₄ H ₁₀ O ₂	85	0.231
N,N-dimethylaniline	C ₈ H ₁₁ N	194.2	0.179
dimethylformamide (DMF)	C ₃ H ₇ NO	153	0.386
dimethylphthalate	C ₁₀ H ₁₀ O ₄	283.8	0.309
dimethylsulfoxide (DMSO)	C ₂ H ₆ OS	189	0.444
dioxane	C ₄ H ₈ O ₂	101.1	0.164
ethanol	C ₂ H ₆ O	78.5	0.654
ether	C ₄ H ₁₀ O	34.6	0.117
ethyl acetate	C ₄ H ₈ O ₂	77	0.228
ethyl acetoacetate	C ₆ H ₁₀ O ₃	180.4	0.577
ethyl benzoate	C ₉ H ₁₀ O ₂	213	0.228
ethylene glycol	C ₂ H ₆ O ₂	197	0.79
glycerin	C ₃ H ₈ O ₃	290	0.812
heptane	C ₇ H ₁₆	98	0.012
1-heptanol	C ₇ H ₁₆ O	176.4	0.549
hexane	C ₆ H ₁₄	69	0.009
1-hexanol	C ₆ H ₁₄ O	158	0.559
methanol	CH ₄ O	64.6	0.762
methyl acetate	C ₃ H ₆ O ₂	56.9	0.253
methyl t-butyl ether (MTBE)	C ₅ H ₁₂ O	55.2	0.124
methylene chloride	CH ₂ Cl ₂	39.8	0.309

Solvent	Formula	Boiling point (°C)	Relative polarity
pentane	C ₅ H ₁₂	36.1	0.009
1-pentanol	C ₅ H ₁₂ O	138	0.568
2-pentanol	C ₅ H ₁₂ O	119	0.488
3-pentanol	C ₅ H ₁₂ O	115.3	0.463
2-pentanone	C ₅ H ₁₀ O	102.3	0.321
3-pentanone	C ₅ H ₁₂ O	101.7	0.265
1-propanol	C ₃ H ₈ O	97	0.617
2-propanol	C ₃ H ₈ O	82.4	0.546
pyridine	C ₅ H ₅ N	115.5	0.302
tetrahydrofuran(THF)	C ₄ H ₈ O	66	0.207
toluene	C ₇ H ₈	110.6	0.099

3.8 Box-Behnken design [36]

The experimental design is a tool to design the experiments to assure the results. The statistical principle is used to find the relation of different parameters, using mathematic equation. This helps to reduce the number of batches of the experiments but cover to study the effect of all parameters. Minitab 17 program is used for the experimental design, using 'Response Surface Design' method. It applied both mathematic and statistical techniques to create the model and analyze the response. The response depends on several parameters and aims to find the optimum of response, as seen in Equation 3.1.

$$y = f(x_1, x_2) + \epsilon \quad \text{Equation (3.1)}$$

The parameters are shown as 'x' and ϵ is the error value of response 'y' which is from the experiment. If $E(y) = f(x_1, x_2) = \eta$, therefore; surface equation can be shown as seen in Equation 2.

$$\eta = f(x_1, x_2) \quad \text{Equation (3.2)}$$

This is called 'Response Surface'. The response surface is often presented using graphic feature. The η is plotted with the level of x_1 and x_2 , in order to more easily observe the shape of response surface. It can be plotted using 'Contour plot' of response surface. As the relation between response and free parameters in most problem is not known, the suitable estimator for expressing the actual relation between y and the set of free parameters have to be considered in the first step. This might be the linear relation between the model of response and free parameter. The function which is used as the model with first order can be expressed in Equation 3.3.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_k x_k + \epsilon \quad \text{Equation (3.3)}$$

Box-Behnken Design composed of 3 level design for fitting response surface. This design is created from the recombination between factorial design ($2k$). The result of design is effective for the number of desired experimental batches. In addition, this design is able to rotate or semi-rotate. The Box-Behnken design for $k=3$ can be seen in Figure 3.2.

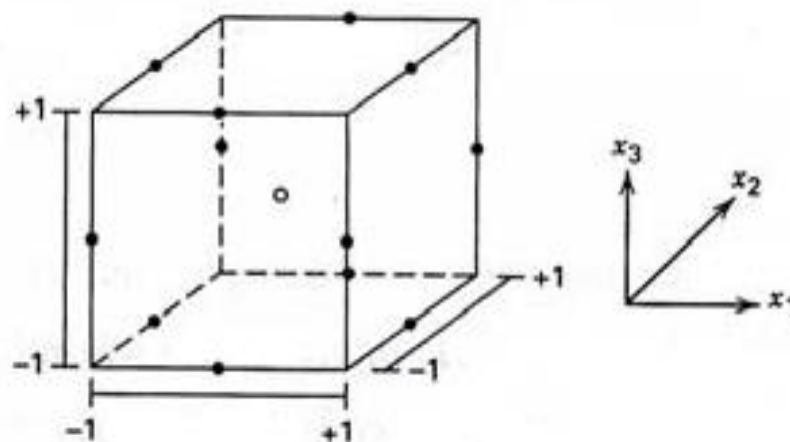
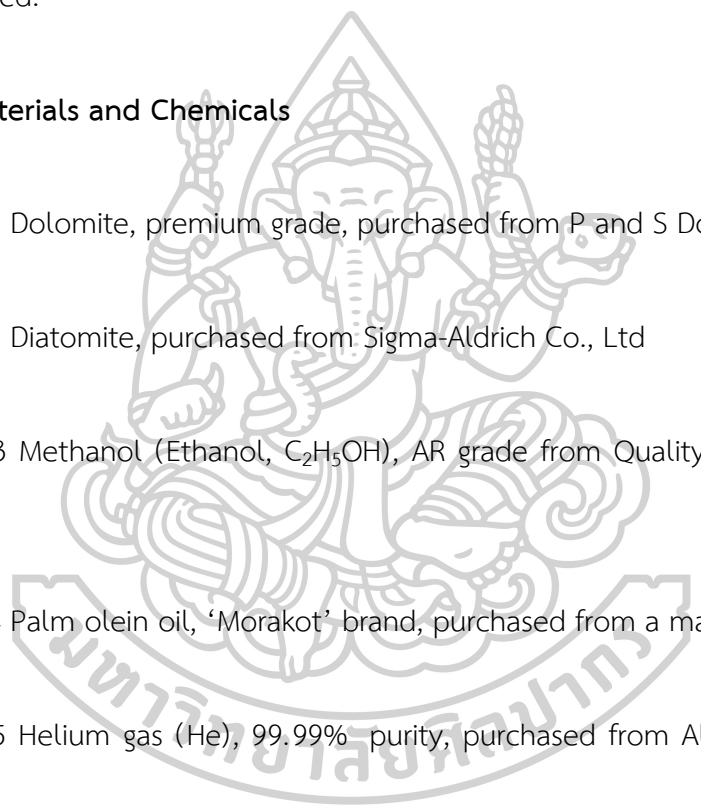


Figure 3.2 Box-Behnken design, for $k = 3$

Chapter 4 Methodology

This chapter mentioned about the experimental design, including experiment procedures to study the effect of calcination temperature and %dolomite doped onto diatomite, %wt. catalyst, methanol to oil molar ratio and reaction time on the transesterification reaction. In addition, the experiment procedure to investigate the effect of co-solvent and reusability of catalysts on transesterification reaction were also explained.

4.1 Raw Materials and Chemicals

- 
- 4.1.1 Dolomite, premium grade, purchased from P and S Dolomite Co., Ltd.
- 4.1.2 Diatomite, purchased from Sigma-Aldrich Co., Ltd
- 4.1.3 Methanol (Ethanol, C_2H_5OH), AR grade from Quality Reagent Chemical Co., Ltd.
- 4.1.4 Palm olein oil, 'Morakot' brand, purchased from a market.
- 4.1.5 Helium gas (He), 99.99% purity, purchased from Alternative Chemical Co., Ltd.
- 4.1.6 Carbon dioxide gas (CO_2), 99.8% purity, purchased from Linde Co., Ltd.
- 4.1.7 Nitrogen gas (N_2), purchased from Alternative Chemical Co., Ltd.
- 4.1.8 Methyl heptadecanoate, analytical grade, purchased from Sigma-Aldrich Thailand Co., Ltd.

4.1.9 Heptane, 99.9% purity, purchased from Quality Reagent Chemical Co., Ltd.

4.1.10 Acetone, AR Grade, purchased from Quality Reagent Chemical Co., Ltd.

4.2 Equipments

4.2.1 Beakers (100, 250, 600 and 1,000 mL)

4.2.2 Measure cylinder (100 mL)

4.2.3 Magnetic bar (2.5-4 cm in length)

4.2.4 Grinding mortar (10 cm in diameter)

4.2.5 Centrifuge vials (2 and 8 mL)

4.2.6 Three-neck flasks (500 mL)

4.2.7 Quartz wool

4.2.8 Syringe (10 μ L)

4.2.9 Ceramic boats

4.3 Experimental apparatuses and analytical Instruments

4.3.1 Hotplate and magnetic stirrer (CMAGHS7 model, IKA Company)

4.3.2 Incubator (FED 240 model)

4.3.3 Centrifuge (XC 80-2 model, Science city Co., Ltd.)

4.3.4 Laboratory chamber furnace (model)

4.3.5 BET (Brunauer-Emmett-Teller) (model)

4.3.6 XRD (X-ray diffraction)

4.3.7 SEM (Scanning electron microscope) (MIRA3 model, TESCAN Company)

4.3.8 TPD (Temperature program desorption) (Autpchem 2910 model, Micromeritics)

4.3.9 Gas Chromatography (GC) (HP model)

4.4 Catalyst preparation

4.4.1 The preparation of dolomite-doped onto diatomite

10 g diatomite was washed using DI water of 50 mL under the stirring at 400 rpm for 10 minutes. Then, the diatomite was filtered using filter paper and dried at 60 °C for 12 hours. For dolomite, dolomite was dried at 60 °C for 12 hours and then calcined at 800 °C for 3 hours. After calcination, 2 g dolomite was mixed in 100 mL DI water with stirring at 700 rpm for 10 minutes. Then, 8 g diatomite was added into the dolomite solution with stirring at 800 rpm for 5 hours. Next, the catalysts were calcined at 800 °C for 3 hours. The 20% dolomite-doped onto diatomite were obtained.

From the scope of the experiment, calcination temperatures of 800 and 900 °C were studied. The % dolomite-doped onto diatomite of 20, 30, 40 and 50% was also investigated by the addition of 2, 3, 4 and 5 g in DI water, respectively.

4.4.2 The study of the effect of calcination temperatures of dolomites

The dolomite which was calcined at 800 °C from 4.4.1 was used as the catalyst for transesterification reaction for biodiesel production in three-neck flask connected with the condenser. The catalyst of 3.6 g and palm oil of 68 mL were added in three-neck flask using stirring rate at 750 rpm. The reaction temperature was controlled at 65 °C, using heat plate. After the mixture temperature reached 65 °C, the methanol of 43 mL was added into the mixture. After 3 hours of reaction time, the mixture was separated, using the centrifuge at rotation speed of 4,000 rpm for 30 minutes. The mixture was separated into 3 layers. The top layer contained glycerin and methanol. The middle layer contained biodiesel and the bottom layer was catalyst. The biodiesel was then dried in the oven at 110 °C for 15 hours before %FAME measurement using GC measurement.

The effect of calcination temperature of dolomite was investigated. The calcination temperatures used were 800, 850 and 900 °C. From GC measurement, %FAME after transesterification reaction using dolomite calcined at 800, 850 and 900 °C were compared.

4.4.3 The study of the effect of %wt dolomite-doped onto diatomite

Dolomite (calcined at 800 °C) and 20% dolomite-doped onto diatomite (from 4.4.1) were used as the catalyst in transesterification reaction for biodiesel production, using three-neck flask connected to the condenser. The catalyst of 3.6 g was added into 68 mL palm oil in three-neck flask with the stirring rate of 750 rpm. The reaction temperature was controlled at 65 °C, using hot plate. After the mixture temperature reached 65 °C, methanol of 43 mL was added into the mixture. After 3 hours of reaction time, the mixture was separated, using the centrifuge at rotation speed of 4,000 rpm for 30 minutes. The mixture was separated into 3 layers. The top layer contained glycerol and methanol. The middle layer contained biodiesel and

the bottom layer was catalyst. The biodiesel was then dried in the oven at 110 °C for 15 hours before %FAME measurement using GC measurement.

The effect of %wt dolomite-doped onto diatomite was investigated. Dolomite (calcined at 800 °C) and 30, 40 and 50% dolomite-doped onto diatomite, were used as the catalyst in transesterification reaction for biodiesel production. From GC measurement, % FAME after transesterification reaction using these catalysts were compared.

4. 4. 4 The effect of reaction conditions used in transesterification reaction, using Box-Behnken design

From 4.4.3, the optimum type of catalyst was chosen to use as the catalyst in transesterification reaction. The several parameters for reaction were investigated which were methanol to oil molar ratios (9-21 molar ratio), %loadings of catalyst (3-9 %wt.) and reaction times (120-240 minutes). The number of batches can be designed using Box-Behnken method, as seen in Table 4.1.

Table 4.1 The number of batch for transesterification, using Box-Behnken design

Batch	Methanol to oil molar ratio (xx:1)	%Amount of catalyst (g)	Time of reaction (minutes)
1	15	9	240
2	15	3	240
3	9	6	120
4	15	6	180
5	9	9	180
6	15	9	120
7	15	3	120
8	15	6	180
9	21	9	180
10	21	6	240
11	21	3	180

Batch	Methanol to oil molar ratio (xx:1)	%Amount of catalyst (g)	Time of reaction (minutes)
12	21	6	120
13	9	6	240
14	15	6	180
15	9	3	180

4.4.5 The effect of acetone used as the co-solvent in transesterification reaction

Dolomite-doped onto diatomite at the optimum amount of %wt dolomite (from 4.4.3) was chosen to be used as the catalyst for transesterification reaction, using the same procedure in 4.4.3 and reaction conditions in 4.4.4. However, the reaction temperature was controlled at 55 °C. The amounts of acetone were varied at 5, 10, 15 and 20 %wt., compared to the amount of palm oil. %FAME was measured using GC measurement.

4.4.6 The study of the reusability of the catalyst

Dolomite-doped onto diatomite at the optimum amount of %wt dolomite (from 4.4.3) was chosen to be used as the catalyst for transesterification reaction, using the same procedure from 4.4.3, reaction conditions from 4.4.4, the optimum amount of acetone from 4.4.5. The catalyst was used to study the reusability of the catalyst. After the reaction, the catalyst was separated and washed with methanol. The catalyst was then dried at 110 °C for 12 hours. Next, the catalyst was used again and again in transesterification reaction. The repeated use of the catalyst was stopped when %FAME was stable.

4.5 Catalyst characterization

4.5.1 Brunauer-Emmett-Teller (BET) measurement

BET technique is used to analyze surface area, volume and pore size of the catalyst. These values were obtained using N_2 physisorption. First of all, the catalysts were pretreated using 50 mL/min of helium gas at 180 °C for 3 hours then the sample cell was equipped in BET equipment. Liquid nitrogen was added into lifting part. The samples were cooled to -196 °C. The nitrogen was fed into sample cell then the volume of N_2 and pressure were measured. Nitrogen was adsorbed onto the catalyst surface. When the catalyst could not adsorb more nitrogen, the desorption happened and BET characterization was finished. The BET instrument can be seen in Figure 4.1.

The preparation of BET characterization is as follow;

1. The catalyst was baked in an oven at 110 °C for 24 hours.
2. 0.1 g catalyst was collected to use for BET characterization.
3. Catalysts were pretreated at 180 °C for 3 hours.
4. Surface area, pore volume, and pore size of catalyst were analyzed using BET program.



Figure 4.1 BET (Brunauer-Emmett-Teller) instrument (BELSORP-mini II Microtrac model, BEL Company)

4.6.2 X-ray diffraction (XRD) measurement

The XRD technique was used to obtain the structure, alignment of atom and crystalline size of the catalyst using the pattern of diffraction and scattering of X-ray. The uniqueness of diffraction can define the composition of the catalyst. The diffraction of X-ray in crystal relies on Bragg's law. In this work, XRD is used to define the presence of calcium oxide and the composition of dolomite.

4.6.3 Scanning electron microscopy (SEM)

Scanning electron microscopy is an instrument for studying the morphology of materials. In addition, EDS technique (Energy Dispersive Spectrometry) coupled with SEM can be used to analyze the composition of materials. The image from SEM measurement shows 2-dimension feature with more than 200,000 times magnification. The electron gun in SEM produces the electron moving with high velocity through condenser lens and transforming into electron beam. The material surface was shined by electron beam and then the secondary electron from the

material surface come out of the surface. The secondary electrons are detected by a detector. This signal is transformed into visual image of the surface. The SEM instrument can be shown in Figure 4.2.

The preparation for SEM characterization is as follow;

1. The samples were attached onto an adhesive sheet and then the sheet was attached onto steel stick.
2. The sample which is non- metal metal needed to be coated with gold layer to clarify the surface and prevent sparking from the electron deposition. The coating process takes about 40 minutes.
3. Steel stick is attached into the sample holder in the SEM instrument for the measurement.



Figure 4.2 SEM (Scanning electron diffraction) instrument (MIRA3 model, TESCAN Company)

4.6.4 Temperature programmed desorption (TPD) measurement

Temperature programmed desorption technique is used to obtain the desorption pattern between absorbent (gas) and absorbate (catalyst) used in the measurement. If acid site of catalyst is measured, the absorbent will be basic gas such as ammonia. This is called NH_3 -TPD. In contrast, the acidic gas such as carbon dioxide is used to determine basic site, known as CO_2 -TPD. The area under the graph plotted between intensity and temperature indicates the amount of active site. The temperature at desorption peak showed the intensity of acid or base site of the catalyst. The TPD instrument can be seen in Figure 4.3.

The preparation for CO_2 -TPD characterization is as follow;

1. 0.1 g catalyst was added into quartz wool. Then quartz wool was placed into U-tube.
2. U-tube was then equipped into TPD instrument.
3. The catalysts in U-tube were heated to 150 °C and held for 1 hour to remove the water in catalysts. Then the catalysts were cooled down to 50 °C.
4. CO_2 was fed into U-tube for adsorption, then the desorption was started by increasing the temperature to 800 °C and held for 1 hour.
5. After the analysis, the graph was used for basic site calculation.



Figure 4.3 TPD (Temperature Programmed Desorption) instrument (Autpchem 2910 model, Micromeritics)

4.6.5 Gas chromatography-Flame ionization detector (GC-FID) measurement

GC technique is used to separate the composition of the mixture using the different movement of each composition on the stationary phase under the convection of mobile phase. For flame ionization detector, the sample was ionized using the flame and then the carrier gas took the ionized sample to the detector. GC-FID instrument is presented in Figure 4.4.

The preparation of sample for GC analysis is as follow;

1. 10 mg/mL methyl heptadecanoate was prepared using 1 g of methyl heptadecanoate dissolved in heptane until the final solution is 100 mL.
2. 0.05 g biodiesel from the reaction was added into a vial.
3. 1 mL of heptadecanoate (1 mg/mL) was added into the biodiesel. The vial was shaken until the mixture was well mixed.

4. The prepared sample was taken into GC-FID. The instrument uses He gas as the carrier. The temperatures of the injector, oven and detector were set at 200, 180 and 230 °C, respectively.
5. The temperature of oven was increased to 220 °C.
6. After analysis, the graph can show the position and area of compositions. This can be used to calculate the amount of composition.



Figure 4.4 GC-FID (Gas Chromatography-Flame ionization) instrument (HP 5890 series II model)

4.6.6 X-ray fluorescence (XRF) measurement

XRF is analytical method to find the composition of materials. After an element in the sample was radiated with X-ray light, the element will emit fluorescence X-ray radiation with discrete energies which are characteristic in each element . The XRF instrument is presented in Figure 4.5

The sample preparation is described below.

1. The catalyst is in the form of powder. Thus, the film was used to support the catalyst powder.

2. The film was stretched covering the one end of the holder. Then, the powder was added into the holder on the film.
3. The powder was equally levelled before another one end of the holder was closed by a lid.
4. The prepared holder was placed in the XRF instrument for the measurement.



Figure 4.5 XRF (X-ray fluorescence) model S8 TIGER, Bruker

Chapter 5 Result and Discussion

5.1 X-Ray Diffraction (XRD) pattern of dolomite, diatomite and dolomite-doped onto diatomite

From XRD results, Fig 5.1 showed X-ray diffraction patterns of dolomite which were calcined at 800, 850 and 900 °C (defined as DM800, DM850 and DM900, respectively), compared to the dolomite which was not calcined (defined as DM No Cal). Uncalcined dolomite presented the peaks of CaCO_3 at $2\theta = 31.2^\circ$ and 51.5° and showed the peak of MgCO_3 at $2\theta = 42.5^\circ$ as seen in Fig 5.1(a). Compared to the dolomites calcined at 800, 850 and 900 °C, calcium and magnesium compounds in dolomite were transformed into CaO and MgO [7, 34]. As seen in Fig 5.1(b), (c) and (d), the peaks of CaO were observed at $2\theta = 32.4^\circ$, 37.5° , 54.0° and 64.4° (JCPD file: 01-082-1691) and the peaks of MgO were noticed at $2\theta = 43.1^\circ$ and 62.4° (JCPD file: 00-065-0476), corresponding to the work from Ngamcharussrivichai et. al. [7, 34] It is well known that CaO is suitable for the use as the catalyst in transesterification reaction because it contains high basic sites used for the catalysis. Therefore, CaO is often chosen as the catalyst in biodiesel production [37].

Fig 5.2(a) showed XRD pattern of diatomite which was not calcined (defined as DI No Cal) while Fig 5.2(b)-(e) presented XRD patterns of dolomite calcined at 800 °C and was then doped onto diatomites using 20, 30, 40 and 50 %wt. dolomite, defined as 20DSD800, 30DSD800, 40DSD800 and 50DSD800, respectively. As seen in Fig 5.2(a), the peaks at $2\theta = 22.0^\circ$, 26.6° , 36.6° and 39.4° were assigned to SiO_2 (JCPD file: 46-1045) which were similar to Fig 5.2(b)-(e). It showed that diatomite contained SiO_2 as the main component [19]. At 40 and 50 %wt. dolomite-doped onto diatomite, the XRD patterns clearly presented the peaks of CaO and MgO. However, the height of the peaks of CaO and MgO from 40 %wt. dolomite-doped onto diatomite were higher than that of 50 %wt. dolomite-doped onto diatomite, due to higher contents of CaO and MgO [8].

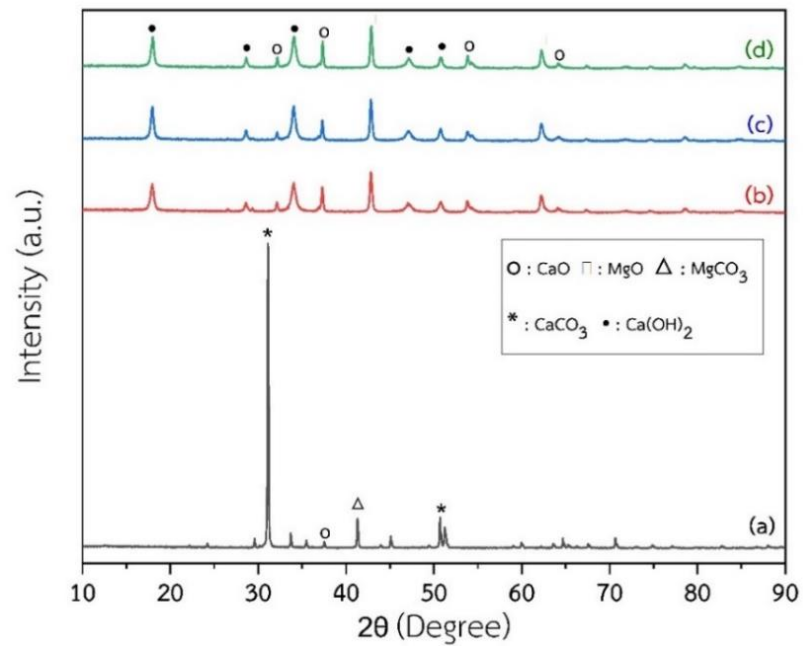


Fig 5.1 XRD pattern (a) dolomite which was not calcined (DM No Cal), (b) dolomite calcined at 800 °C (DM800), (c) dolomite calcined at 850 °C (DM850) and (d) dolomite calcined at 900 °C (DM900)

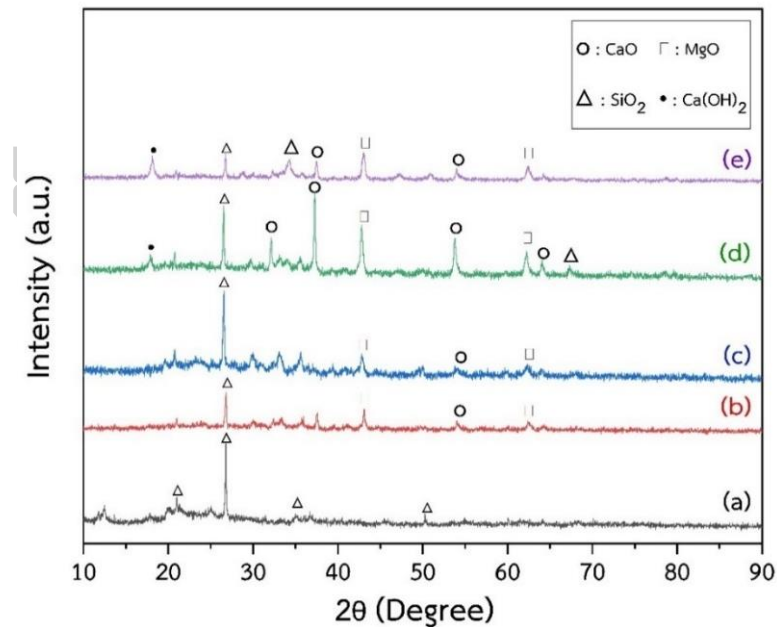


Fig 5.2 XRD patterns (a) diatomite which was not calcined (DI No Cal), (b) dolomite calcined at 800 °C and doped onto diatomite using 20 %wt. dolomite (20DSD800), (c) dolomite calcined at 800 °C and doped onto diatomite using 30 %wt. dolomite (30DSD800), (d) dolomite calcined at 800 °C and doped onto diatomite using 40 %wt. dolomite (40DSD800) and (e) dolomite calcined at 800 °C and doped onto diatomite using 50 %wt. dolomite (50DSD800)

5.2 X-ray fluorescence (XRF) measurement of dolomite, diatomite and dolomite-doped onto diatomite

From X-ray fluorescence measurement, uncalcined dolomite contained Ca content around 80.48% while dolomites calcined at 800, 850 and 900 °C contained Ca contents at 76.6, 76.82 and 77.04%, as seen in Fig 5.3. The Ca in uncalcined dolomite was in the form of CaCO_3 . After calcinations at 800, 850 and 900 °C, most CaCO_3 were transformed into CaO . Therefore, the content of Ca from uncalcined dolomite was more than those of Ca from dolomites calcined at 800, 850 and 900 °C. In addition, there were not much different in Ca contents among calcined dolomites at these temperatures (Fig 5.3). As a result, calcined dolomites showed the potential to be used as the catalyst for biodiesel production since CaO in calcined dolomites offered high basic sites to catalyze transesterification reaction [13].

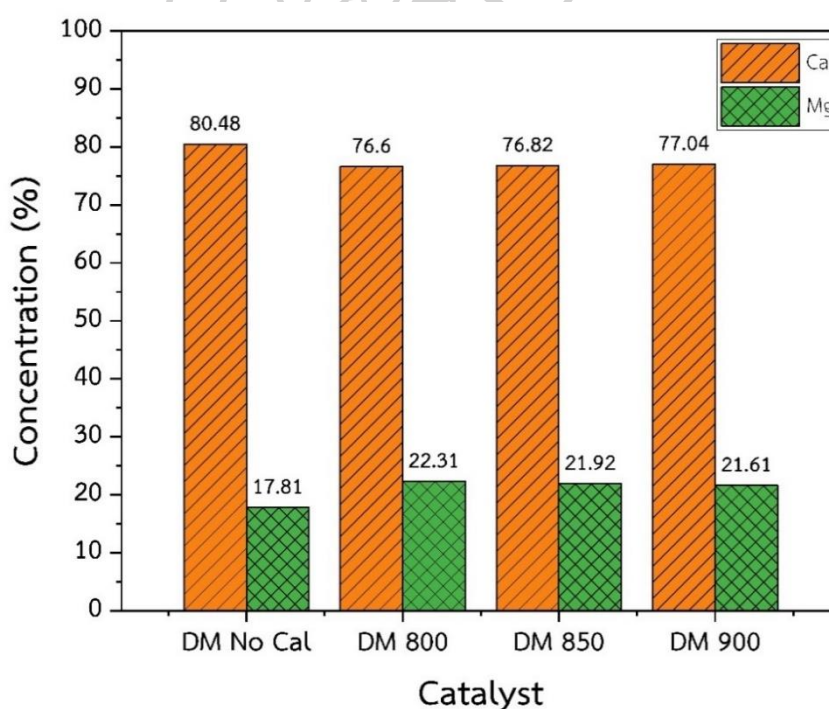


Fig 5.3 XRF measurement for Ca and Mg contents from diatomite which was not calcined (defined as DM No Cal), dolomite calcined at 800, 850 and 900 °C (defined as DM800, DM850 and DM900, respectively)

As seen in Fig 5.4, diatomite contained high content of SiO₂ and small amounts of Fe and Al, while less Ca and Mg contents were found in diatomite. Dolomite calcined at 800 °C and doped onto diatomite using 20, 30, 40 and 50 %wt. dolomite, showed Ca contents at 25.2, 30.33, 39.24 and 42.54%, respectively. These Ca contents corresponded to the dolomite contents used for doping onto diatomite, except at 50%. The Ca content from 50 %wt. dolomite doped onto diatomite was around 42.54%. Therefore, dolomite doping onto diatomite was limited at 40 %wt.

From Fig 5.4 it showed that the content of Fe and Al decreased after dolomite was doped onto diatomite at several contents. The addition of dolomite content in doping increased the content of Ca and Mg onto the catalyst as dolomite composed of Ca and Mg. Thus, Ca was observed at 25.2, 30.33, 39.24 and 42.54% and Mg was noticed at 2.91, 4.74, 8.69 and 9.72% from doping dolomite at 20, 30, 40 and 50 %wt onto diatomite. As a result, the percentage of Fe and Al was decreased from the addition of dolomite because the content proportion of Fe and Al reduced after the doping.

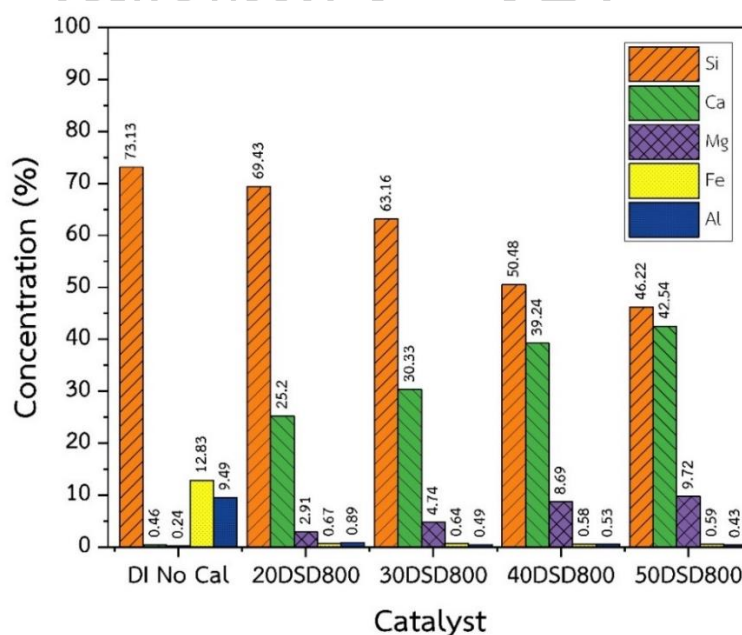


Fig 5.4 XRF measurement for element contents from diatomite which was not calcined (defined as DI No Cal), dolomite calcined at 800 °C and doped onto diatomite using 20, 30, 40 and 50 %wt. dolomite (defined as 20DSD800, 30DSD800, 40DSD800 and 50DSD800, respectively).

5.3 Scanning electron microscopy (SEM) of dolomite, diatomite and dolomite-doped onto diatomite

The surface of uncalcined dolomite and dolomites calcined at 800, 850 and 900 °C can be seen in Fig 5.5, using SEM measurement. The surface of uncalcined dolomite presented several big particles, seen in Fig 5.5(a). Compared to dolomites calcined at 800, 850 and 900 °C, the surface showed a large numbers of tiny particles, clumped together, showed in Fig 5.5(b)-(d). However, at higher temperatures in calcination, some tiny particles can aggregate into several big clumps of particles. This might be from the melting of particles at high temperature in calcination [38].

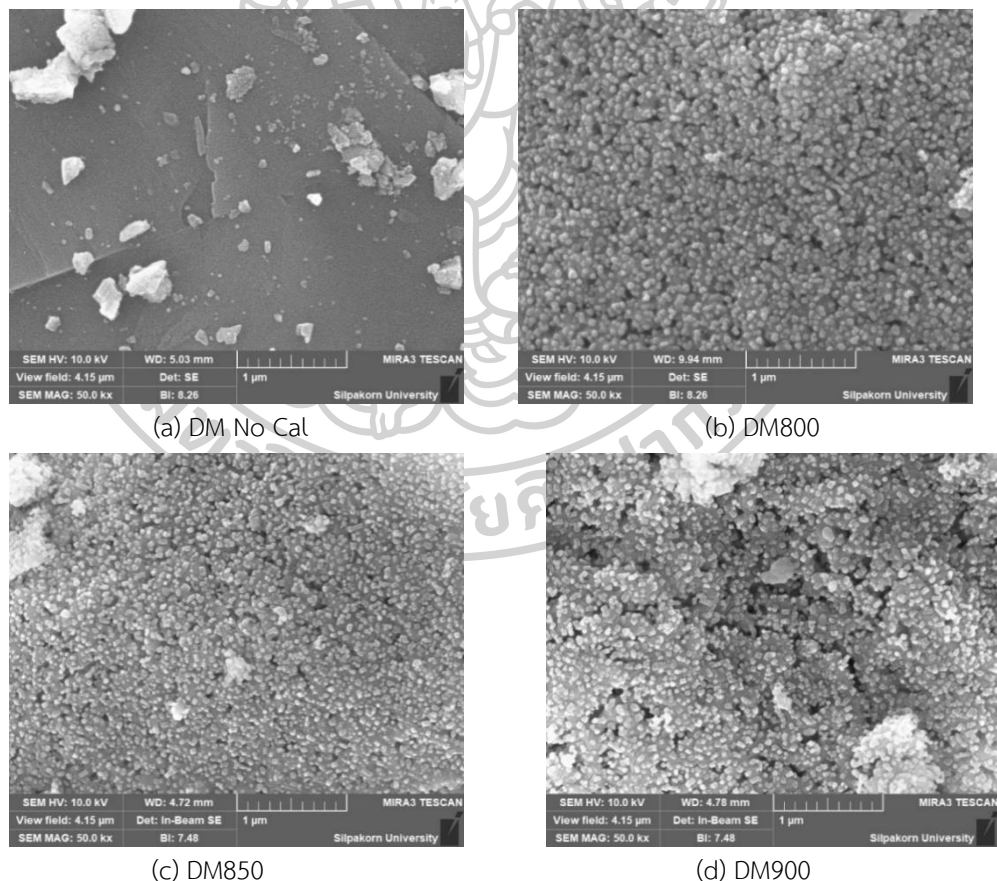


Fig 5.5 SEM measurement (a) uncalcined dolomite (DM No Cal), (b) dolomite calcined at 800 °C (DM800), (c) dolomite calcined at 850 °C (DM850) and (d) dolomite calcined at 900 °C (DM900)

From Fig 5.6(a), it showed the surface of diatomite. The surface of diatomite looked like living cell of organism in cylindrical shape with porous surface. After doping using 20, 30, 40 and 50 %wt. dolomite onto diatomite, small particles were found on the surface of diatomite as seen in Fig 5.6(b)-(e). Higher contents of dolomite doped onto diatomite presented a large amount of small particles attached on the diatomite surface.

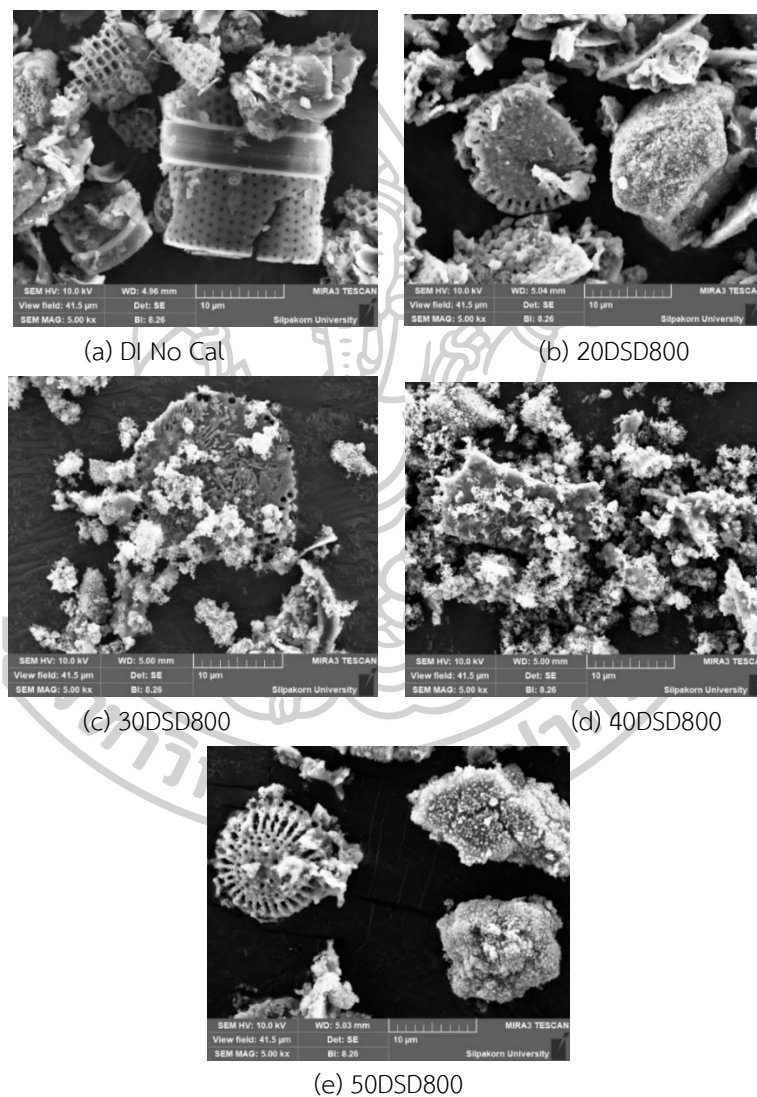


Fig. 5.6 SEM measurement (a) diatomite which was not calcined (DI No Cal), (b) dolomite calcined at 800 °C and doped onto diatomite using 20 %wt. dolomite (20DSD800), (c) dolomite calcined at 800 °C and doped onto diatomite using 30 %wt. dolomite (30DSD800), and (d) dolomite calcined at 800 °C and doped onto diatomite using 40 %wt. dolomite (40DSD800), and (e) dolomite calcined at 800 °C and doped onto diatomite using 50 %wt. dolomite (50DSD800).

5.4 Brunauer-Emmett-Teller (BET) measurement of dolomite, diatomite and dolomite-doped onto diatomite

BET measurement was used to obtain the amounts of surface area. Uncalcined dolomite occupied the surface area of $5.189 \text{ m}^2/\text{g}$ and mean pore size of 5.6091 nm (seen in Fig 5.7). Dolomite calcined at 800 , 850 and $900 \text{ }^\circ\text{C}$ showed the surface areas of 21.304 , 21.207 and $19.234 \text{ m}^2/\text{g}$ and mean pore sizes of 8.6032 , 8.565 , and 8.3936 nm , respectively. The surface areas and mean pore sizes of calcined dolomites were slightly different. However, dolomite calcined at $900 \text{ }^\circ\text{C}$ showed less surface area and mean pore size than those of lower temperatures in calcination. Some parts of dolomite were melted at high temperature, resulting to less surface area and mean pore size [17], as seen in Fig 5.7.

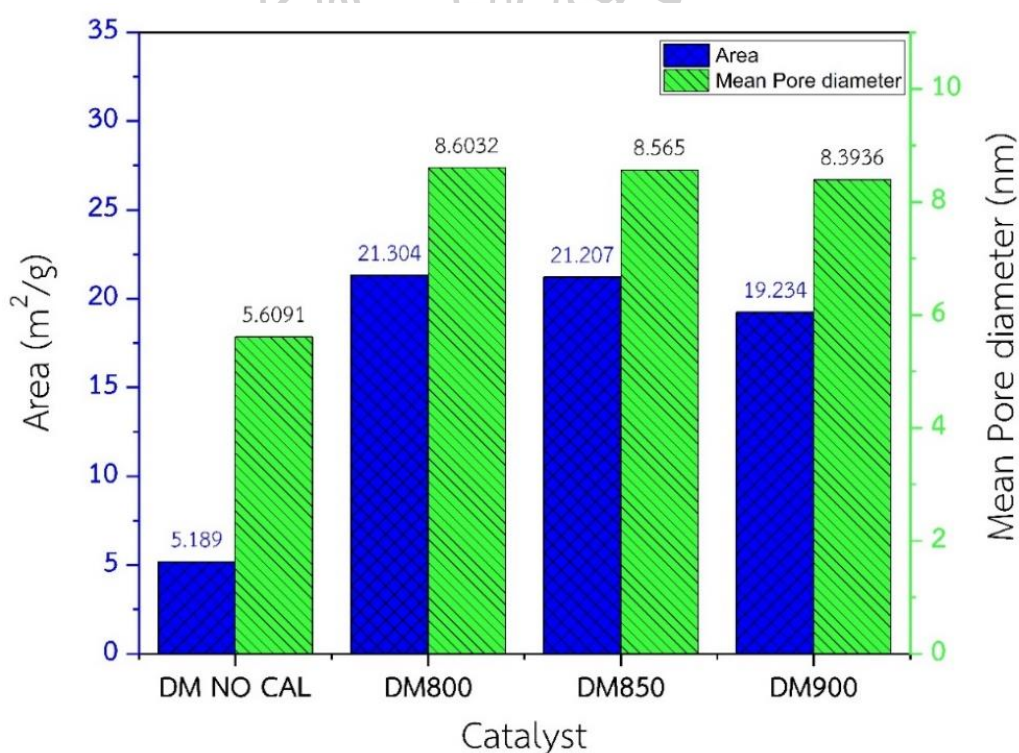


Fig. 5.7 Surface areas and mean pore sizes of uncalcined dolomite (defined as DM No Cal), dolomite calcined at 800 , 850 and $900 \text{ }^\circ\text{C}$ (defined as DM800, DM850 and DM900, respectively)

Fig 5.8 showed the surface area of 44.118 m²/g and mean pore size of 6.8266 nm from uncalcined diatomite. After doping using 20, 30, 40 and 50 %wt. dolomite onto diatomite, the surface areas were 11.47, 12.649, 15.761 and 15.821 m²/g and mean pore sizes of 7.793, 9.7163, 9.7349 and 9.1952 nm, respectively. The surface area of uncalcined diatomite decreased after doping using dolomite because the surface of diatomite was covered with dolomite which has less surface area. However, the surface area of dolomite-doped onto diatomite increased when higher content of dolomite was used. After doping, mean pore size of dolomite-doped onto diatomite increased when higher content of dolomite was used for doping, compared to uncalcined diatomite [39, 40].

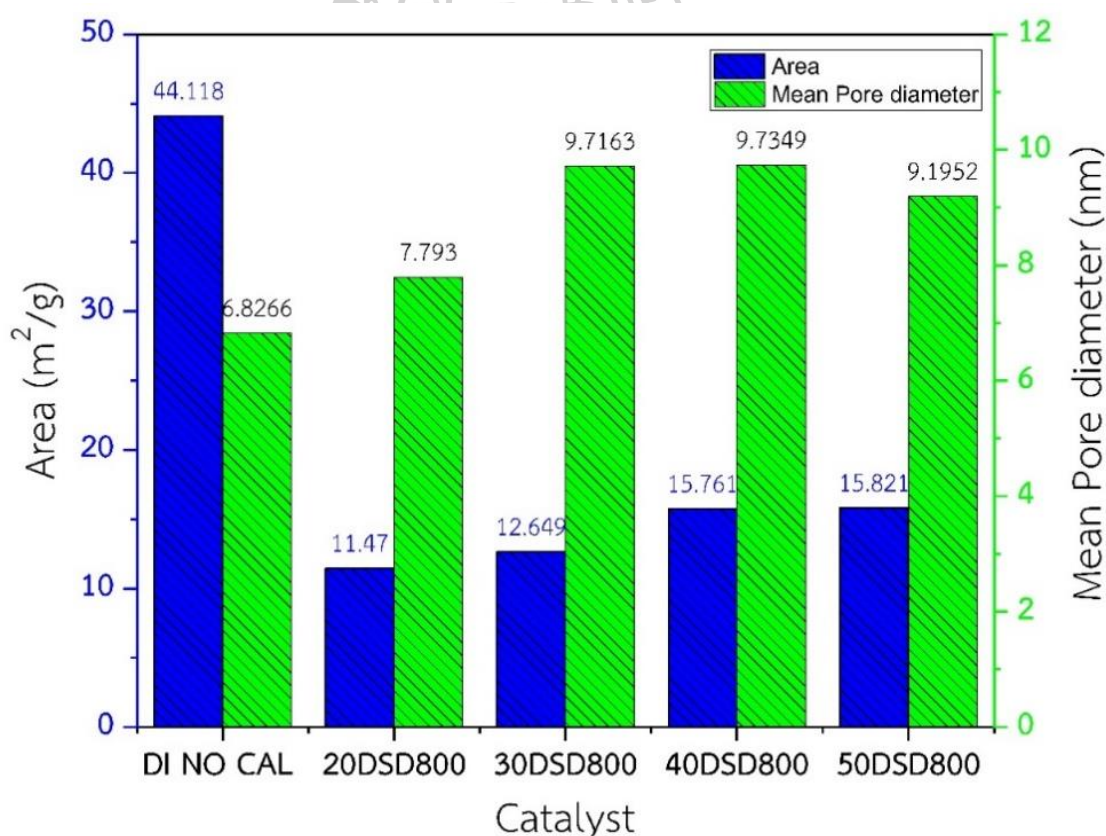


Fig. 5.8 Surface areas and mean pore sizes of uncalcined diatomite (defined as DI No Cal), dolomite calcined at 800 °C and doped onto diatomite using 20, 30, 40 and 50 %wt. dolomite (defined as 20DSD800, 30DSD800, 40DSD800 and 50DSD800, respectively)

5.5 Temperature programmed desorption (TPD) measurement of dolomite, diatomite and dolomite-doped onto diatomite

TPD measurement was used to obtain basic sites of the catalysts. The TPD- CO_2 patterns of uncalcined dolomite, dolomite calcined at 800, 850 and 900 °C were presented in Fig 5.9. It showed that the desorption temperature were at 0, 648, 632 and 630 °C for uncalcined dolomite, dolomite calcined at 800, 850 and 900 °C, respectively. From Fig 5.10, The amount of desorbed CO_2 were 0, 6.98, 5.58 and 5.05 mmol CO_2/g for uncalcined dolomite, dolomite calcined at 800, 850 and 900 °C, respectively. As a result, dolomite calcined at 800 °C offered the highest amount of basic sites. In addition, it showed the strongest bonds to CO_2 due to higher desorption temperature [8, 41].

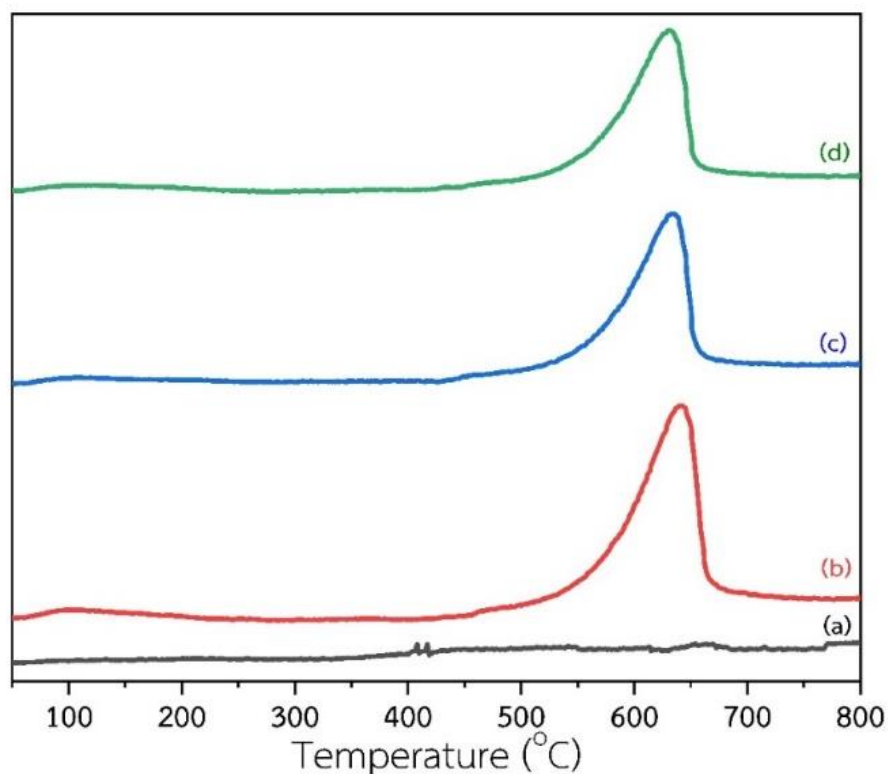


Fig. 5.9 TPD- CO_2 patterns (a) uncalcined dolomite (DM No Cal), (b) dolomite calcined at 800 °C (DM800), (c) dolomite calcined at 850 °C (DM850) and (d) dolomite calcined at 900 °C (DM900)

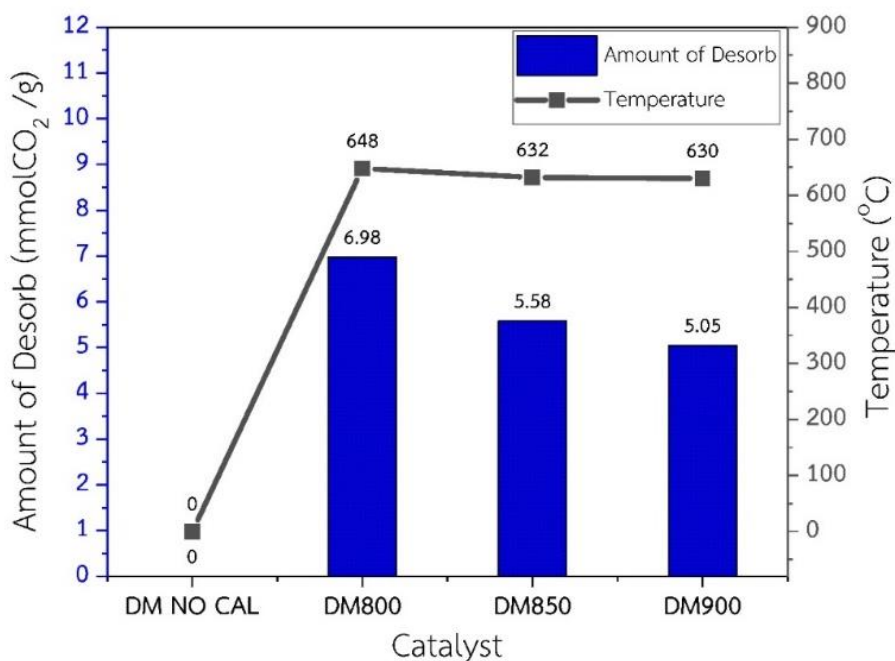


Fig. 5.10 Amount of desorbed CO₂ and desorption temperatures of uncalcined dolomite (defined as DM No Cal), dolomite calcined at 800, 850 and 900 °C (defined as DM800, DM850 and DM900, respectively)

From Fig 5.11, it showed TPD-CO₂ patterns of uncalcined diatomite, dolomite calcined at 800 °C and doped onto diatomite using 20, 30, 40 and 50 %wt. dolomite. As seen in Fig 5.12, uncalcined diatomite, dolomite calcined at 800 °C and doped onto diatomite using 20, 30, 40 and 50 %wt. dolomite presented desorption temperatures of 0, 629, 617, 679 and 632 °C, respectively, and showed the amount of desorbed CO₂ of 0, 2.33, 2.74, 5.55 and 4.31 mmol CO₂/g, respectively. The higher content of dolomite which was doped onto diatomite increased the amount of desorbed CO₂. However, doping at the highest content of dolomite (50 %wt.) showed less amount of desorbed CO₂ than that of 40 %wt. due to less mean pore size (seen in Fig 5.8). This might obstruct CO₂ to diffuse through the pore to attach the basic sites, leading to less amount of desorbed CO₂. As a result, dolomite calcined at 800 °C and doped onto diatomite using 40 %wt. dolomite (defined as 40DSD800) contained the highest basic sites (highest amount of desorbed CO₂) and showed strong bonds (highest desorption temperature) [8, 41].

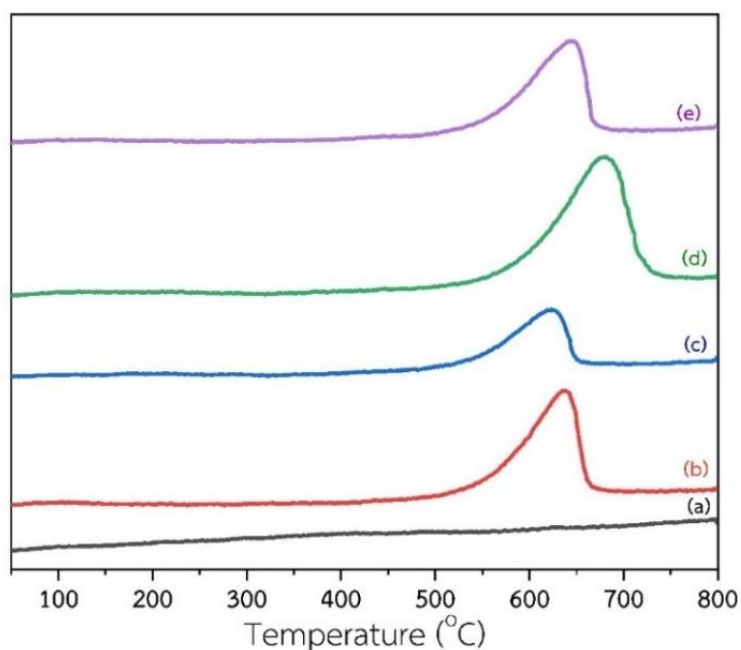


Fig. 5.11 TPD- CO_2 patterns of (a) uncalcined diatomite (DI No Cal), (b) dolomite calcined at 800 °C and doped onto diatomite using 20 %wt. dolomite (20DSD800), (c) dolomite calcined at 800 °C and doped onto diatomite using 30 %wt. dolomite (30DSD800), (d) dolomite calcined at 800 °C and doped onto diatomite using 40 %wt. dolomite (40DSD800) and (e) dolomite calcined at 800 °C and doped onto diatomite using 50 %wt. dolomite (50DSD800)

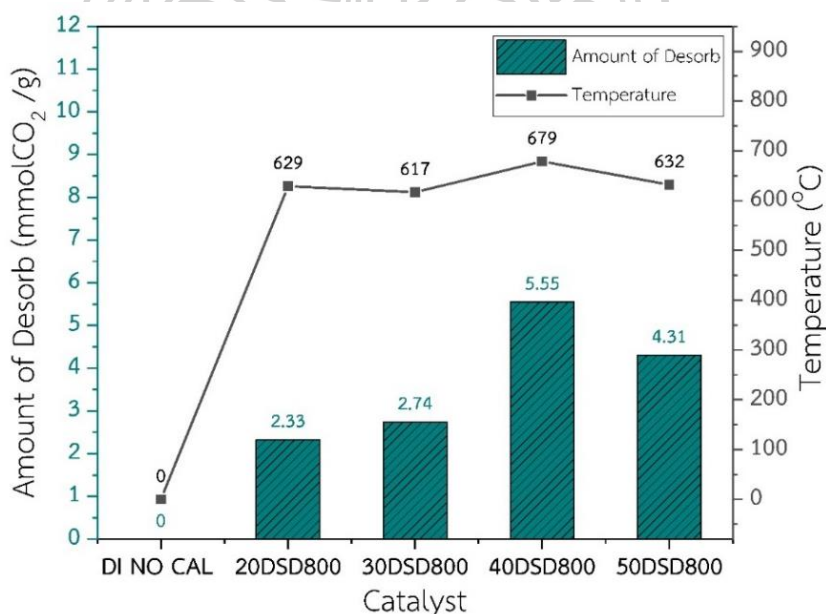


Fig. 5.12 Amount of desorbed CO_2 and desorption temperatures of uncalcined diatomite (defined as DI No Cal), dolomite calcined at 800 °C and doped onto diatomite using 20, 30, 40 and 50 wt% dolomite (defined as 20DSD800, 30DSD800, 40DSD800 and 50DSD800, respectively)

5.6 The use of dolomite, diatomite and dolomite-doped onto diatomite as the catalyst in transesterification reaction

From Fig 5.13, it showed %FAME obtained from the use of uncalcined dolomite, dolomite calcined at 800, 850 and 900 °C as the catalyst in transesterification reaction for biodiesel production. The highest %FAME of 95% was obtained using dolomite calcined at 800 °C. Uncalcined dolomite offered only 2.94 %FAME which was lowest because the main compound of dolomite before calcination was CaCO_3 . After dolomite was calcined at high temperatures, CaCO_3 was transformed into CaO which offered high basic sites (active sites) to catalyse transesterification reaction. Therefore, calcined dolomites showed higher %FAME, compared to uncalcined dolomites. However, the use of high calcination temperature might decrease %FAME due to less basic sites [8, 41]. Dolomite calcined at 850 and 900 °C offered 81.76 and 56.09 %FAME, respectively, which were less than 95 %FAME obtained from dolomite calcined at 800 °C. The melting of dolomite in some parts might occur when high temperature in calcination was used. This decreased the surface area, resulting to less basic sites and less %FAME [16].

%FAME obtained from the use of uncalcined diatomite, dolomite calcined at 800 °C and doped onto diatomite using 20, 30, 40 and 50 %wt. dolomite as the catalyst in transesterification reaction for biodiesel production can be seen in Fig 5.14. The results showed that uncalcined diatomite offered the lowest %FAME of 0.62% because the main compound in diatomite was Si which was not active site for transesterification reaction. After diatomite was doped using 20, 30, 40 and 50 %wt. dolomite, %FAME increased to 19.28, 21.76, 92.38 and 74.64%, respectively. The increase in %FAME was that dolomite contained CaO which was doped onto diatomite, resulting to the increase of basic sites as seen in Fig 5.12. The 40 %wt. dolomite doped onto diatomite offered the highest %FAME due to highest basic sites. However, at 50 %wt. dolomite doped onto diatomite, it offered less %FAME than that of 40 %wt. This might be that the mean pore size of 50 %wt. dolomite doped onto diatomite was less than that of 40 wt%. Therefore, there were some

limitation of mass transfer into the pores [1, 42], resulting to less basic sites for catalysis. In addition, higher mean pore size could promote the mass transfer for reaction. As a result, 40 %wt. dolomite-doped onto diatomite which had higher basic sites and bigger mean pore size offered the highest %FAME [43].

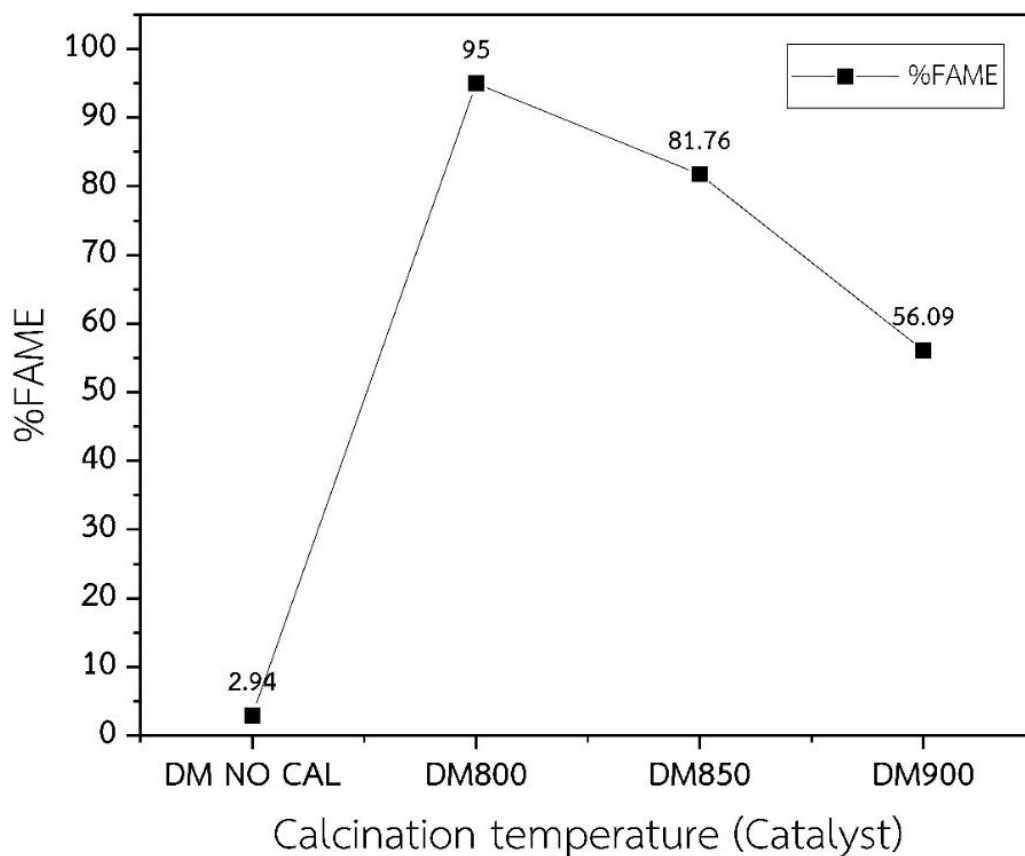


Fig. 5.13 %FAME obtained from uncalcined dolomite (defined as DM No Cal), dolomite calcined at 800, 850 and 900 °C (defined as DM800, DM850 and DM900, respectively), used as the catalyst in transesterification reaction. The reaction conditions were at 6% catalyst loading, methanol to oil molar ratio of 15:1, reaction temperature of 65 °C and reaction time of 3 hours

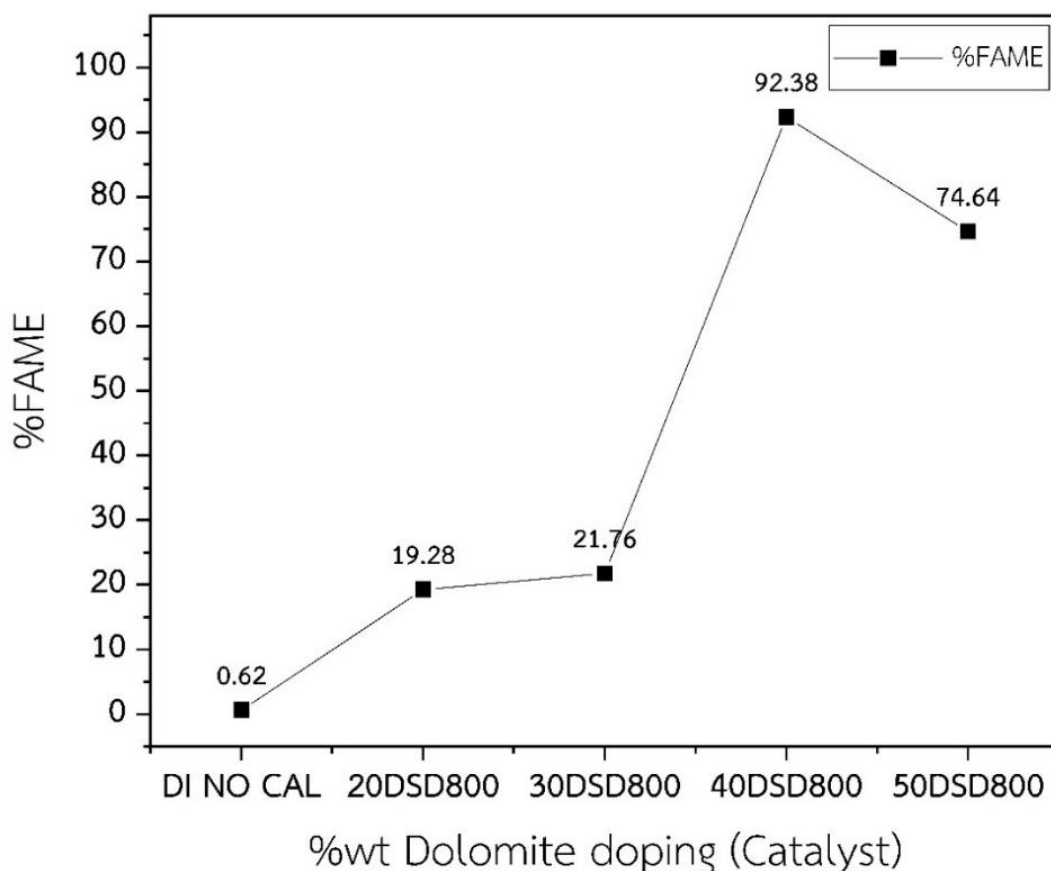


Fig. 5.14 %FAME obtained from uncalcined diatomite (defined as DI No Cal) and dolomite calcined at 800 °C and doped onto diatomite using 20, 30, 40 and 50 wt% dolomite (defined as 20DSD800, 30DSD800, 40DSD800 and 50DSD800, respectively), used as the catalyst in transesterification reaction. The reaction conditions were at 6% catalyst loading, methanol to oil molar ratio of 15:1, reaction temperature of 65 °C and reaction time of 3 hours

5.7 The study of reaction conditions in transesterification reaction for the use of dolomite-doped onto diatomite as the catalyst using Box-Behnken method for experimental design

As dolomite calcined at 800 °C and doped onto diatomite using 40% dolomite (defined as 40DSD800) was the suitable catalyst to obtain high %FAME, it was chosen to be used in this section. There are several parameters studied for suitable reaction conditions in biodiesel reaction, such as amount of catalyst, methanol to oil molar ratio, reaction temperature, reaction time, etc. Many works showed that reaction temperature was suitable at 65 °C [19] when CaO compound

was used as the catalyst. Therefore, this work aimed to use Box-Behnken method for experimental design to study the effect of amount of catalyst, methanol to oil molar ratio and reaction time on biodiesel production with the use of reaction temperature at 65 °C, in order to find the suitable reaction conditions.

From Box-Behnken experimental design, 3 parameters (amount of catalyst, methanol to oil ratio and reaction time) were studied. There were 15 batches obtained from Box-Behnken experimental design. Each parameter was divided into 3 levels; $X_1(-1)$, $X_2(0)$ and $X_3(1)$. The %FAME obtained from 15 batches of the experiment was showed in Table 5.1

Table 5.1 %FAME from 15 batches designed using Box-Behnken method

Batch	Methanol to oil molar ratio (A_1)	Amount of catalyst (%wt.) (A_2)	Time reaction (hr.) (A_3)	%FAME
1	15 (0)	6 (0)	3 (0)	90.91
2	15 (0)	9 (1)	4 (1)	67.85
3	21 (1)	6 (0)	2 (-1)	2.43
4	15 (0)	6 (0)	3 (0)	92.88
5	9 (-1)	6 (0)	2 (-1)	4.02
6	15 (0)	9 (1)	2 (-1)	14.11
7	21 (1)	3 (-1)	3 (0)	81.57
8	15 (0)	3 (-1)	4 (1)	27.85
9	9 (-1)	3 (-1)	3 (0)	55.11
10	9 (-1)	6 (0)	4 (1)	68.86
11	21 (1)	6 (0)	4 (1)	70.32
12	15 (0)	6 (0)	3 (0)	95.69
13	21 (1)	9 (1)	3 (0)	67.18
14	15 (0)	3 (-1)	2 (-1)	69.73
15	9 (-1)	9 (1)	3 (0)	69.66

From Table 5.1, Minitab program was used to analyze the data from Box-Behnken experimental design to find the relationship between %FAME and 3

parameters used for reaction conditions of transesterification reaction, as presented in Equation 5.1.

$$\begin{aligned} \%FAME = & -349 + 16.4 A_1 - 7.7 A_2 + 209.1 A_3 - 0.462 A_1 * A_1 - 0.91 A_2 * A_2 - 40.1 A_3 * A_3 \\ & - 0.402 A_1 * A_2 + 0.13 A_1 * A_3 + 7.97 A_2 * A_3 \end{aligned} \quad (\text{Eq.1})$$

which A_1 = Methanol to oil molar ratio

A_2 = Amount of catalyst (%wt.)

A_3 = Time reaction (hr.)

From Eq. 5.1, the statistical value of P-value was evaluated to show confidential value of parameters which affected to the results from interested parameters, as showed in Table 5.2. Normally, confidential value was accepted at 95%. Therefore, P-value should be lower than 0.05. From Table 5.2, both A_3 and $A_3 * A_3$ showed P-values lower than 0.05. The A_3 parameter was defined as reaction time. Therefore, reaction time was the parameter which affected to %FAME with statistically confidential value higher than 95%. In addition, the coefficient from this parameter (reaction time) reached the maximum value of 209.1. Hence, it was confident that reaction time influenced %FAME for transesterification reaction in biodiesel production.

From the main effect plot for %FAME seen in Fig 5.15, it found that the increase of methanol to oil molar ratio from 9:1 to 15:1 showed the potential to raise up %FAME. However, when methanol to oil molar ratio reached at 21:1, %FAME decreased because higher amount of methanol would dilute the concentration of oil, resulting to low reaction rate [1, 44]. It was similar to the increase of catalyst loading from 3% to 6% to obtain higher %FAME. However, when catalyst loading was 9%, %FAME decreased. This might be that the increase of catalyst loading could raise up the viscosity, leading to poor mixing in the reaction and then lower reaction rate [45, 46]. As mentioned before, reaction time strongly influence %FAME. Different reaction times showed a wide range of %FAME. Transesterification reaction is

reversible reaction. Therefore, longer reaction time might result to the decrease of %FAME [47, 48].

Table 5.2 Coefficient and P-value from relationship equation

Factor	Coefficient	P-value
Constant	-349	0.000
A_1	16.4	0.687
A_2	-7.7	0.793
A_3	209.1	0.049
$A_1 * A_1$	-0.462	0.166
$A_2 * A_2$	-0.91	0.463
$A_3 * A_3$	-40.1	0.011
$A_1 * A_2$	-0.402	0.496
$A_1 * A_3$	0.13	0.941
$A_2 * A_3$	7.97	0.060

Fig 5.16 showed the optimization results from relationship equation using Minitab program. The results presented that expected maximum %FAME of 95.84% can be obtained using methanol to oil molar ratio of 15.18:1, catalyst loading of 7.06% and reaction time of 3.33 hours (199 minutes). When these conditions were used for the actual experiment, %FAME reached to 94.56%. It was only 1.35% different from the expected optimization result (95.84 %FAME). Therefore, the relationship equation from Box-Behnken method can predict %FAME which was close to that from the actual experiment.

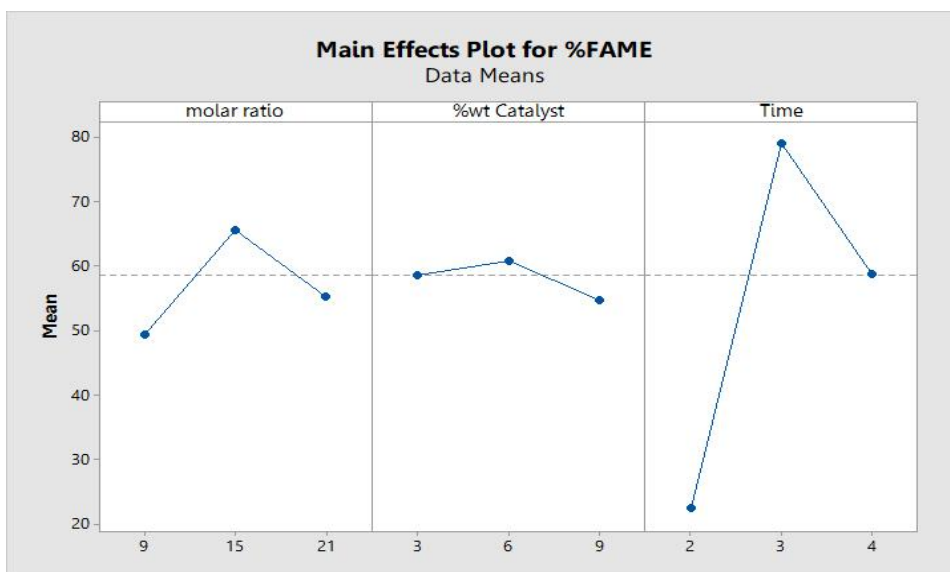


Fig. 5.15 Main effect plot for %FAME with reaction conditions (methanol to oil molar ratio, %wt catalyst loading and reaction time)

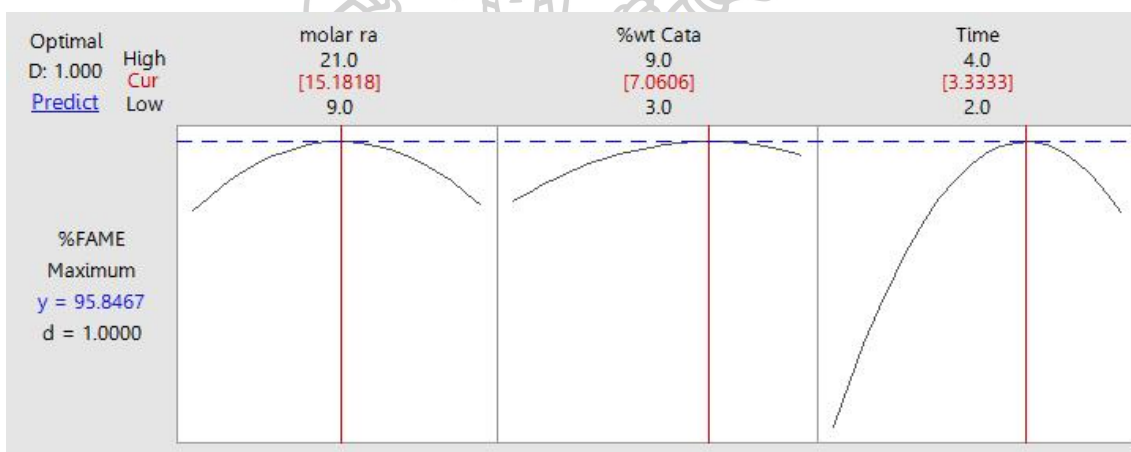


Fig. 5.16 Optimization results using Box-Behnken method to obtain the highest %FAME

5.8 The reuse of the catalysts

Fig 5.18 showed %FAME obtained from the reuse of dolomite calcined at 800 °C (defined as DM800) and dolomite calcined at 800 °C and doped onto diatomite using 40 wt% dolomite (defined as 40DSD800). As seen in Fig. 5.18, %FAME decreased after both catalysts were reused several times. 40DSD800 catalyst showed more %FAME at each reuse than that of DM800 catalyst. %FAME considerably decreased from 1-4 times of reuse, but less difference in %FAME from 5-7 times. The decrease

of %FAME was from the leaching of Ca in the catalyst. However, when dolomite was doped onto diatomite, the leaching of Ca was reduced [19]. Therefore, 40DSD800 showed more %FAME than that of DM800 due to less Ca leaching. This can be confirmed from XRD pattern of reused 40DSD800 and DM800 in Fig. 5.19. The Ca peaks were still observed in reused 40DSD800 but not in reused DM800.

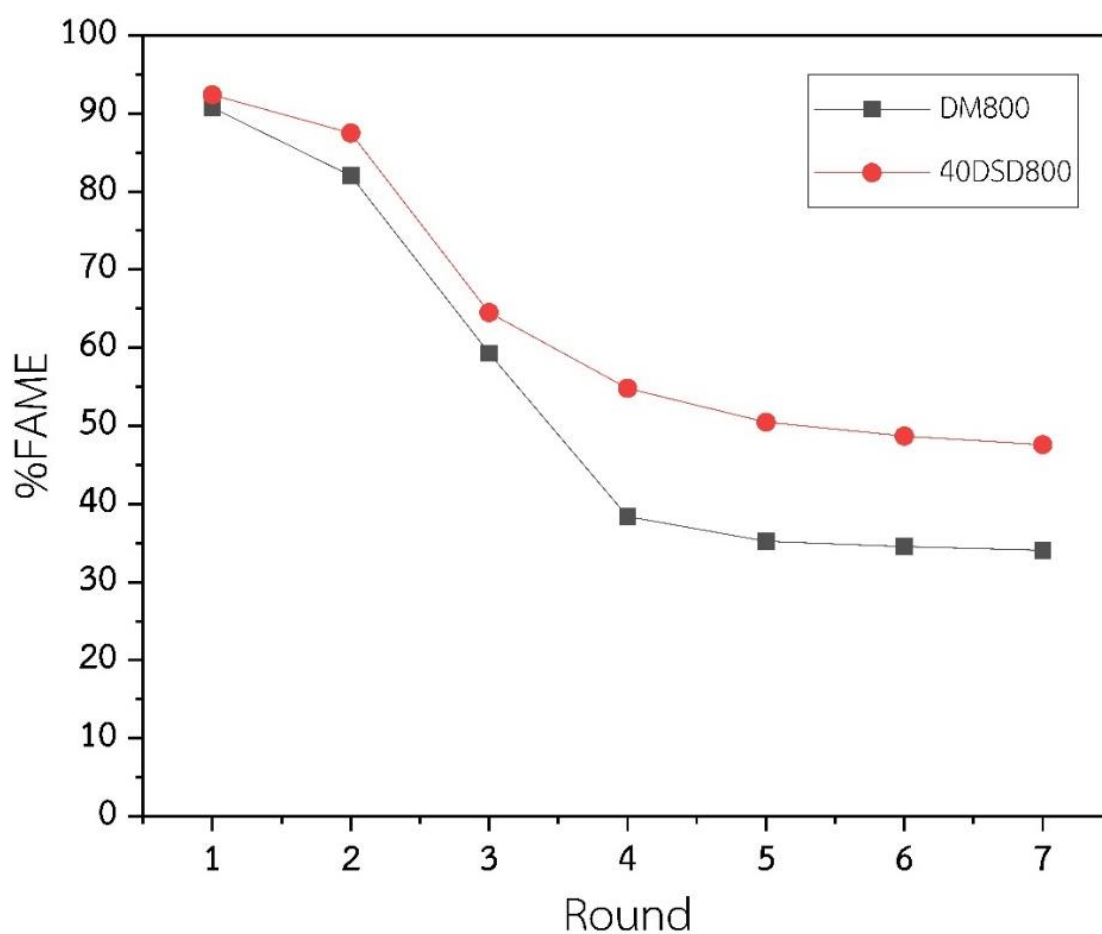


Fig. 5.18 %FAME from the re-use of the catalysts

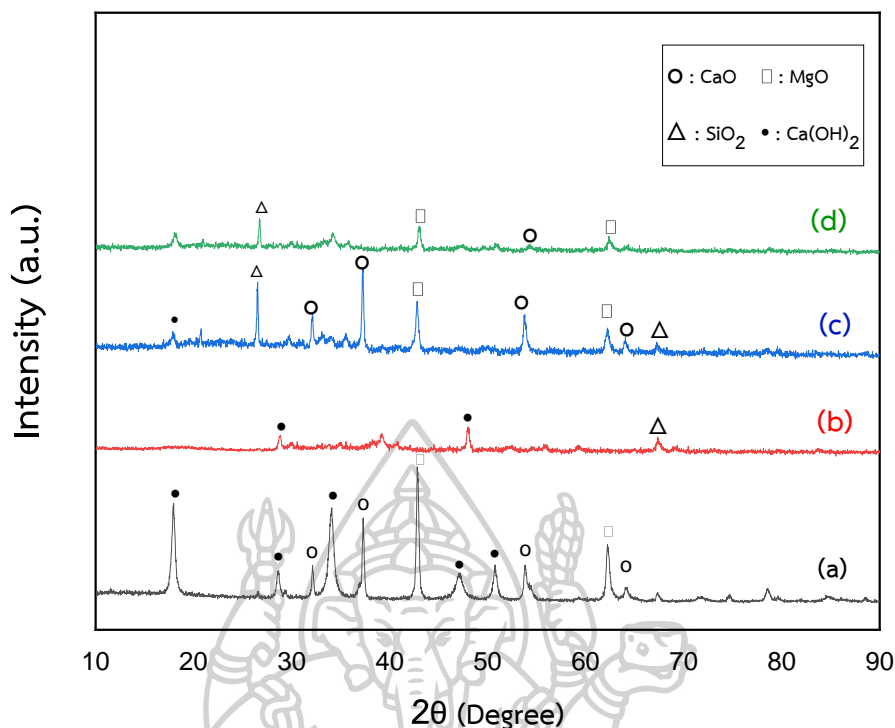


Fig 5.19 XRD patterns (a) dolomite calcined at 800 °C, (b) reused dolomite (calcined at 800 °C), (c) dolomite calcined at 800 °C and doped onto diatomite using 40 %wt. dolomite and (d) reused dolomite calcined at 800 °C and doped onto diatomite using 40 %wt. dolomite (reaction conditions were catalyst loading of 7 %wt., methanol to oil molar ratio of 15:1, reaction temperature of 65 °C and reaction time of 3 hours)

Fig 5.20 and Fig 5.21 showed the amount of basic site of the catalyst after 7 cycles of use, measured using TPD technique. The results showed that the basic sites from dolomite calcined at 800 °C (DM800) of 6.98 mmol CO₂/g decreased to 2.88 mmol CO₂/g after 7 cycles. In addition, the basic sites of 5.55 mmol CO₂/g from 40 %wt dolomite (calcined at 800 °C) doped onto diatomite (40DSD800) was also reduced to 3.63 mmol CO₂/g after 7 cycles. However, the basic sites of dolomite doped onto diatomite after reuse at 7 cycles was slightly higher than that of dolomite. This implied that the doping of dolomite onto diatomite help to prevent the leaching of CaO from the catalyst which was important to catalyse the transesterification reaction for biodiesel production.

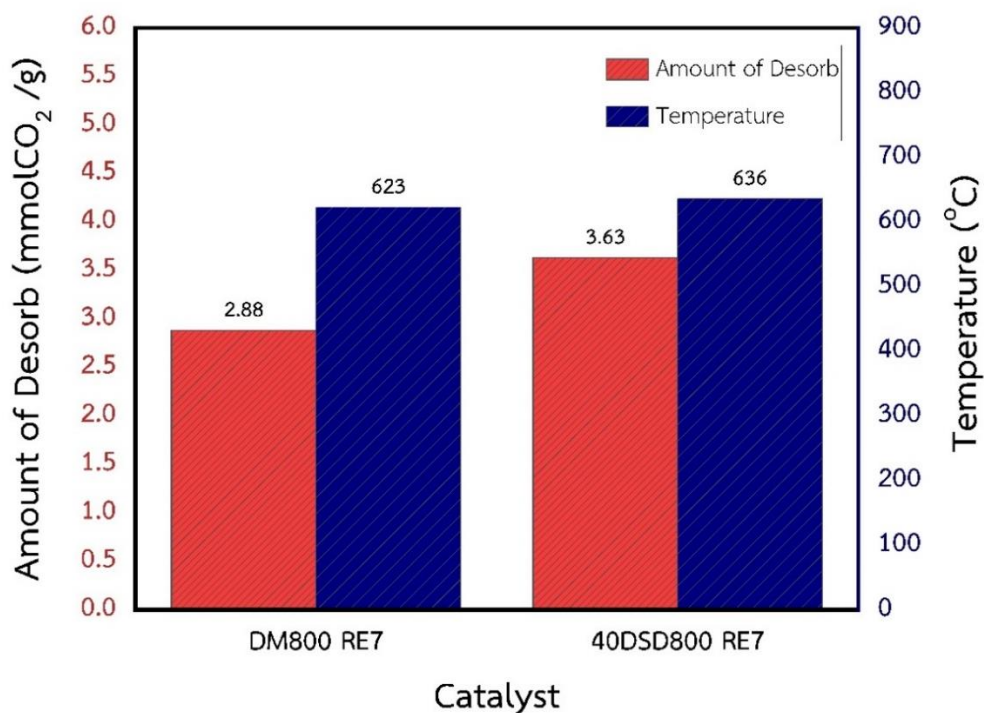


Fig. 5.20 Amount of desorbed CO₂ and desorption temperature of reused dolomite (calcined at 800 °C) (DM800 RE7) and reused dolomite calcined at 800 °C and doped onto diatomite using 40 %wt. dolomite (40DSD800 RE7). Both samples were measured after reuse at 7 cycles.

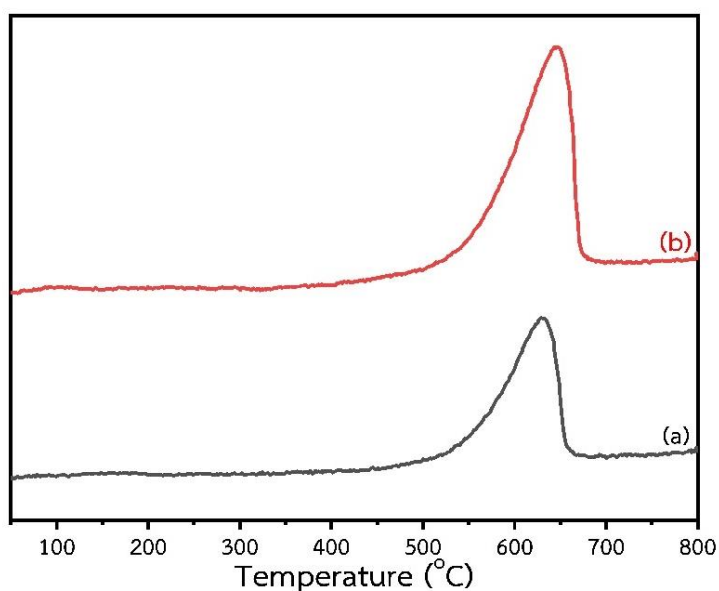


Fig. 5.21 TPD-CO₂ patterns of (a) reused dolomite (calcined at 800 °C) (DM800 RE7), (b) reused dolomite calcined at 800 °C and doped onto diatomite using 40 %wt. dolomite (40DSD800 RE7). Both samples were measured after reuse at 7 cycles.

5.9 The effect of co-solvent in transesterification reaction for biodiesel production

5.9.1 The effect of the amount of acetone used as co-solvent in transesterification reaction for biodiesel production.

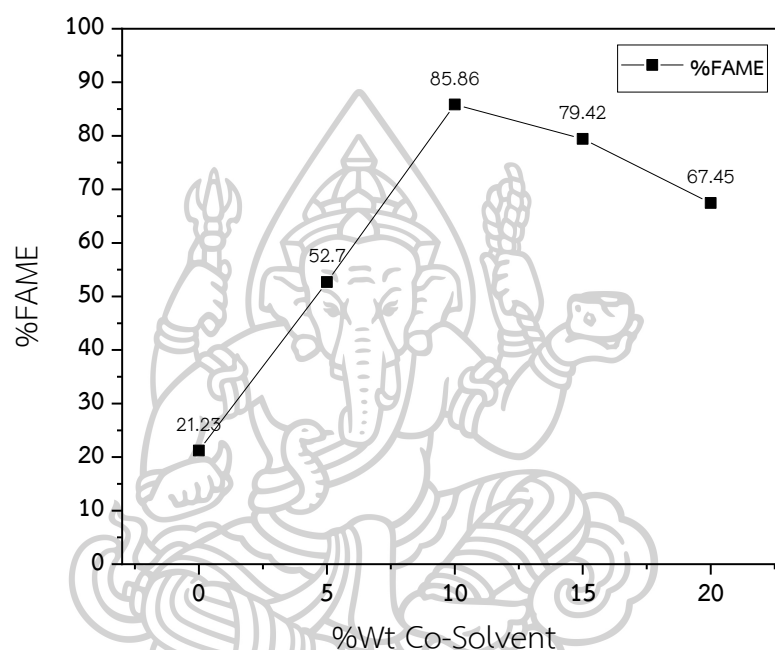


Fig 5.22 %FAME obtained from the addition of acetone used as the co-solvent using different amounts of acetone (The reaction conditions were as follows; catalyst loading of 7 %wt., methanol to oil molar ratio of 15:1, reaction temperature of 55 °C and reaction time of 3 hours)

From Fig. 5.22, it showed %FAME obtained from the use of different amount of acetone (0, 5, 10, 15 and 20 %wt.) used as the co-solvent for biodiesel production under the reaction conditions as follow; catalyst loading of 7 %wt. (40 %wt. dolomite-doped onto diatomite), methanol to oil molar ratio of 15:1, reaction temperature of 55 °C and reaction time of 3 hours. The results showed that the increase of acetone provided higher %FAME. The highest %FAME of 85.86% was observed at 10 %wt. acetone. Acetone used as co-solvent promoted the solubility between methanol (polar compound) and palm oil (non-polar compound), resulting to the increase of reaction efficiency [11, 12, 49]. However, %FAME decreased when

the amounts of acetone were at 15 and 20 %wt., respectively. It implied that more amounts of acetone would dilute the solution and then low concentration of the reactants reduced the efficiency of reaction [12].

5.9.2 The effect of reaction temperatures in transesterification reaction for biodiesel production, using acetone as the co-solvent.

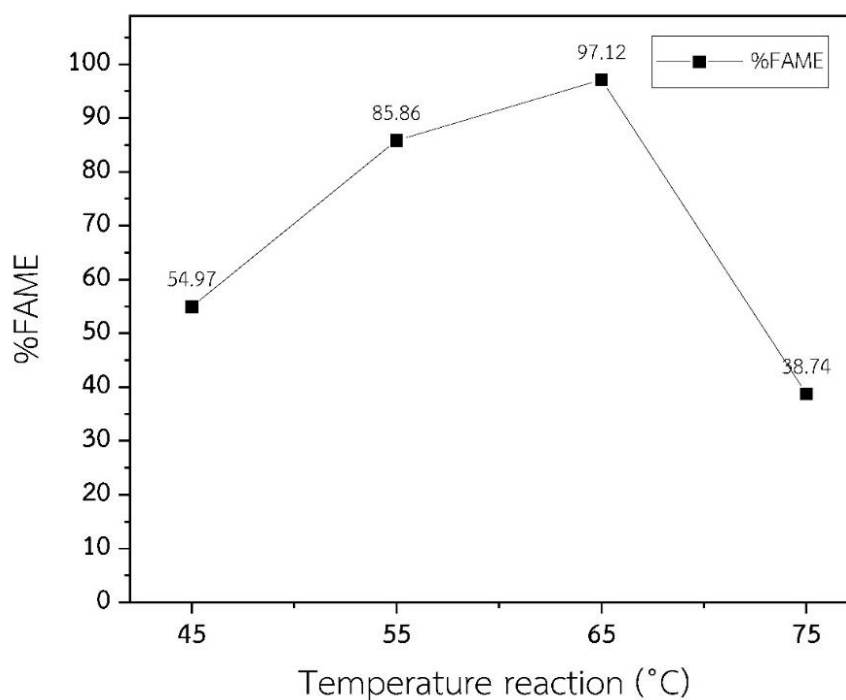


Fig 5.23 %FAME obtained from the use of different reaction temperatures (The reaction conditions were as follows; amount of acetone used as the co-solvent at 10 %wt., catalyst loading of 7 %wt., methanol to oil molar ratio of 15:1 and reaction time of 3 hours)

For transesterification reaction, 10 %wt. acetone was used as the co-solvent in order to study the effect of reaction temperatures of 45, 55, 65 and 75 °C for biodiesel production. The results showed that the reaction temperature of 65 °C offered the highest %FAME of 97.12%. Higher reaction temperature decreased the viscosity of the solution and then enhanced the mixing between methanol and palm oil. Therefore, the addition of 10 %wt. acetone used as the co-solvent promoted the solubility between methanol and palm oil and then high %FAME can be obtained.

However, %FAME decreased when reaction temperature of 75 °C was used. Although the condenser was used to prevent the loss of acetone and methanol in the gas form, more amount of acetone and methanol can still be evaporated and then flowing out the system, compared to those of lower reaction temperatures. This might lower %FAME due to the loss of methanol and acetone in the system.

From Fig 5.24, it showed %FAME from the use of 40 %wt. dolomite-doped onto diatomite and the use of acetone as the co-solvent at 10 %wt. At 60, 120, 180 and 240 minutes, %FAME were obtained at 65.47, 87.71, 97.12 and 76.55%, while %yield were observed at 58.74, 76.42, 95.84 and 65.29, respectively. It implied that %FAME and %yield increased in the range of 60-180 minutes. However, %FAME and %yield decreased at 240 minutes. This might be that the transesterification reaction can be reversed at the longer time of the reaction [19], resulting to the decrease of %FAME and %yield.

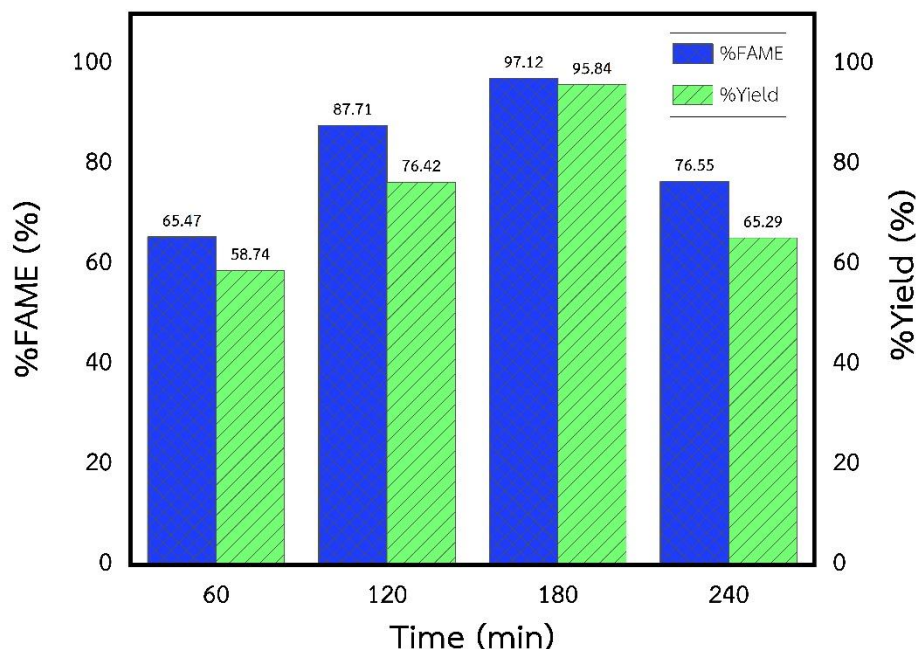


Fig 5.24 %FAME and %yield obtained from the use of co-solvent at different reaction times (The reaction conditions were as follows; amount of acetone used as the co-solvent at 10 %wt., catalyst loading of 7 %wt., methanol to oil molar ratio of 15:1 and reaction temperatures 65 °C)

Chapter 6 Conclusion

This work studied the synthesis of dolomite which was calcined at 800 °C and doped onto diatomite for the use as the catalyst in transesterification reaction for biodiesel production. Palm oil and methanol were used as the reactants. In addition, acetone used as co-solvent in transesterification reaction was studied in order to increase the efficiency of transesterification reaction

6.1 The effect of calcination temperatures for dolomite used as the catalyst for biodiesel production

Before calcination, dolomite composed of CaMgCO_3 as the main compound. Therefore, dolomite needed to be calcined to be transformed into CaO and MgO which was able to be used as the catalyst in transesterification reaction for biodiesel production. Uncalcined dolomite, dolomite calcined at 800, 850 and 900 °C were used to catalyze transesterification under the reaction conditions; catalyst loading of 6 %wt, methanol to palm oil ratio of 15:1, reaction temperature of 65 °C and reaction time of 3 hours. The results showed that dolomite calcined at 800 °C offered the highest %FAME at 95% because it provided highest amount of basic sites (6.98 mmol CO_2/g). Basic sites played the main role to promote the reaction rate. Therefore, dolomite calcined at 800 °C was then used for the next experiment.

6.2 The effect of dolomite content used for doping onto diatomite for the used as the catalyst for biodiesel production

Diatomite, which composed of SiO_2 as the main component, was doped using 20, 30, 40 and 50 %wt. dolomite which was calcined at 800 °C. The results showed that 40 %wt. dolomite-doped onto diatomite used as the catalyst gave the highest %FAME at 92.38%. However, the use of 50 %wt. dolomite-doped onto diatomite offered less %FAME than that of 40 %wt. due to less amount of basic sites and

smaller mean pore size. Therefore, 40 %wt. dolomite-doped onto diatomite was the suitable catalyst for biodiesel production in this work.

6.3 The study on suitable conditions in transesterification reaction for biodiesel production using 40 wt% dolomite-doped onto diatomite as the catalyst

The suitable conditions in transesterification reaction for biodiesel production were studied using 40 %wt. dolomite which was calcined at 800 °C and doped onto diatomite and reaction temperature of 65 °C. The Box-Behnken method was used for experimental design. The results demonstrated that the suitable conditions were at methanol to oil ratio of 15.18:1, catalyst loading of 7.06 %wt. and reaction time of 3.33 hours (199 minutes), to obtain %FAME of 94.56% which differentiated from predicted value only 1.35%. In addition, the reusability of 40 %wt. dolomite-doped onto diatomite was studied, compared to dolomite calcined at 800 °C. It found that 40 %wt. dolomite-doped onto diatomite gave more efficiency on reusability than that of dolomite calcite at 800 °C for every round of reuse.

6.4 The study on the effect of the amount of co-solvent and reaction temperature in transesterification reaction for biodiesel production.

Acetone was used as the co-solvent in transesterification reaction for biodiesel production. It was found that the use of 10 %wt. acetone and reaction temperature of 65 °C provided the highest %FAME of 97.12%. Therefore, the addition of acetone used as the co-solvent in transesterification reaction was able to promote the efficiency of the reaction.

6.5 Recommendations

1. The comparison on several types of co-solvents should be studied using dolomite calcined at 800 °C used as the catalyst for biodiesel production.

2. The comparison on several types of co-solvents should be studied using 40 %wt. dolomite-doped onto diatomite used as the catalyst for biodiesel production.



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Appendix A

The basic site calculation

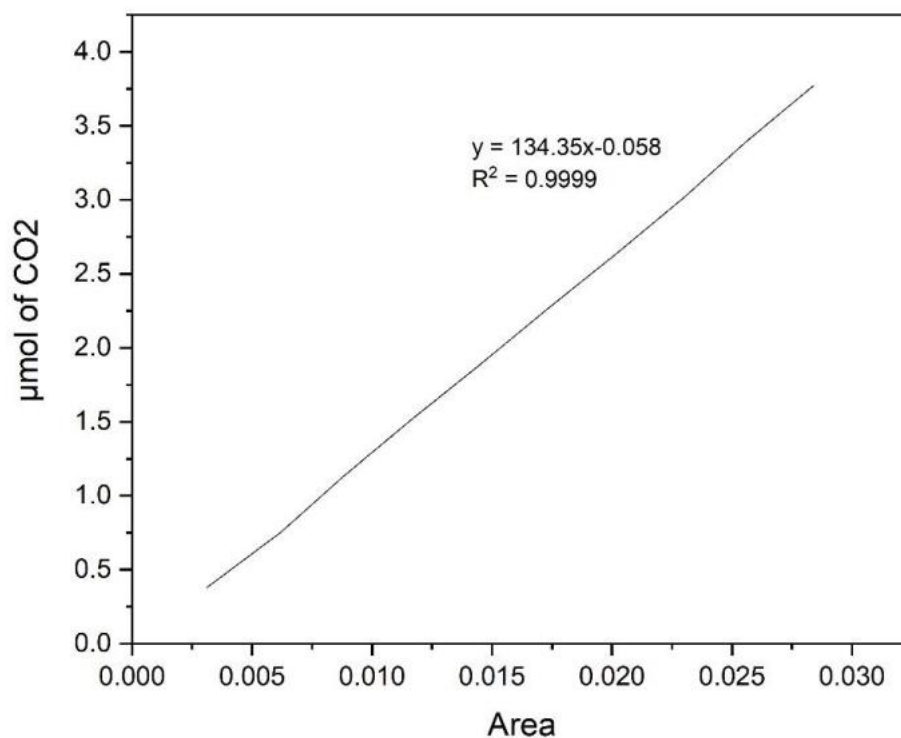


Fig A.1 Calibration curve of CO₂

The calibration curve was plotted using CO₂ injection which varied volume from 10-100 μL. After the injection, the area in various value occurred. The volume of CO₂ injection was converted into mol CO₂ using ideal gas equation. The graph was plotted between area and mol of CO₂ as seen in Figure A.1

The result of CO₂-TPD was presented in the form of area. The equation in Figure A.1 was used to calculate mol of CO₂ by replacing x with the area from CO₂-TPD result.

Example: Find basic site of 40DSD800

CO₂-TPD area is 5.4457

Weight of characterized catalyst is 0.1316 g.

$\mu\text{mol of CO}_2 = 134.35 (x) - 0.058$

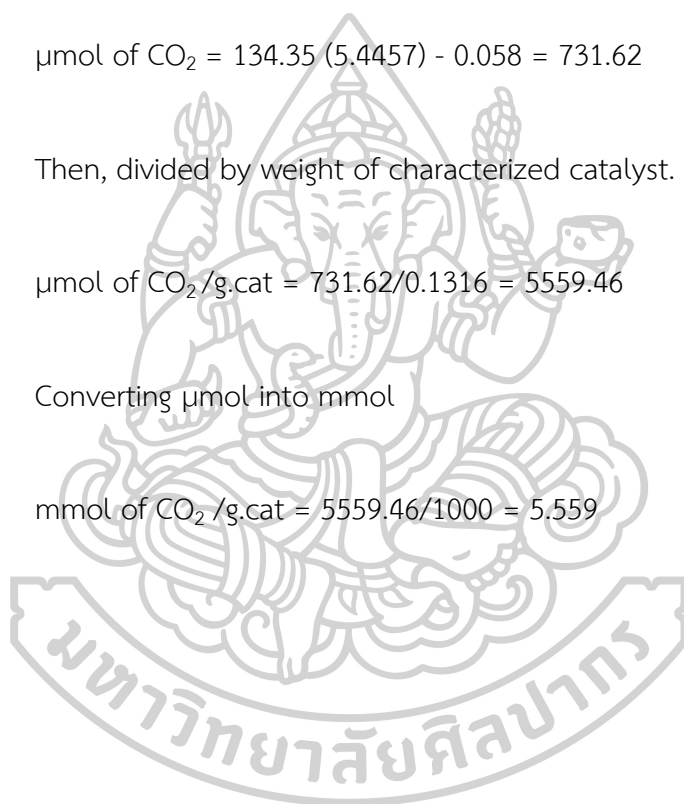
$\mu\text{mol of CO}_2 = 134.35 (5.4457) - 0.058 = 731.62$

Then, divided by weight of characterized catalyst.

$\mu\text{mol of CO}_2/\text{g.cat} = 731.62/0.1316 = 5559.46$

Converting μmol into mmol

$\text{mmol of CO}_2/\text{g.cat} = 5559.46/1000 = 5.559$



Appendix B

The percent of methyl ester calculation

The %FAME was calculated, following the EN14103 standard method. Methyl heptadecanoate was used as internal standard.

%FAME can be calculated following the below equation:

$$\%FAME = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{W_{EI}}{W_{Biodiesel}} \times 100 = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100$$

when C is the percent of methyl ester

$\sum A$ is total area from C12 – C24

A_{EI} is area of methyl heptadecanoate

C_{EI} is concentration of methyl heptadecanoate solution (mixed with heptane, mg/mL)

V_{EI} is volume of methyl heptadecanoate (mL)

m is mass of biodiesel sample (mg)

Example: %FAME area from the batch which use 40DSD800

$$\sum A = 17367471$$

$$A_{E1} = 2485738$$

$$C_{E1} = 10.57 \text{ mg/mL}$$

$$V_{E1} = 1 \text{ mL}$$

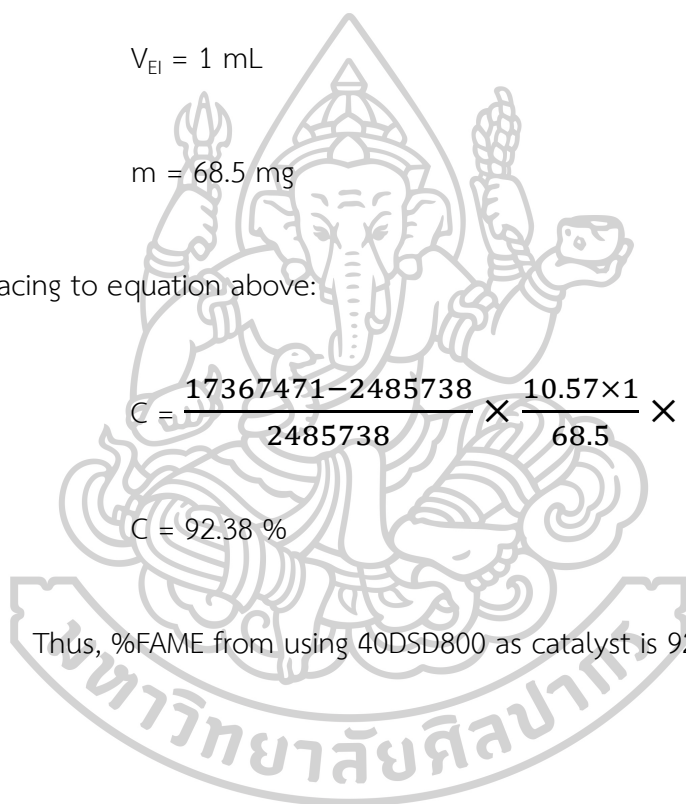
$$m = 68.5 \text{ mg}$$

Replacing to equation above:

$$C = \frac{17367471 - 2485738}{2485738} \times \frac{10.57 \times 1}{68.5} \times 100$$

$$C = 92.38 \%$$

Thus, %FAME from using 40DSD800 as catalyst is 92.38%



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