EFFECT OF SILVER DOPING ON TITANIUM DIOXIDE NANO POWDER ON THE QUALITY OF BIODIESEL PRODUCTION

KITTIPONG KAPANYA
RUNGNAPA PISSATAN
SUPINYA PUNYAPASO

[illegible]

A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF BACHERLOR OF SCIENCE
INTERNATIONAL PROGRAMS, FACULTY OF SCIENCE,
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG 2008

Special Project Title The effect of Ag doping TiO_2 nano powder on the quality of Biodiesel production

Students	Mr. Kittipong Kapanya	ID. 48050435
	Miss. Rungnapa Pissatan	ID. 48050467
	Miss. Supinya Punyapaso	ID. 48050473

Program Petrochemical Technology

Faculty Science

Academic Year 2008

Special Project Advisor Dr. Samart Kongtaweeleart

ABSTRACT

In this experiment, we used NaOH and Ag doped TiO_2 catalyst for biodiesel production. The Ag doped TiO_2 catalyst powder was prepared by sol-gel method with calcining at temperature 400°C for 24 hours. The Ag doped TiO_2 was tested by X-ray diffraction (XRD). The anatased structure of TiO_2 was found in calcined powder. The biodiesel using NaOH catalyst and Ag doped TiO_2 catalyst was compared by Nuclear Magnetic Spectrometer (NMR). The NMR results was shown 98.68% yield of NaOH catalyst biodiesel and ineffective with Ag doped TiO_2 catalyst biodiesel. The results were confirmed that the yield of biodiesel using Ag doped TiO_2 catalyst was lower than using NaOH catalyst, and it also reduce the cost of production.

Acknowledgement

We would like to thank and express a profound gratitude to our advisor, Dr. Samart Kongtaweelcrt for encouraging guidance, advice, discussion throughout this special project. We are also grateful to Assoc.Prof.Dr.Somsak Woramongkolchai and Dr. Pisek Rungrojchaiporn for serving as the examiners, and their valuable comments. We would like to thank and express for Kai Tod Had Yai restaurant for waste cooking oil.

Finally, we dedicate the work to our parents and family for their support.

Thank you so much

Kittipong Kapanya
Rungnapa Pissatan
Supinya Punyapaso

Table of Contents

Page

Chapter I Introduction

Chapter II Theory

Chapter III Experimental details

Chapter IV Results and Discussion

Chapter V Conclusions and Recommendations

List of Tables

Table **Page**

List of Figures

Chapter I

Introduction

1.1 Motivations

The present, an economy has growth rapidly and consumed in high proportion of the natural resource. The fuel is essential natural resource. That has limit and use up by the time. The quantity of fuel will be decreased by many consumers. That is a reason why we are lacking the fuel recently. Hence, we should to reduce the consumption of fuel and find a new alternative fuel or a new alternative energy for saving the natural resources.

Using the vegetable oil as a fuel for diesel engine was started with making the diesel engine in the same time. Since 1895, Dr. Rudolf Diesel who designed and developed the diesel engine by uses vegetable oil as a fuel. He presented the working of engine to the public in World Exhibition, Paris, France 1900 by using the soybean oil as a fuel. Until 1911, Dr. Rudolf diesel promoted the diesel engine which is used the vegetable oil as a fuel to become popular. [1], [2] Afterwards, the petroleum and coals were developed to be main fuel until now.

The Bio-fuel is one kind of the alternative fuel which is made from vegetable oil or animal oil. The combustion of bio-fuel is clean and release low amount of poison gas. That can help to reduce pollution problem. The biodiesel could produce by Esterification and Transesterification reaction of vegetable oil or animal oil, depend on the type of catalyst (Base or Acid catalyst). Mostly, it is produced by transesterification with base catalyst, such as, NaOH, KOH. The base catalyst is effective though transesterificaton reaction between oil and alcohol. That is faster than acid catalyst and higher yield as well. However, the use of a homogeneous base catalyst will cause saponification, which creates a serious problem of product separation and will ultimately substantially decrease methyl ester yield of NaOH, ZnO and CaO as the alternatively heterogeneous base catalyst for biodiesel production. The result from using Ag doped TiO_2 catalyst has many advantages or many benefits for biodiesel production. Firstly, it may reduce the cost of biodiesel. Secondly, the biodiesel production using Ag doped TiO_2 catalyst is not being popular. So we will make people know that the biodiesel production using Ag doped TiO_2 catalyst have many advantages and instead of using other base catalyst. Thirdly, the catalyst is not waste, it can reuse for biodiesel production. Fourthly, the biodiesel production using Ag doped TiO_2 catalyst may increase of yield, reducing free fatty acid and faster reaction.

In this experiment, we study the preparing Ag doped TiO_2 catalyst powder and use it for biodiesel production. That is different from conventional process which is using general base catalyst. The Ag doped TiO_2 catalyst was tested by X-ray diffraction (XRD) and biodiesel was tested by 1H-NMR and FT-IR spectrometer. We expect the results to get high yield of biodiesel, reduce

free fatty acid and can reuse the Ag doped TiO_2 catalyst. All components proportion was also varied to study the biodiesel, adjust the rate of reaction.

1.1 Objectives

1. To prepare Ag doped TiO_2 catalyst powder by Sol-gel method.
2. To study the effect of Ag doped TiO_2 catalyst in biodiesel production.
3. To compare production quality between general catalyst and Ag and TiO_2 catalyst in biodiesel production.

1.2 Scopes

1. To study the biodiesel production.
2. To preparating of the Ag doped TiO_2 catalyst powder by sol-gel technology
3. To study characterized Ag doped TiO_2 catalyst by X-ray diffraction (XRD)

1.3 Expected results

1. To reduce the cost of biodiesel by using Ag doped TiO_2 catalyst.
2. To produce high yield of biodiesel.
3. Using shorter time than using general catalyst.
4. Reduction of the environmental impact.

Chapter II

Literature review and theory

2.1 Definition of Biodiesel

Biodiesel is a diesel fuel substitute produced from renewable sources such as vegetable oils, animal fats, and recycled cooking oils. Chemically, it is defined as the mono alkyl esters derived from renewable sources. Biodiesel is typically produced through the transesterification reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield glycerin and biodiesel (chemically called methyl or ethyl esters). Biodiesel can be used in neat form, or blended with petroleum diesel for use in (the) diesel engines. Biodiesel has similar physical and chemical properties to petroleum diesel with reference to the operation of a diesel motor. Its physical and chemical properties as it relates to operation of diesel engines are similar to petroleum based diesel fuels. [1]

The concept of using vegetal oil as an engine fuel likely dates when Rudolf Diesel (1858-1913) developed the first engine to run on peanut oil, as he demonstrated at the World Exhibition in Paris in 1900. Unfortunately, R. Diesel died 1913 before his vision of a vegetable oil powered engine was fully realized. [2]

Modern diesels are now designed to run on a less viscous fuel than vegetable oil but, in times of fuel shortages, cars and trucks were successfully run on preheated peanut oil and animal fat. It seems that the upper rate for inclusion of rapeseed oil with diesel fuel is about 25% but crude vegetal oil as a diesel fuel extender induces poorer cold-starting performance compared with diesel fuel or biodiesel made with fatty esters. [3]

Biodiesel can also be made from other feed stocks:

- Other vegetable oils such as corn oil, canola (an edible variety of rapeseed) oil, cottonseed oil, mustard oil, palm oil, etc.
- Restaurant waste oils such as frying oils.
- Animal fats such as beef tallow or lard.
- Trap grease (from restaurant grease traps), float grease (from waste water treatment plants), etc. [5]

All vegetable oils and animal fats consist primarily of ***triglyceride*** molecules such as that shown schematically below. [5]

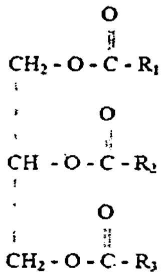
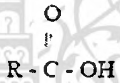


Figure 2.1 Triglyceride [5]

R1, R2, and R3 represent the hydrocarbon chains of the fatty acyl groups of the triglyceride. In their free form, fatty acids have the configuration shown below where R is a hydrocarbon chain > 10 carbon atoms. [5]



$$R-\overset{\overset{O}{\|}}{C}-OH$$

Figure 2.2 ROOH molecule [5]

Transesterification is the process of reacting a triglyceride molecule with an excess of alcohol in the presence of a catalyst (KOH, NaOH, $NaOCH_3$, etc.) to produce glycerol and fatty esters. The chemical reaction with methanol is shown schematically below. [5]

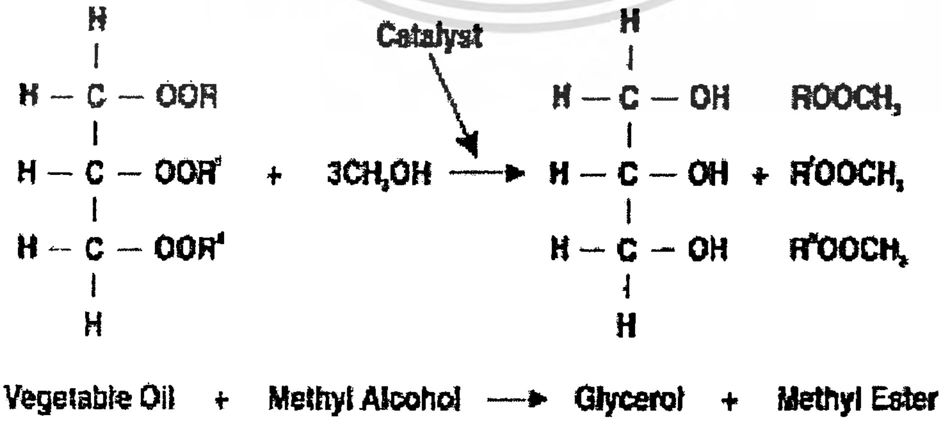


Figure 2.3 Transesterification reaction [5]

Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace. Biodiesel can be employed as a fuel for unmodified diesel engines. [6]

Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix: fuel containing 20% biodiesel is labeled B20, while pure biodiesel is referred to as B100. It is common to see B99, since 1% petrodiesel is sufficiently toxic to retard mold. Blends of 20 percent biodiesel with 80 percent petroleum diesel (B20) can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems. Blending B100 with petro diesel may be accomplished by:

- Mixing in tanks at manufacturing point prior to delivery to tanker truck.
- Splash mixing in the tanker truck (adding specific percentages of Biodiesel and Petro Diesel).
- In-line mixing, two components arrive at tanker truck simultaneously. [7]

Biodiesel can test the properties by NMR Spectroscopy Instrument and Fourier Transform Infrared Spectrometer. [29], [30]

They defined the biodiesel specified shall be mono-alkyl esters of long chain fatty acids derived from vegetable oils and animal fats. [29], [30]

2.2 Raw materials for Biodiesel production

2.2.1 Vegetable oil

Vegetable fats and oils are lipid materials derived from plants. Physically, oils are liquid at room temperature, and fats are solid. Chemically, both fats and oils are composed of triglycerides, as contrasted with waxes which lack glycerin in their structure. Although many different parts of plants may yield oil, in commercial practice, oil is extracted primarily from seeds. [9]

The melting temperature distinction between oils and fats is imprecise, since definitions of room temperature vary, and typically natural oils have a *melting range* instead of a single melting point. [9]

Vegetable fats and oils may be edible or inedible. Examples of inedible vegetable fats and oils include processed linseed oil, tung oil, and castor oil used in lubricants, paints, cosmetics, pharmaceuticals, and other industrial purposes. Although thought of as esters of glycerin and a varying blend of fatty acids, fats and oils also typically contain free fatty acids, monoglycerides, and diglycerides. [9]

2.2.1.1 Palm oil [10]

Palm oil is edible plant oil derived from the fruit of the Arecaceae Elaeis oil palm. Previously the second-most widely produced edible oil, after soybean oil, 28 million tonnes was produced worldwide in 2004. It may have now surpassed soybean oil as the most widely produced vegetable oil in the world. It is also an important component of much soaps, washing powders and personal care products, is used to treat wounds, and has controversially found a new use as a feedstock for biofuel.

The palm fruit is the source of both palm oil (extracted from palm fruit) and palm kernel oil (extracted from the fruit seeds). Palm oil itself is reddish because it contains a high amount of beta-carotene. It is used as cooking oil, to make margarine and is a component of many processed foods. Boiling it for a few minutes destroys the carotenoids and the oil becomes colourless. Palm oil is one of the few vegetable oils relatively high in saturated fats (like coconut oil) and thus semi-solid at room temperature.

Palm oil and palm kernel oil are composed of fatty acids, esterified with glycerol just like any ordinary fat. Both are high in saturated fatty acids, about 50% and 80%, respectively. The oil palm gives its name to the 16 carbon saturated fatty acid palmitic acid found in palm oil; monounsaturated oleic acid is also a constituent of palm oil while palm kernel oil contains mainly lauric acid. Palm oil is the largest natural source of tocotrienol, part of the vitamin E family. Palm oil is also high in vitamin K and dietary magnesium.

Napalm derives its name from naphthenic acid, palmitic acid and pyrotechnics or simply from a recipe using naphtha and palm oil. Splitting of oils and fats by hydrolysis, or under basic conditions saponification, yields fatty acids; with glycerin (glycerol) as a by-product. The split-off fatty acids are a mixture of fatty acids ranging from C6 to C18 depending on the type of Oil / Fat.

Palm oil products are made using milling and refining processes; first using fractionation, with crystallization and separation processes to obtain a solid stearin, and liquid olein. By melting and degumming, impurities can be removed and then the oil filtered and bleached. Next, physical refining removes odours and colouration, to produce *refined bleached deodorized palm oil*, or RBDPO, and free pure fatty acids, used as an important raw material in the manufacture of soaps, washing powder and other hygiene and personal care products. RBDPO is the basic oil product which can be sold on the world's commodity markets; although many companies fractionate it out further into palm olein, for cooking oil, or other products.

Palm is also used in biodiesel production, as either a simply-processed palm oil mixed with petrodiesel, or processed through transesterification to create a palm oil methyl ester blend which meets the international EN 14214 specification, with glycerin as a by-product. The actual process used varies between countries and the requirements of any export markets. Second-generation biofuel production processes are also being trialled in relatively small quantities.

Although palm oil has a comparatively high yield, the problems that organisations such as Greenpeace have linked to palm cultivation on newly-cleared plantations have encouraged research into alternative vegetable fuel oil sources with less potential for environmental damage, such as jatropha. Although palm requires less manual labor to harvest a given amount of oil than jatropha, the latter grows well in more marginal areas and requires less water.

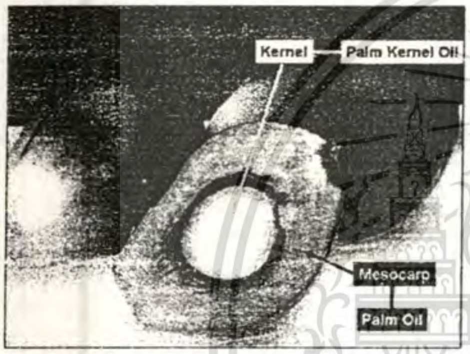


Figure 2.4 Kanel and Palm Kanel Oil [11]

Figure 2.5 Biodiesel from Palm oil [11]

However, regardless of these new innovations, first generation biodiesel production from palm oil is still in demand globally and will continue to increase. Palm oil is also a primary substitute for rapeseed oil in Europe, which too is experiencing high levels of demand for biodiesel purposes. Palm oil producers are investing heavily in the refineries needed for biodiesel. In Malaysia companies have been merging, buying others out and forming alliances in order to obtain the economies of scale needed to handle the high costs caused by increased feedstock prices. New refineries are being built across Asia and Europe. [10]

Nowadays, the area plant for palm tree in Thailand is 0.84 million acres and can made crude palm oil 700,000-800,000 tons per years. [8] It's fourth rank next to Malaysia, Indonesia and Nigeria. The provinces that produce high amount of palm oil are Krabi , Surat Thani and Chum porn. [8]

2.2.1.2 Waste vegetable oil (WVO)

Many vegetable oils have similar fuel properties to diesel fuel, except for higher viscosity and lower oxidative stability. If these differences can be overcome, vegetable oil may substitute for Diesel fuel, most significantly as engine fuel or home heating oil. For engines designed to burn diesel fuel, the viscosity of vegetable oil must be lowered to allow for proper atomization of fuel; otherwise incomplete combustion and carbon build up will ultimately damage the engine. Many enthusiasts refer to vegetable oil used as fuel as waste vegetable oil (WVO) if it is oil that was discarded from a restaurant or straight vegetable oil (SVO) or pure plant oil (PPO) to distinguish it from biodiesel. [13]

Proper disposal of used cooking oil is an important waste-management concern. Oil is lighter than water and tends to spread into thin and broad membranes which hinder the oxygenation of water. Because of this, a single litre of oil can contaminate as much as 1 million litres of water. Also, oil can congeal on pipes provoking blockages. [14]

Because of this, cooking oil should never be dumped on the kitchen sink or in the toilet bowl. The proper way to dispose of oil is to put it in a sealed non-recyclable container and discard it with regular garbage. [14]

Figure 2.6 Biodiesel, Waste Vegetable Oils and Vegetable Oils [15]

Figure 2.7 Waste Vegetable Oils [16]

Cooking oil can be recycled. It can be used to produce soap and biodiesel. [14]

The major steps required to synthesize biodiesel are as follows:

Purification

If waste vegetable oil (WVO) is used, it is filtered to remove dirt, charred food, and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to give biodiesel. At home, this is often accomplished by heating the filtered oil to approximately 120 °C. At this point, dissolved or suspended water will boil off. When the water boils, it spatters (chemists refer to it as "bumping"). To prevent injury, this operation should be done in a sufficiently large container (at most two thirds full) which is closed but not sealed. [17]

In the laboratory, the crude oil may be stirred with a drying agent such as magnesium sulfate to remove the water in the form of water of crystallization. The drying agent can be separated by decanting or by filtration. However, the viscosity of the oil may not allow the drying agent to mix thoroughly. [17],[18]

Neutralization of free fatty acids

A sample of the cleaned oil is titrated against a standard solution of base in order to determine the concentration of free fatty acids (RCOOH) present in the waste vegetable oil sample. The quantity (in moles) of base required to neutralize the acid is then calculated. [17], [18]

And after that through the transesterification reaction later.

2.3 Biodiesel production

Biodiesel is commonly produced by the transesterification of the vegetable oil or animal fat feedstock. There are several methods for carrying out this transesterification reaction including the common batch process, supercritical processes, ultrasonic methods, and even microwave methods. [12]

Chemically, transesterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. The most common form uses methanol (converted to sodium methoxide) to produce methyl esters as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester biodiesel and higher alcohols such as isopropanol and butanol have also been used. Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester, at the cost of a less efficient transesterification reaction. A lipid transesterification production process is used to convert the base oil to the desired esters. Any Free fatty acids (FFAs) in the base oil are either converted to soap or removed from the process, or they are esterified (yielding more biodiesel) using an acidic catalyst. After this processing, unlike straight vegetable oil, biodiesel has combustion properties very similar to those of petroleum diesel, and can replace it in most current uses. [12]

There are 2 chemical reactions for obtaining Ester as follows.

1. Esterification: a process using of acid as catalyst.

2. Transesterificaion: a process using of alkaline as catalyst to form up Ester by its equation.

There are 5 significant factors effecting to biodiesel production as follows:

- Temperature at chemical reaction.
- A ratio of oil and alcohol.
- Catalyst type and concentration.
- Blending of the base agent.
- Purity of reactants. [19]

2.3.1 Transesterification reaction

Animal and plant fats and oils are typically made of triglycerides which are esters of free fatty acids with the trihydric alcohol, glycerol. In the transesterification process, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol is used. As can be seen, the reaction has no other inputs than the triglyceride and the alcohol. [20]

Normally, this reaction will proceed either exceedingly slowly or not at all. Heat, as well as an acid or base are used to help the reaction proceed more quickly. It is important to note that the acid or base are not consumed by the transesterification reaction, thus they are not reactants but catalysts. [20]

Almost all biodiesel is produced from virgin vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids). However, biodiesel produced from other sources or by other methods may require acid catalysis which is much slower. [19], [21] Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification and will be discussed below, based on the type of catalyst used. [21]

Mechanism:

Transesterification reaction equation, shown in skeletal formulas:

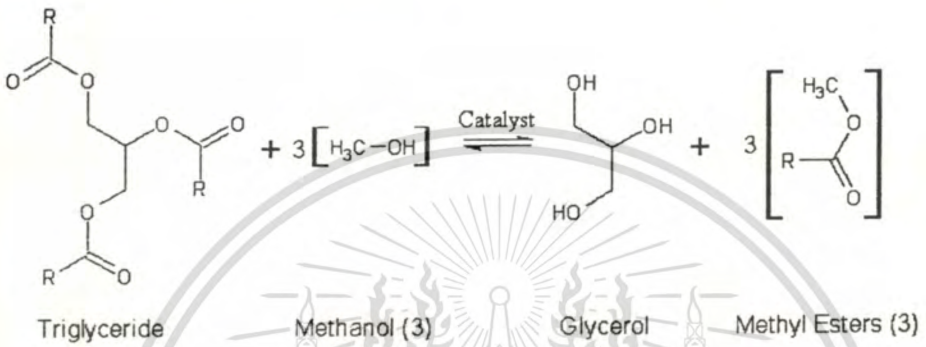


Figure 2.8 Transesterification reactions [20]

Since natural oils are typically used in this process, the alkyl groups of the triglyceride are not necessarily the same. Therefore, distinguishing these different alkyl groups, we have a more accurate depiction of the reaction: [8]

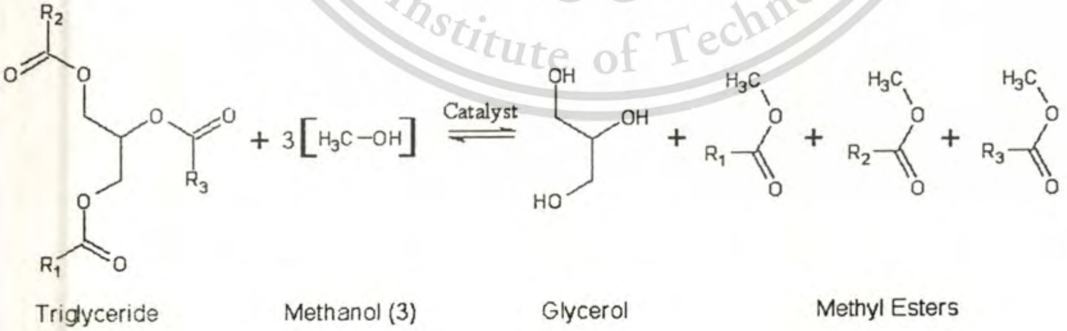


Figure 2.9 Transesterification reactions [20]

R_1, R_2, R_3 : Alkyl group.

During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline (NaOH, KOH, or Alkoxides). The main reason for doing a titration to produce biodiesel, is to find out how much alkaline is needed to completely neutralize any free fatty acids present, thus ensuring a complete transesterification. Empirically 6.25 g / L NaOH produces a very usable fuel. One uses about 6 g NaOH when the WVO is light in colour and about 7 g NaOH when it is dark in colour.

The alcohol reacts with the fatty acids to form the mono-alkyl ester (or biodiesel) and crude glycerol. The reaction between the biolipid (fat or oil) and the alcohol is a reversible reaction so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion. [20]

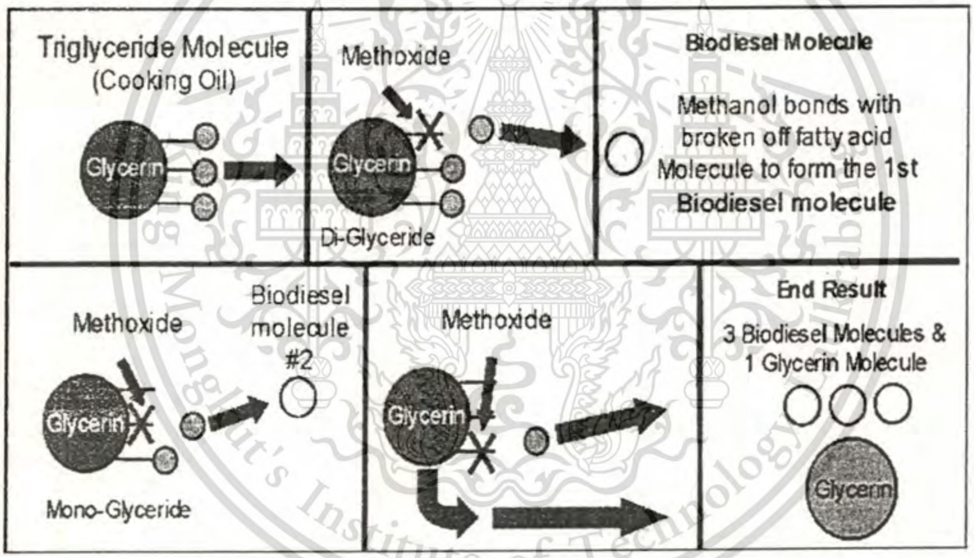


Figure 2.10 Molecules reaction of biodiesel production [8]

2.3.2 Base-Catalyzed Processes [21]

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Fig.2.11. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

$$\mathrm{ROH} + \mathrm{B} \rightleftharpoons \mathrm{RO^-} + \mathrm{BH^+} \qquad (1)$$

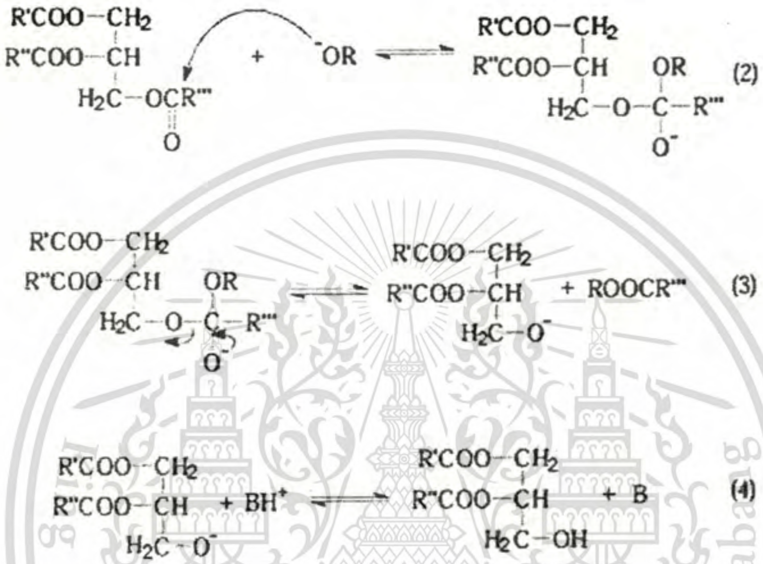
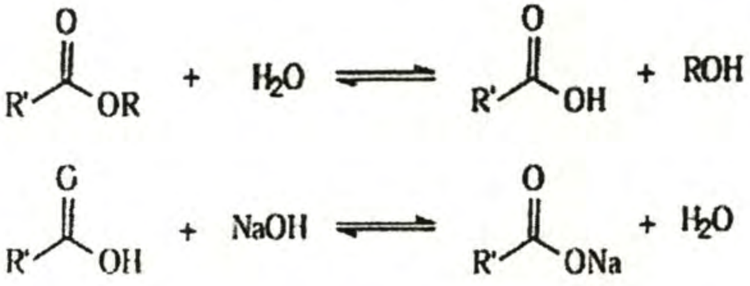


Figure 2.11 Mechanism of the base-catalyzed transesterification of vegetable oils [21]

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation (Fig.2.12). This undesirable saponification reaction reduces the ester yields and considerably difficults the recovery of the glycerol due to the formation of emulsions.



R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Figure 2.12 Saponification reactions of the produced fatty acid alkyl esters [21]

Potassium carbonate, used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation. This can be explained by the formation of bicarbonate instead of water (Fig.2.13), which does not hydrolyze the esters.

$$K_2CO_3 + ROH \rightleftharpoons ROK + KHCO_3$$

R = alkyl group of the alcohol

Figure 2.13 Reaction of potassium carbonate with the alcohol [21]

2.3.3 Heterogeneously Catalyzed Processes for biodiesel production [21]

The advantage of using guanidines in the transesterification of vegetable oils is the possibility to heterogenize them on organic polymers. Schuchardt *et al.* tested principally cellulose and poly(styrene/divinylbenzene), but also polyuretanes and other organic polymers allow the suitable incorporation of guanidines.

The heterogenization of unsubstituted guanidines can be achieved by their reaction with microcrystalline cellulose activated by cyanuric chloride at the C-6 position (Fig.2.14.). After deprotonation of the guanidinium salt formed, the guanidine-containing cellulose shows a slightly reduced activity, compared to guanidine in homogeneous phase, giving a conversion of 30% after 1 h, when used at 5 mol%. This guanidine-containing cellulose was used in a continuous reactor containing 100 g of the catalyst. An alcohol/oil mixture of 2:1 was pumped at 60 °C with a rate of 0.48 L/h. In the first hour the methyl esters were obtained with high yields and the phase separation was quick. After this, however, the reaction was incomplete and the phase separation difficult.

This could be due either to leaching of the catalyst or to its irreversible protonation. As no leaching tests were performed, no definite reason can be given at this point.

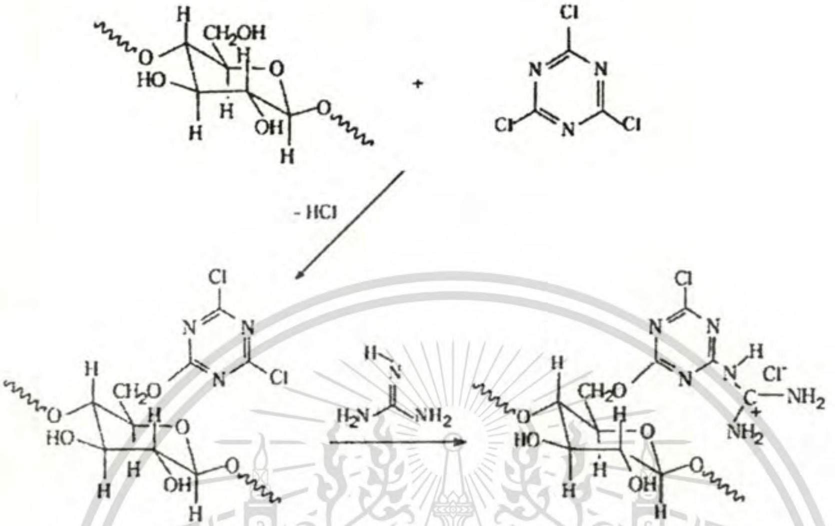
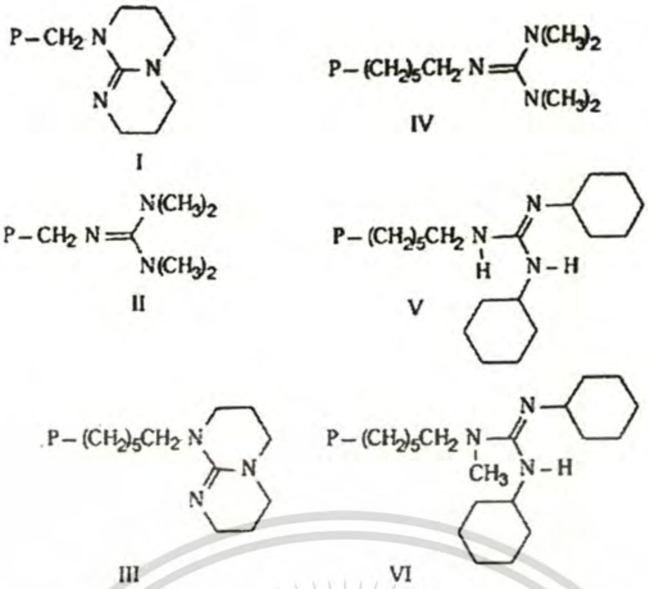


Figure 2.14 Heterogenization of guankline on activated microcrystalline cellulose [21]

The catalytic performance of some alkylguanidines heterogenized on different substituted polystyrenes was investigated. The guanidine-containing polymers (Fig.2.15) were used in the transesterification of soybean oil with methanol in several consecutive catalytic cycles. The guanidines heterogenized on gel-type poly (styrene/divinylbenzene) with 1 meq Cl/g (polymers I and II) showed a slightly lower activity than their homogeneous analogues but allowed the same high conversions after prolonged reaction times. However, they slowly leached from the polymers, allowing only nine catalytic cycles. The guanidines heterogenized on linear polystyrene with the use of a 'spacer-arm' (polymers III, IV), were less active. Polymer V, which is symmetrically substituted, showed an activity as high as polymer I. When another methyl group was introduced (polymer VI) its activity was slightly reduced. Furthermore, all polymers with a 'spacer-arm' suffered substitution reactions during the recycling experiments to form inactive hexasubstituted guanidinium compounds.



P = polymer chain

Figure 2.15 Molecular structures of some guanidine-containing polystyrene [21]

The lower activity of the guanidine-containing polymers I and II, when compared to their homogeneous analogues, is probably due to the hydrophobicity of the polymer chain which reduces the concentration of the methanol at the active sites. However, at prolonged reaction times, the efficiency of the anchored catalysts is practically the same. The use of a 'spacer-arm' (polymers III-VI) was expected to improve the performance of the heterogenized catalyst. However, polymer IV showed the same activity as polymer II and polymer III was even less active than polymer.

Despite less active than their homogeneous analogues, all polymer-containing guanidines could be reused in several consecutive reaction cycles. However, a loss of activity was observed, mainly due to leaching of the anchored base from the polymers, as mentioned above. Polymers I and II have the guanidine moiety bound to the benzylic CH_2 group of the polystyrene. After the protonation of the base, the electrophilic character of the methylene group is increased, thus becoming more susceptible to nucleophilic attack by methoxide ions present in the reaction medium. This attack results in the removal of the guanidine moiety from the polymer as shown in Fig.2.16. The leaching of the guanidines from the other polymers follows a similar mechanism.

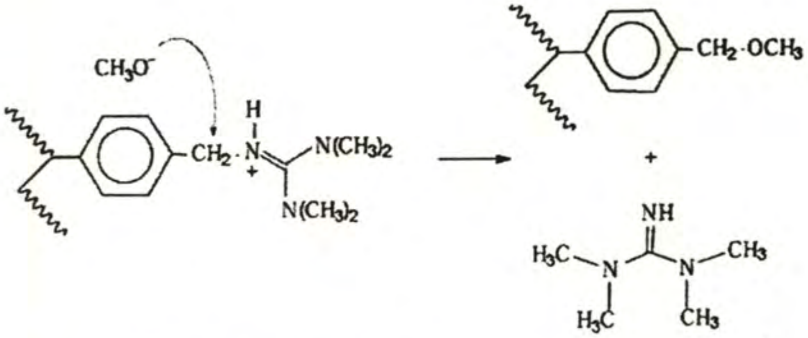


Figure 2.16 Leaching of the guanidine molety from the polymers [21]

For the polymers containing a 'spacer-arm', there is an additional factor that accelerates the deactivation of the supported catalysts. The anchored bases can react with electrophilic functional groups which are further away on the polymer chain, producing inactive hexasubstituted guanidinium compounds, as shown in Fig.2.17. However, it is possible to deprotonate these hexasubstituted guanidinium compounds, which should give doubly anchored active guanidines whose leaching is less probable.

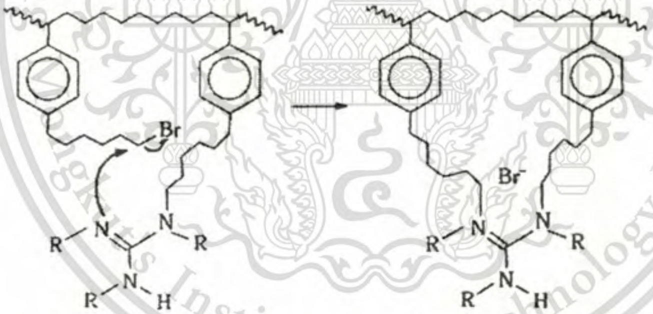


Figure 2.17 Reaction of the heterogenized guanidines III-VI with unreacted 6-bromohexyl substituenes [21]

In order to circumvent the leaching of the guanidines from the polymers, Schuchardt *et al.* encapsulate TCG by the reaction of dicyclohexylcarbodiimide and cyclohexylamine in the supercages of a hydrophobic Y zeolite. The encapsulated guanidine showed a good catalytic activity in the addition reaction of benzaldehyde to acetone. However, its activity in the transesterification of vegetable oils is low (14% conversion after 5 h), as the diffusion of the triglycerides through the channels of the Y zeolite is slow due to steric hindrance.

2.4 Chemical substances in Biodiesel production

2.4.1 General types of alcohol

2.4.1.1 Methanol [22]

Figure 2.18 Structure of methanol or methyl alcohol [22]

Methanol, also known as methyl alcohol, carbinol, wood alcohol, wood naphtha or wood spirits, is a chemical compound with chemical formula CH_3OH (often abbreviated MeOH). It is the simplest alcohol, and is a light, volatile, colourless, flammable, poisonous liquid with a distinctive odor that is somewhat milder and sweeter than ethanol (ethyl alcohol). At room temperature it is a polar liquid and is used as an antifreeze, solvent, fuel, and as a denaturant for ethyl alcohol. It is also used for producing biodiesel via transesterification reaction.

Methanol is produced naturally in the anaerobic metabolism of many varieties of bacteria. As a result, there is a small fraction of methanol vapor in the atmosphere. Over the course of several days, atmospheric methanol is oxidized by oxygen with the help of sunlight to carbon dioxide and water.

Properties: Melting point –97 °C, -142.9 °F (176 K)

Boiling point 64.7 °C, 148.4 °F (337.8 K)

2.4.2 Catalyses in biodiesel production

2.4.2.1 Sodium Hydroxide (NaOH) [23]

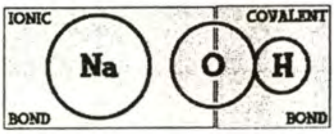


Figure 2.19 Structure of sodium hydroxide [23]

Sodium hydroxide (NaOH), also known as lye, caustic soda and (incorrectly, according to IUPAC nomenclature) as sodium hydrate, is a caustic metallic base. Sodium hydroxide forms a strong alkaline solution when dissolved in a solvent such as water. It is used in many industries, mostly as a strong chemical base in the manufacture of pulp and paper, textiles, drinking water, soaps and detergents and as a drain cleaner. Worldwide production in 1998 was around 45 million tonnes. Sodium hydroxide is the most used base in chemical laboratories.

Pure sodium hydroxide is a white solid; available in pellets, flakes, granules and as a 50% saturated solution. It is deliquescent and readily absorbs carbon dioxide from the air, so it should be stored in an airtight container. It is very soluble in water with liberation of heat. It also dissolves in ethanol and methanol, though it exhibits lower solubility in these solvents than potassium hydroxide. It is insoluble in ether and other non-polar solvents. A sodium hydroxide solution will leave a yellow stain on fabric and paper.

For the manufacture of biodiesel, sodium hydroxide is used as a catalyst for the transesterification of methanol and triglycerides. This only works with anhydrous sodium hydroxide, because combined with water the fat would turn into soap, which would be tainted with methanol. It is used more often than potassium hydroxide because it is cheaper and a smaller quantity is needed.

2.5 Important catalyst which is used in experiment

2.5.1 TiO_2- *Titanium Dioxide*

Figure 2.20 Titanium dioxide powders and Structure of Titanium dioxide [24]

2.5.1.1 History of TiO_2 [24], [25]

The element Titanium was discovered in 1791 by William Gregor, in England. Gregor spent much of his time studying mineralogy, which led him to his discovery. This happened when he discovered a sample of a black sandy substance in his neighborhood. He studied this substance and after he was assured that it was a mineral, he called it menachanite. Four years later a man named Martin H. Klaproth, recognized that there was a new chemical element in this mineral, he later named it Titanium after the Titans, which were humongous monsters that ruled the world in Greek mythology. Martin H. Klaproth was not able to make the pure element of titanium however; he was only able to produce TiO_2, or Titanium Dioxide.

Titanium dioxide (TiO_2) is a multifaceted compound. It's the stuff that makes toothpaste white and paint opaque. TiO_2 is also a potent photocatalyst that can break down almost any organic compound when exposed to sunlight, and a number of companies are seeking to capitalize on TiO_2's reactivity by developing a wide range of environmentally beneficial products, including self-cleaning fabrics, auto body finishes, and ceramic tiles. Also in development is a paving stone that uses the catalytic properties of TiO_2 to remove nitrogen oxide from the air, breaking it down into more environmentally benign substances that can then be washed away by rainfall. Other experiments with TiO_2 involve removing the ripening hormone ethylene from areas where perishable fruits, vegetables, and cut flowers are stored; stripping organic pollutants such as trichloroethylene and methyl-tert-butyl ether from water; and degrading toxins produced by blue-green algae. It remains to be seen, however, whether the formation of undesirable intermediate products during these processes outweighs the benefits offered by TiO_2's photocatalytic properties.

2.5.1.2 Crystal structureTiO_2 [25]

Titanium dioxide occurs in nature as the well-known naturally occurring minerals rutile, anatase and brookite, additionally two high pressure forms, the monoclinic baddeleyite form and the orthorhombic α -PbO_2 form have been found at the Ries crater in Bavaria. The most common form is rutile, which is also the most stable form. Anatase and brookite both convert to rutile upon heating. Rutile, anatase and brookite all contain six coordinates titanium. Additionally there are three metastable forms produced synthetically and five high pressure forms:

The TiO_2 group is composed of rutile, anatase, and brookite.

Figure 2.21 (a)The crystal structure of rutile , (b) The crystal structure of anatase and (c)The crystal structure of brookite.[26]

2.5.1.3 Production [25]

Crude titanium dioxide is purified via titanium tetrachloride in the chloride process. In this process, the crude ore (containing at least 90% TiO_2) is reduced with carbon, oxidized with chlorine to give titanium tetrachloride. This titanium tetrachloride is distilled, and re-oxidized with oxygen to give pure titanium dioxide.

Another widely used process utilizes ilmenite as the titanium dioxide source, which is digested in sulfuric acid. The by-product iron (II) sulfate is crystallized and filtered-off to yield only the titanium salt in the digestion solution, which is processed further to give pure titanium dioxide. Another method for upgrading ilmenite is called the Becher Process.

2.5.1.4 Chemical properties

Table 2.1 Properties of rutile, anatase and brookite TiO_2 [26]

Properties	Rutile TiO_2	Anatase TiO_2	Brookite TiO_2
Form.Wt.	79.890	79.890	79.890
Z	2	4	8
CrystalSystem	Tet	Tet	Orth
PointGroup	4/mmm	4/mmm	mmm
SpaceGroup	$P4_2/mnm$	$I4_1/amd$	Pbca
UnitCell			
a(Å)	4.5845	3.7842	9.184
b(Å)		5.447	
c(Å)	2.9533	9.5146	5.145
Vol.	62.07	136.25	257.38
MolarVol	18.693	20.156	19.377
Density	4.2743	3.895	4.123
Thermal Expansion (Volumetric)			
Alpha 28.9			
a_0 0.2890			

<u>As a photocatalyst</u> [25]

Titanium dioxide, particularly in the anatase form, is a photocatalyst under ultraviolet light. Recently it has been found that titanium dioxide, when spiked with nitrogen ions, or doped with metal oxide like tungsten trioxide, is also a photocatalyst under visible and UV light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. Titanium dioxide is thus added to paints, cements, windows, tiles, or other products for sterilizing, deodorizing and anti-fouling properties and is also used as a hydrolysis catalyst. It is also used in the Graetzel cell, a type of chemical solar cell.

As TiO_2 is exposed to UV light, it becomes increasingly hydrophilic; thus, it can be used for anti-fogging coatings or self-cleaning windows. TiO_2 incorporated into outdoor building materials, such as paving stones in noxer blocks or paints can substantially reduce concentrations of airborne pollutants such as volatile organic compounds and nitrogen oxides.

Photocatalyst: [24]

A substance that helps bring about a light-catalyzed reaction, such as chlorophyll in photosynthesis. Like photosynthesis, the reaction continues throughout the day once begun.

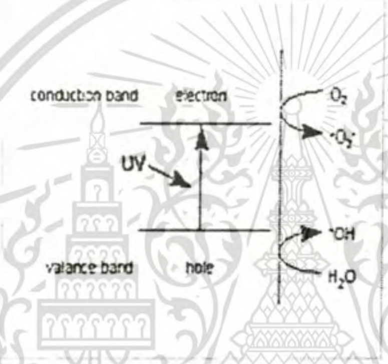


Figure 2.22 Mechanism of TiO_2 photocatalysis [24]

TiO_2 (titanium dioxide) is an oxide of the metal titanium which occurs naturally as a rutile in some acid igneous rocks and metamorphic rocks, and is also in sedimentary rocks and beach sands. TiO_2 (titanium dioxide) is found in heavy mineral sand deposits rutile and is often associated with a common titanium mineral, ilmenite, together with zircon, monazite and magnetite.

In air purification technology, a TiO_2 photocatalytic action is achieved when titanium dioxide is combined with a properly balanced light source and the moisture in the air. The result creates oxidizers that convert harmful microorganisms and chemicals that are constantly circulating through the air into harmless CO_2 (carbon dioxide, which is expelled during respiration) and H_2O (water).

2.5.2 Silver (Ag) [27]

Silver is a chemical element with the symbol "Ag"and atomic number 47. A soft, white, lustrous transition metal, it has the highest electrical conductivity of any element and the highest thermal conductivity of any metal. It occurs as a pure free metal (native silver) and alloyed with gold (electrum), as well as in various minerals, such as argentite and chlorargyrite. Most silver is produced as a by-product of copper, gold, lead, and zinc mining.

Silver has been known since ancient times and has long been valued as a precious metal, used to make ornaments, jewellery, high-value tableware and utensils (hence the term "silverware") and currency coins. Today, silver metal is used in electrical contacts and conductors, in mirrors and in catalysis of chemical reactions. Its compounds are used in photographic film and dilute solutions of silver nitrate and other silver compounds are used as disinfectants. Although the antimicrobial uses of silver have largely been supplanted by the use of antibiotics, further research into its clinical potential is in progress.

2.5.2.1 Characteristics [27]

Silver is a very ductile and malleable (slightly harder than gold) monovalent coinage metal with a brilliant white metallic luster that can take a high degree of polish. It has the highest electrical conductivity of all metals, even higher than copper, but its greater cost and tarnishability have prevented it from being widely used in place of copper for electrical purposes, though 13540 tons were used in the electromagnets used for enriching uranium during World War II (mainly because of the wartime shortage of copper). Another notable exception is in high-end audio cables.

Among metals, pure silver has the highest thermal conductivity (only the non-metal diamond's is higher), the whitest color, and the highest optical reflectivity (although aluminium slightly outdoes it in parts of the visible spectrum, and it is a poor reflector of ultraviolet light). Silver also has the lowest contact resistance of any metal. Silver halides are photosensitive and are remarkable for their ability to record a latent image that can later be developed chemically. Silver is stable in pure air and water, but tarnishes when it is exposed to air or water containing ozone or hydrogen sulfide. The most common oxidation state of silver is +1 (for example, silver nitrate: $AgNO_3$); in addition, +2 compounds (for example, silver (II) fluoride: AgF_2) and +3 compounds (for example, potassium tetrafluoroargentate: $K[AgF_4]$)

Figure 2.23 Electron shell diagram of silver [27]

Figure 2.24 Time trend of silver production [27]

2.5.2.2 Doping [44]

Doping is the process of intentionally introducing impurities into an extremely pure (also referred to as *intrinsic*) semiconductor in order to change its electrical properties. The impurities are dependent upon the type of semiconductor. Lightly and moderately doped semiconductors are referred to as *extrinsic*. A semiconductor which is doped to such high levels that it acts more like a conductor than a semiconductor is called *degenerate*.

Some do pants are generally added as the (usually silicon) boule is grown, giving each wafer an almost uniform initial doping. To define circuit elements, selected areas (typically controlled by photolithography) are further doped by such processes as diffusion and ion implantation, the latter method being more popular in large production runs due to its better controllability.

The number of dopant atoms needed to create a difference in the ability of a semiconductor to conduct is very small. Where a comparatively small number of dopant atoms are added (of the order of 1 every 100,000,000 atoms) then the doping is said to be low, or light. Where many more are added (of the order of 1 in 10,000) then the doping is referred to as heavy, or high. This is often shown as n+ for n-type dopant or p+ for p-type doping. A more detailed description of the mechanism of doping can be found in the article on semiconductors.

2.5.2.3 Prepare of nano powder by sol-gel method [44]

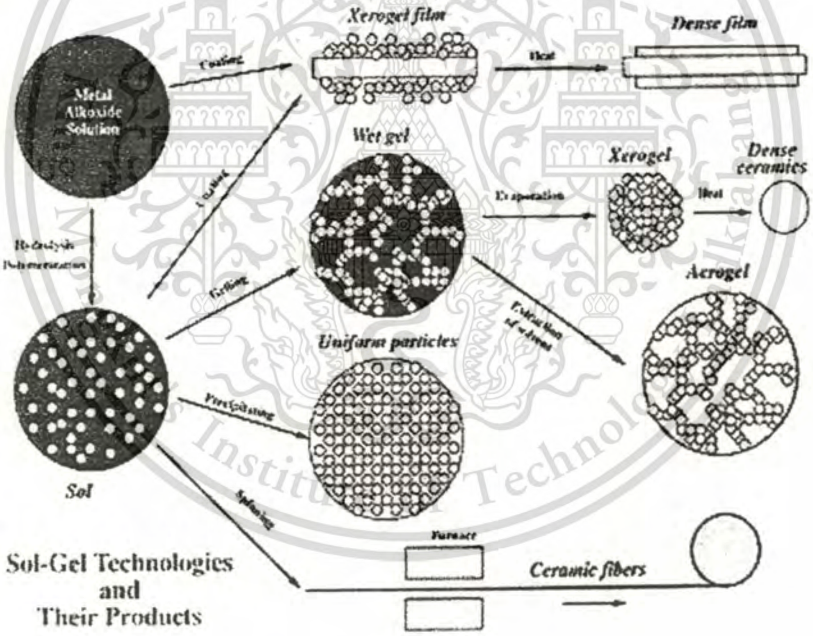


Figure 2.25 Sol-gel methods [44]

The sol-gel process is a versatile solution process for making advanced materials, including ceramics and organic-inorganic hybrids. In general, the sol-gel process involves the transition of a solution system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. Utilizing the sol-gel process, it is possible to fabricate advanced materials in a wide variety of forms: ultrafine or spherical shaped powders, thin film coatings, fibers, porous or dense materials, and extremely porous aerogel materials. An overview of various sol-gel processes is illustrated below in a graphical form.

The starting materials used in the preparation of the "sol" are usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, or a "sol". Further processing of the "sol" makes it possible to make materials in different forms.

Durable thin films with a variety of properties can be deposited on a substrate by spin-coating or dip-coating. When the "sol" is cast into a mold, a "wet gel" will form. With further drying and heat treatment, the "gel" is converted into dense materials. If the liquid in a wet "gel" is extracted under a supercritical condition, a highly porous and extremely low-density material called "aerogel" is obtained. As the viscosity of a "sol" is adjusted into a given viscosity range, fibers can be drawn from the "sol". Ultrafine and uniform powders are formed by precipitation, spray pyrolysis, or emulsion techniques.

In offering a Total Sol-Gel Solution, Chemat supplies precursors and equipment specifically suited for sol-gel processing, together with the R&D Services to assist customers in developing entire systems for production of unique advanced material.

2.6 Test Methods

2.6.1 X-ray Powder Diffraction (XRD) Instrument [28]

Fundamental Principles of X-ray Powder Diffraction (XRD)

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d\sin\theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

Figure 2.26 X-ray Powder Diffraction Instruments [28]

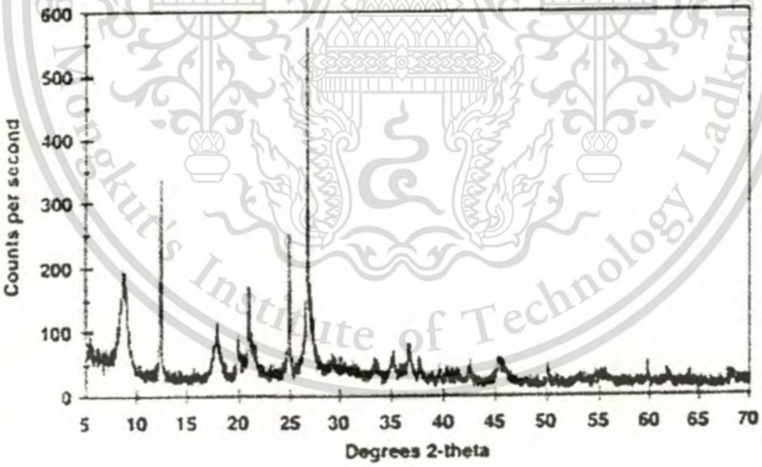


Figure 2.27 X-ray powder diffractogram. Peak positions occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacings derived from this patter can be used to 'fingerprint' the mineral [28]

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected.

A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.

2.6.2 Nuclear Magnetic Resonance Spectrometer [29], [30]

Figure 2.28 Nuclear Magnetic Resonance Spectrometer, Bruker Avance™ 300 MHz (^{1}H Frequency) NMR Instruments [29]

Nuclear magnetic resonance (NMR) is the name given to a physical resonance phenomenon involving the observation of specific quantum mechanical magnetic properties of an atomic nucleus in the presence of an applied, external magnetic field. Many scientific techniques exploit NMR phenomena to study molecular physics, crystals and non-crystalline materials through NMR spectroscopy. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI).

All nuclei that contain odd numbers nucleons have an intrinsic magnetic moment and angular momentum, in other words a spin > 0. The most commonly studied nuclei are ^{1}H (the most NMR-sensitive isotope after the radioactive ^{3}H and the stable ^{13}C nuclei), although nuclei from isotopes of many other elements (e.g. ^{2}H, ^{10}B, ^{11}B, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{23}Na, ^{29}Si, ^{31}P, ^{35}Cl, ^{113}Cd, ^{195}Pt) are readily studied by high-field NMR spectroscopy as well.

A key feature of NMR is that the resonance frequency of a particular substance is directly proportional to the strength of the applied magnetic field. It is this feature that is exploited in imaging techniques; if a sample is placed through a non-uniform magnetic field then the resonance frequencies of the sample's nuclei depends on where in the field they are located. Since the resolution of the imaging techniques depends on how big the gradient of the field is, thus many efforts are made to develop more powerful magnets, often using superconductors. The effectiveness of NMR can also be improved using hyper polarization, or using two-dimensional and three-dimensional imagines techniques.

The principle of NMR usually involves two sequential steps:

- The alignment (polarization) of the magnetic nuclear spins in an applied, constant magnetic field $\mathbf{H}_0$.
- The perturbation of this alignment of the nuclear spins by employing radio frequency (RF) photon pulse.

The two fields are usually chosen to be perpendicular to each other as this maximizes the NRM signal strength. The resulting response by the total magnetization (**M**) of the nuclear spins is the phenomenon that is exploited in NMR spectroscopy and magnetic resonance imaging. Both use intense applied magnetic fields ($\mathbf{H}_0$) in order to achieve high spectral resolution, the details of which are described by chemical shifts, the Zeeman effect, and Knight shifts (in metals). NMR phenomena are also utilized in low-field NMR, in NMR investigations of Earth's magnetic field (referred to as Earth's field NMR), and in several types of magnetometers.

2.6.3 Fourier Transform Infrared Spectrometer (FT-IR) [30], [31]

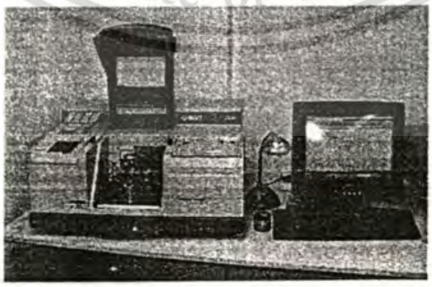


Figure 2.29 Fourier transform infrared (FTIR) spectrometer [30]

Fourier transform infrared (FTIR) spectroscopy is a measurement technique for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied (monochromator), the IR light is guided through an interferometer. After passing through the sample, the measured signal is the interferogram. Performing a mathematical Fourier transform on this signal results in a spectrum identical to that from conventional (dispersive) infrared spectroscopy.

FTIR spectrometers are cheaper than conventional spectrometers because building of interferometers is easier than the fabrication of a monochromator. In addition, measurement of a single spectrum is faster for the FTIR technique because the information at all frequencies is collected simultaneously. This allows multiple samples to be collected and averaged together resulting in an improvement in sensitivity. Because of its various advantages, virtually all modern infrared spectrometers are FTIR instruments.

2.7 Literature reviews

Thiam Leng Chew, Subhash Bhatia , Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery , Bioresource Technology journal homepage: www.elsevier.com/locate/biortech [32]

Biodiesel, produced from transesterification of vegetable oils or animal fats, is used in compression–ignition (diesel) engines. The heterogeneous catalysts such as zeolites. hydrotalcites, oxides, c-alumina, appears to be promising catalysts for transesterification of vegetable oil. There are number of solid heterogeneous catalysts reported for acid-catalyzed as well as alkali-catalyzed transesterification processes. Hence, there is still need of low cost efficient heterogeneous catalysts with high conversion in transesterification of vegetable oil to be explored. There is need of research to reduce the reaction time using proper technology with or without catalyst. Catalytic cracking of vegetable oils is one route to convert the vegetable oil or waste used cooking oil into gasoline and other hydrocarbons. The yields of hydrocarbon in catalytic cracking depend on the choice of shape selective catalyst as well as acidity of the catalysts. Mass and heat transfer in a reactor are essential in achieving the required reactor performance and thus these should be incorporated in the design of reactors. There is a need to integrate process operation, reactor and catalyst design to improve the effectiveness of different processes used for biofuels production in a typical biorefinery.

Ayhan Demirbas, Comparison of transesterification methods for production of biodiesel from vegetable oils and fats, Energy Conversion and Management 49 (2008) 125–130 [33]

Various vegetable oil transesterification methods are currently used in the production of biodiesel fuel. As an alternative fuel, vegetable oil is one of the renewable fuels. Chemically, biodiesel is a fatty acid (m)ethyl ester. Biodiesel plays an important role in meeting future fuel requirements in view of its ability to reduce emissions from Diesel engines for many air pollutant precursors, and the lower toxicity of the Diesel particulate matter emissions have an edge over conventional Diesel as they are obtained from renewable sources.

The parameters affecting the methyl esters formation are reaction temperature, pressure, molar ratio, water content and free fatty acid content. It is evident that at a subcritical state of alcohol, the reaction rate is very low and gradually increases as either the pressure or temperature rises. It was observed that increasing the reaction temperature, especially to supercritical conditions, had a favorable influence on the yield of ester conversion. The yield of alkyl ester increased with increasing molar ratio of oil to alcohol.

Joelianingsiha,b,c,e, Hitoshi Maedaa,c, Shoji Hagiwaraa, Hiroshi Nabetania,_Yasuyuki Sagarac, Tatang H. Soerawidjayad, Armansyah H. Tambunane, Kamaruddin Abdullahe , Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure: A kinetic study , Renewable Energy 33 (2008) 1629–1636 [34]

Transesterification of palm oil with superheated MeOH vapor has been carried out at 523–563K reactor temperature under atmospheric pressure in the absence of a catalyst. Evaluation on the reaction kinetic based on changes of the uME concentration shows that reaction rate constant at 523, 543 and 563K was 0.0034, 0.0051 and 0.0056 min_1, respectively, activation energy was 31 kJ/mol, and frequency factor was 4.2. The rate constant, conversion and yield of ME showed an increase trend with the reaction temperature, but the ME content in the reaction product decreased as the reaction temperature was increased. The optimum reaction temperature which gives the highest ME content (95.17% w/w) was 523 K, while the rate constant of the total system increased as the reactiontemperature was increased. Experimental results indicated that in order to increase process efficiency showed by the value of rate constant, conversion and yield of ME the interfacial area of gas–liquid phase should be enlarged.

Michael K. Seery a, Reenamole George a, Patrick Floris a, Suresh C. Pillai b , Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis , Journal of Photochemistry and Photobiology A: Chemistry 189 (2007) 258–263 [35]

This paper describes the synthesis of TiO_2 containing different amounts of silver metal by the sol–gel route. The synthetic method where the silver nitrate was not reduced by light before calcination resulted in a slightly more efficient photocatalysis over that which did. All materials with added silver showed visible light activation in both the Q-Sun solar simulator and Dublin sunlight, with the activity increasing with increasing amounts of silver.

Chia-Hsin Li , Yung-Hsu Hsieh, Wan-Ting Chiu, Chin-Chuan Liu, Chao-Lang Kao , Study on preparation and photocatalytic performance of Ag/TiO2 and Pt/TiO2 photocatalysts , Separation and Purification Technology 58 (2007) 148–151 [36]

In this study, the TiO_2 film was deposited on the internal surface of the pyrex glass tubes by the CVD technique and then modified with the photoreduction method. Based on the results of the orthogonal array test, the optimal condition in terms of photocatalytic degradation efficiency of salicylic acid, for the preparation of both the Ag/ TiO_2 and the Pt/ TiO_2 photocatalysts were 1.5mM of silver or platinum ion concentration,3.0mWcm—2 of light intensity. But irradiation time were 4 h for the Ag/ TiO_2 and 8 h for the Pt/ TiO_2. The results of XRD and SEM–EDX analyses suggested that the photoreduction deposition method did indeed deposit silver and platinum on the surface of the TiO_2 catalysts and that the crystal structure of the photocatalysts remained in the anatase form after modification. Results of photocatalytic experiments indicated that high pH and low initial concentrations of salicylic acid led to high removal efficiencies. The formation of the intermediate products, 2,5- DHBA and 2,3-DHBA, was observed. 2,5-DHBA concentration was higher than 2,3-DHBA concentration except at pH 11.

L.A. Brook, P. Evans, H.A. Foster, M.E. Pemble 1, A. Steele, D.W. Sheel , H.M. Yates , Highly bioactive silver and silver/titania composite films grown by chemical vapour deposition , Journal of Photochemistry and Photobiology A: Chemistry 187 (2007) 53–63 [37]

Silver molecules can be oxidised at the silver/titania interface, we have designed the multi-layer system to incorporate diffusion based replenishment capability, thus giving the potential for extended activity. It is interesting to note that atomic absorption measurements of the bacteria solutions above the films showed concentrations below 1 ppm (atomic abs. detection limit). The Ag– TiO_2 film has "dual activity" and "dual functionality". The film dual biocidal activity comes from both Ag toxicity to bacteria, and also from the photo-activity of the TiO_2. The dual functionality comes from combining Ag derived bio-activity along with the self-regeneration capability of the photo-active TiO_2.

Qilin Cheng a,b, Chunzhong Li a, Vladimir Pavlinek b,Petr Saha b, Huanbing Wang a , Surface-modified antibacterial TiO2/Ag+ nanoparticles: Preparation and properties , Applied Surface Science 252 (2006) 4154–4160 [38]

APS-grafted antibacterial TiO_2 /Ag+ nanoparticles were prepared and tested by various methods with the following conclusions:APS is chemically bonded on the surface of inorganic particles, the layer thickness being ca 25 nm., Surface treatment of the particles does not deteriorate antibacterial properties of TiO_2 /Ag+nanoparticles,Surface modification can assure better affinity of the particles to organic matrix, in our case PVC.

Ayato Kawashima *, Koh Matsubara, Katsuhisa Honda, Development of heterogeneous base catalysts for biodiesel production, Bioresource Technology 99 (2008) 3439–3443 [39]

Investigations were conducted on heterogeneous base catalysts for the transesterification of oil aimed at effective production of biodiesel. Thirteen different kinds of metal oxides containing calcium, barium, magnesium, or lanthanum were prepared as catalysts. Their catalytic activities were tested for transesterification at 60 _C with a 6:1 molar ratio of methanol to oil and a reaction time of 10 h. The calcium-containing catalysts – CaTiO3, CaMnO3, Ca2Fe2O5, CaZrO3, and CaO–CeO2 – showed high activities and approximately 90% yields of methyl ester. Furthermore, catalytic durability tests were performed by repeating the transesterification reaction several times with the calcium-containing catalysts recovered from the previous reaction mixture. It was found that CaZrO3 and CaO–CeO2 show high durability and have the potential to be used in biodiesel production processes as heterogeneous base catalysts.

Rusiene M. de Almeida a,*, Lu´ cia K. Noda b, Norberto S. Gonc¸alves b,Simoni M.P. Meneghetti a, Mario R. Meneghetti a , Transesterification reaction of vegetable oils, using superacid sulfated TiO2–base catalysts, Applied Catalysis A: General 347 (2008) 100–105 [40]

Superacid sulfated titania catalyst, TiO2/SO4 (TS-series), have been prepared via the sol–gel technique, with different sulfate concentrations. The relation of structure and catalytic activity of the prepared material have been evaluated. The obtained material was characterized by several techniques, as infrared and Raman absorption spectroscopy, pyridine-adsorption infrared spectroscopy, thermogravimetric analyses and obtention of N2 adsorption–desorption isotherms. The catalyst that exhibits the highest catalytic activity in the methanolysis of soybean and castor oils at 120 8C, for 60 min (40% and 25%, respectively) was that which displayed the highest specific surface area, average pores diameter and pore volume, and highest percentage in sulfate groups (TS-5).

B. Bonelli a,b, M. Cozzolino c, R. Tesser c, M. Di Serioc, M. Piumetti a, E. Garrone a,b,E. Santacesaria c, Study of the surface acidity of TiO2/SiO2 catalysts by means of FTIR measurements of CO and NH3 adsorption, Journal of Catalysis 246 (2007) 293–300 [41]

Samples were prepared by grafting different amounts of titanium isopropoxide (Ti(O–Pr*i*)4) onto silica surface in N2 atmosphere, followed by steam hydrolysis and calcination. Either dioxane or toluene was used as a solvent. The surface properties of TiO2/SiO2 catalysts were studied by means of FTIR spectroscopy of adsorbed probe molecules, CO, and ammonia. Adsorption of CO at nominal 77 K exhibited different surface sites: (i) two families of Ti4+ cations, namely associated and isolated sites, with bands in the 2183–2194 and 2173–2177 cm□1 ranges respectively, shifting with coverage; (ii) surface Si–OH groups; and (iii) at titanium loadings >8 wt%TiO2, corresponding to the alkoxide monolayer coverage of silica, TiOH species exhibiting an acidity higher than expected probably due to interaction with the support. With increasing the titanium loading, the band at 2176 cm 1 disappears, indicating that associated Ti4+ sites form at the expense of isolated ones. Adsorption of ammonia at room temperature confirms the data obtained with CO. The use of apolar solvents seems to cause anchoring of the Ti alkoxide on the dehydrated portions of the silica surface, with consequences for the final state of the catalyst. In agreement with this observation, activity was lower for catalysts prepared in toluene than in those prepared using dioxane. Prepared catalysts were rather effective in the transesterification of refined oils with methanol.

Bao-Xiang Peng, Qing Shu, Jin-Fu Wang, Guang-Run Wang, De-Zheng Wang, Ming-Han Han, Biodiesel production from waste oil feedstocks by solid acid catalysis, process safety and environment protection 8 6 (2 0 0 8) 441–447 [42]

Biodiesel is a non-toxic and biodegradable substitute for petroleum-based diesel. However, it is impractical to use refined edible oils to produce biodiesel due to its high cost and priority for food products, especially in China, while waste oils with high free fatty acids (FFAs) can be considered as the raw materials. In the present work, a solid acid catalyst comprising SO4/TiO2–SiO2 was prepared, characterized and studied for its activity for the production of biodiesel from several low cost feedstocks with high FFAs. The solid acid catalyst can be recycled, easily removed and can simultaneously catalyze esterification and transesterification. The influence of reaction parameters was studied, and the optimized reaction parameters are reaction temperature 200 °C, molar ratio of methanol to oil 9:1 and catalyst concentration 3 wt.%. The catalyst showed good stability. A continuous process for biodiesel production from cheap raw feedstocks was proposed, and a 10,000-tonnes/year biodiesel production demonstration plant has been built.

Chapter III

Experimental

3.1. Materials

1. NaOH, Italma Company Limited.
2. Waste Vegetable Oil obtained from the KAI –TOD- HAD-YAI restaurant.
3. Methanol 99.8% Molecular Weight 32.04, Density 0.792g/cc,

   . Boiling Point 64.7 ° C
4. 2-propanal, ($CH_3CH(OH)CH_3$) Merek company.
5. Glacial Acitic acid, CH_3COOH Carlo ERBA company .
6. Acetylacetone,($C_5H_8O_2$) 2 ml.
7. Titanium (IV) isopropoxide ($C_{12}H_{28}O_4$) 97% Aldrich company.
8. Silver (I) nitrate ($AgNO_3$) 99.9% Merck company.
9. Distillation water.
10. Paraffin
11. acetone, Fisher scientific company (CH_3COCH_3) Mw.58.08

3.2. Equipments and test method

1. Laboratory glass wares.
2. Hot plate, Fisher scientific company.
3. Mortar.
4. Aluminum foil.
5. Stirrer.
6. Magnetic stirrer bar.
7. Furnace 6000 model, Thermolyne Company.
8. Oven Isotemp model, Fisher scientific company.
9. X-ray diffraction (XRD, Brucker AXs GmbH) D8 Advance model.

10. Scale Denver Instrument TC-254 model.
11. NMR spectroscopy, Bruker 300 MHz/52mm Ultra shield
12. Fourier Transform Infrared Spectrometer, spectrum GX, Perkin Elmer instrument Ltd
13. Centrifuge, Centurion 1000 series ,Mfr : centurion sciencetific Ltd
14. Heating Mantle, Glas-col , Terre haute in USA
15. Aspirator A-35, Eyela Tokyo rikakikai Co,Ltd
16. Filter paper quantitative ashless 5A, 70mm 100circles, Tokyo Roshi kaisha Ltd, Japan
17. Protector Laboratory hood, science technology
18. UV-Visible reactor

3.3. Experimental procedure

Part I: Treatment of waste vegetable oil and preparation a TiO_2/Ag catalyst

3.3.1. Treatment of waste vegetable oil

1. Waste vegetable oil is filtered withfilter cloth.
2. Heating the filtered oil to approximately 120°C to remove water.
3. Allow to cool the mixture.

3.3.2 Preparation a TiO_2/Ag catalyst [44]

1. Blend an isopropanal 50 ml with 10 ml of acetic acid and 2 ml acytylacetone in a 100 ml volumetric flask.
2. Pipet Titanium (IV) isopropoxide about 3.0686 and Siver nitrate 0.017 ml to the mixer in 100 ml volumetric flask.
3. Adjusts to 100 ml with isopropanal.
4. Stirred on hot plate with magnetic bar and control temperature at 50°C for 30 min.
5. Leave in temperature room for 6 hours and then dry on the oven at 100°C for 24 hours.
6. Calcining at 400°C for 2 hours.
7. Grinding the catalyst with a mortar.
8. Analysis with XRD method.

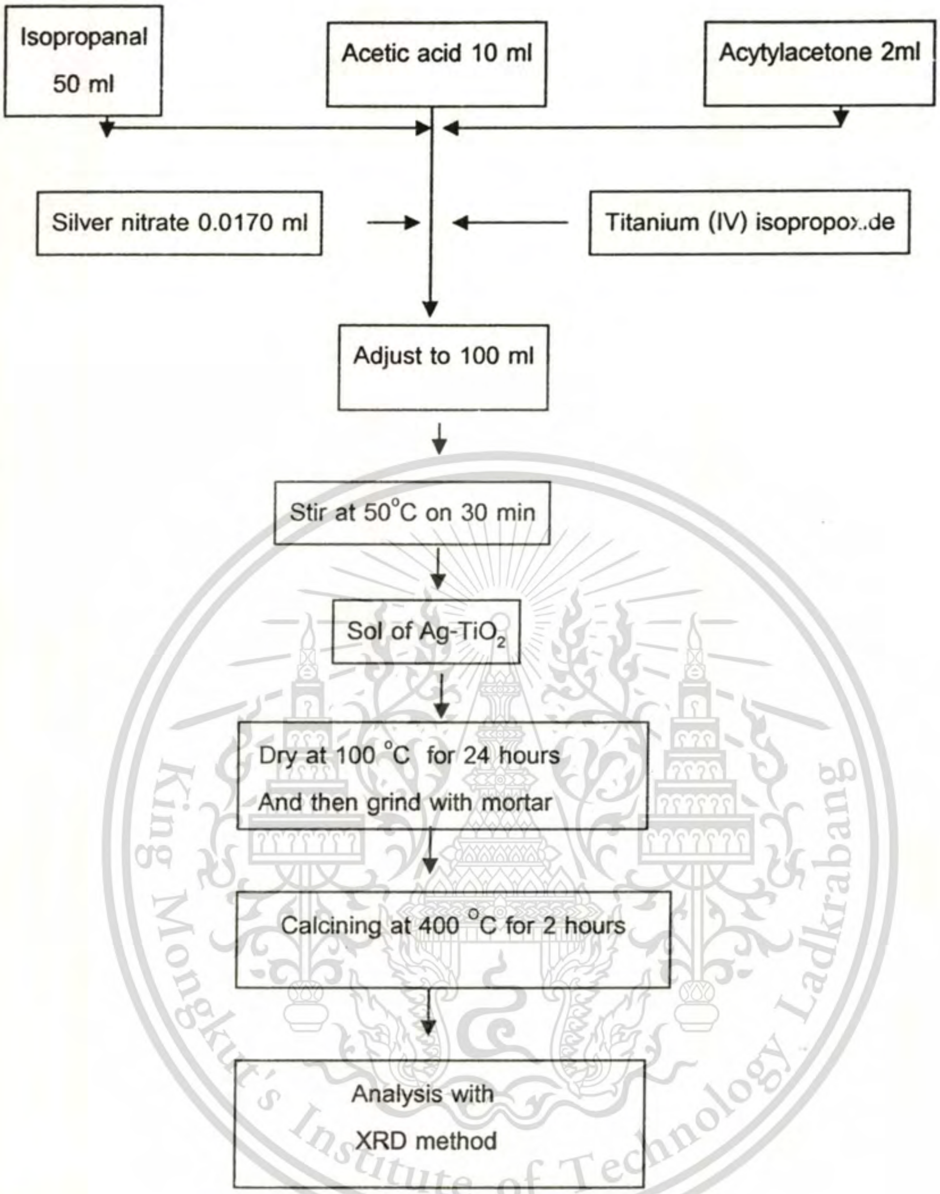


Figure 3.1 Flow chart of TiO_2/Ag preparation [44]

Figure 3.2 TiO_2/Ag catalysts

Part II: production of biodiesel

3.3.3. Production of biodiesel which using NaOH catalyst

1. Calculated 40 ml of Methanol, 90 ml of the WVO and 0.6 g of NaOH to 1% by weight per volume of WVO in g/ml.
2. Add 0.6 g of NaOH to methanol.
3. Heat the WVO up to 45-50 °C.
4. Pour methanol/NaOH (Methoxide solution) to the WVO at 50 °C for 1 hour.
5. Leave Biodiesel and after 10 minutes the glycerin or "soap" will settle from mixture.
6. Take a day or two day for the Biodiesel to completely separate.
7. See two defined layers - the Biodiesel and the glycerin. Then drain off glycerin layer out. Now remove the Biodiesel from the container leaving the glycerin and that are ready for the wash.

7. Pour 90 ml of biodiesel into 500 ml separation funnel and Add 100 ml of water
8. Shake it for about 10 seconds. Water and Biodiesel will separate immediately and then drain off the water layer.
9. Wash for four times or if the washing has been completed successfully the water should be neutron (pH 7.0)

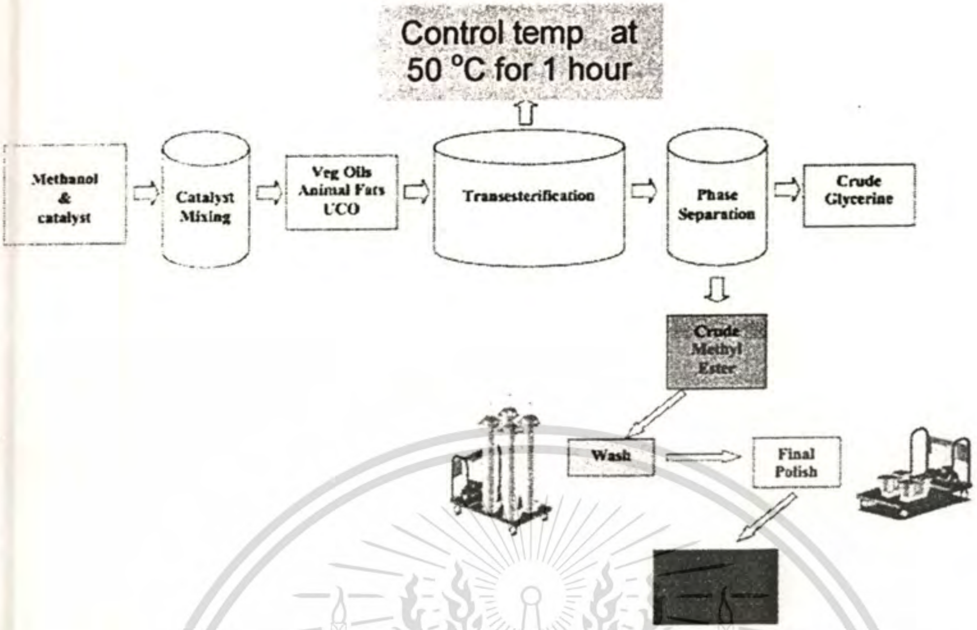


Figure 3.3 Simple flow diagram of biodiesel production [43]


(a) (b)

Figure 3.4 (a) waste vegetable oil, (b) biodiesel with NaOH catalyst

3.3.4 Production of biodiesel with TiO_2/Ag catalyst by heat treatment with various reaction times

1. Molar ratio of methanol / oil / catalyst at 120 : 20 : 1 are calculate into stoichiometric volume. [40]

2. Add 10 ml to WVO in 500 ml three-neck flask then heat up to 60°C.

3. Pour the catalyst (TiO_2/Ag) to the methanol then stir by stirrer rod. After that, pour its into the three-neck flask which is contained filter waste vegetable oil and heat it up to 120° C.

4. Do the experiment for 3 times: 1hour, 2hours and 3 hours.

5. Take a day for the biodiesel to separate completely.

6. If the biodiesel is not separate, it can be done by centrifugation for separation catalyst and product from biodiesel production.

7. Take the biodiesel from centrifugation to filter by aspirator and to characterize it by NMR spectrometer and Fourier Transform Infrared Spectrometer to calculate yield percentage of biodiesel.

8. Filtration of TiO_2/Ag catalyst by using filter paper 5A,70 mm in aspirator machine. Next, washing by acetone for 5 times (10 ml per time) , to dry its up to 80° C for 2 hours. Finally, to check the purity by X-ray powder diffraction.

(a) (b)

Figure 3.5 (a) waste vegetable oil, (b) the product from biodiesel production with TiO_2/Ag catalyst by hot plate (heat treatment) for 1 hour and 2, 3 hours.

3.3.5 Production of biodiesel with TiO_2/Ag catalyst by using heating mantle with various reaction times

1. To set an apparatus. Then to put the three-neck flask which is connected with condenser and thermometer on heating mantle. The heat is generated by heating mantle using condenser to condense the hot oil and hot methanol vapors and using the molar ratio of methanol/ oil/ catalyst are 60 ml /10 ml / 0.5 g respectively.

2. Heating the filtered waste vegetable oil (WVO) to 60° C in the three-neck flask

3. Pour the catalyst (TiO_2/Ag) to the methanol then stir by stirrer rod. After that, pour its into the three-neck flask which is contained filter waste vegetable oil and heat it up to 120° C

.

4. Do the experiment for 3 times: 1hour, 2hours and 3 hours.

5. Take a day for the biodiesel to separate completely.

6. If the biodiesel is not separate, it can be done by centrifugation.

7. Take the biodiesel from centrifugation to filter by aspirator and to calculate percentage of yield and to check it by NMR spectrometer and Fourier Transform Infrared Spectrometer.

8. Take the TiO_2/Ag catalyst from centrifugation that mixed with methanol to recovery by means of boiling 60° C for 30 minutes to evaporate methanol out ,and filtration of TiO_2/Ag catalyst by using filter paper 5A,70 mm in aspirator machine. Next, washing by acetone for 5 times (10 ml per time) , to dry its up to 80° C for 2 hours. Finally, to check the purity by X-ray powder diffraction again.


(a) (b)

Figure 3.6 (a) waste vegetable oil, (b)) the product from biodiesel production with TiO_2/Ag catalyst by heating mantle for 1 hour.

3.3.6 Production of biodiesel with TiO_2/Ag catalyst by using UV-Visible reactor with various the weight of TiO_2/Ag catalyst

1. All reaction was performed in 10 hours at 120° C, using a methanol/oil/catalyst;

60 ml / 10 ml / 0.25 g for first volumetric flask (100ml)

60 ml / 10 ml / 0.50 g for second volumetric flask (100ml)

60 ml / 10 ml / 0.75 g for third volumetric flask (100ml)

2. Leave the mixture under UV-VIS reactor and stir it for 10 hours.
3. Then, separate catalyst and biodiesel product from biodiesel production by centrifugation.
4. When the centrifugation was finished, take the top layer (biodiesel layer) to filter by aspirator with filter paper 5A ,70 mm.
5. Check the biodiesel by NMR spectrometer and Fourier Transform Infrared Spectrometer.
6. Filtration of TiO_2/Ag catalyst by using filter paper 5A,70 mm in aspirator machine. Next, washing by acetone for 5 times (10 ml per time) , to bake its up to 80° C for 2 hours. Finally, to check the purity by X-ray powder diffraction.

(a) (b)

Figure 3.7 (a) waste vegetable oil and (b) the product from biodiesel production with 0.25, 0.50 and 0.75 g of TiO_2/Ag catalyst for 10 hours.

3.4 Test Method [8]

3.4.1 Litmus paper

Test proceeding water with Litmus paper until the water is neutralization (PH 7).

Figure 3.8 Hydrion pH Strips in Vials

3.4.2 X-ray Powder Diffraction Instrument (XRD) [28]

We use X-ray Powder Diffraction (XRD) for analysis a catalyst. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

- Determine crystal structures using Rietveld refinement
- Determine of modal amounts of minerals (quantitative analysis)

Characterize thin films samples by:

- Determining lattice mismatch between film and substrate and to inferring stress and strain
- Determining dislocation density and quality of the film by rocking curve measurements
- Measuring super lattices in multilayered epitaxial structures
- Determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurement.

Figure 3.9 X-ray Powder Diffraction (XRD) [28]

3.4.3 Nuclear Magnetic Resonance Spectrometer (NMR spectrometer) [29]

We use Nuclear Magnetic Resonance Spectrometer (NMR spectrometer) to identify the information and we also know the yield percentage of biodisel product also.

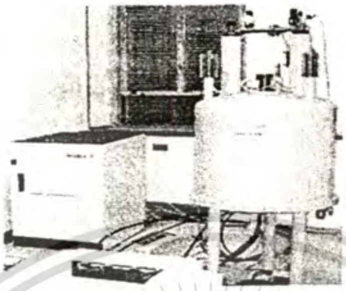


Figure 3.10 Nuclear Magnetic Resonance Spectrometer, Bruker Avance™ 300 MHz (^{1}H Frequency) NMR Instrument [29]

3.4.4 Fourier Transform Infrared spectrometer (FT-IR) [30], [31]

FT-IR is used for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied (monochromator), the IR light is guided through an interferometer. After passing through the sample, the measured signal is the interferogram. Performing a mathematical Fourier transform on this signal results in a spectrum identical to that from conventional (dispersive) infrared spectroscopy.

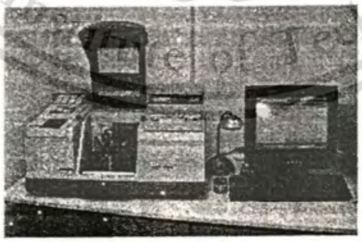


Figure 3.11 Fourier Transform Infrared Spectrometer, spectrum GX, Perkin Elmer instrument Ltd [30]

Chapter IV

Results and Discussion

The objectives of this experiment to study the biodiesel production which using titanium doped silver for improvement the production of biodiesel. The variable of this experiment is compared with three methods; (1.)Reflux System by hot plate, (2.)Reflux System by heating mantle and (3.)UV-Visible reactor. The Nuclear Magnetic Resonance (NMR) Spectroscopy instrument and Fourier Transform Infrared (FT-IR) Spectrometer were used to analysis these methods.

4.1 Analysis of raw material (Waste vegetable oil or WVO)

The raw material of this experiment was waste vegetable oil from Kai- Tod- Had –Yai restaurant. The raw material was analyzed by Nuclear Magnetic Resonance Spectroscopy Instrument (NMR) and Fourier Transform Infrared Spectrometer (FT-IR).

Figure 4.1 Waste vegetable oil

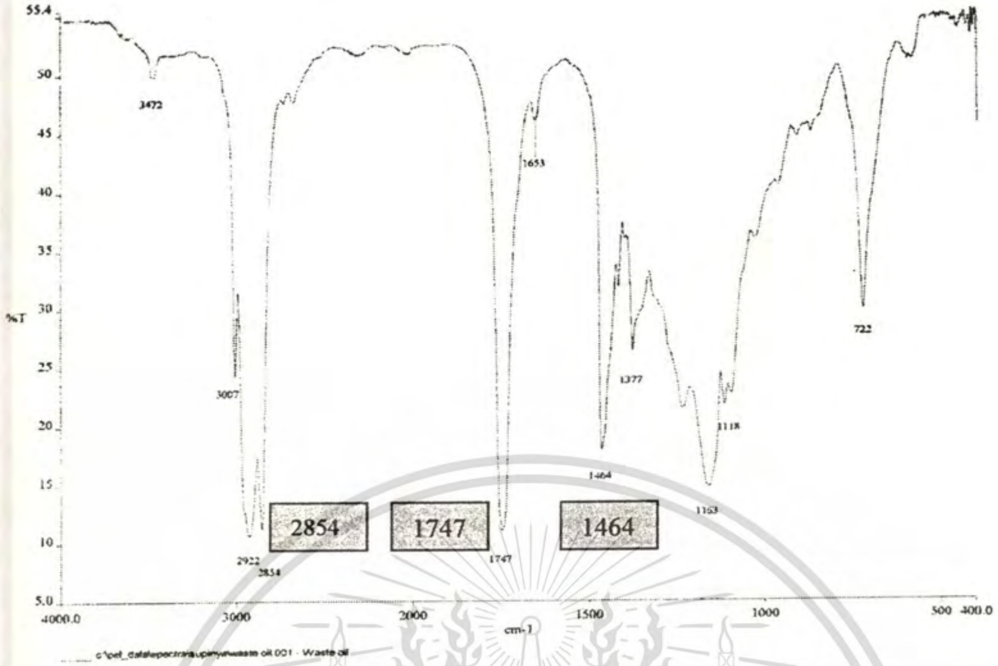


Figure 4.2 Waste vegetable oil, checked by Fourier Transform Infrared Spectrometer.

From the Figure 4.2 the gap spectrum in the raw material or WVO before reaction have a spectrum at 1744 cm^{-1} as C=O and at 2854 cm^{-1}as functional class of alkane CH_3, CH_2 and CH stretching, and1464 cm^{-1} is functional class of CH_2 stretching. Hence, it can be concluded that the structure of waste vegetable oil is a triglyceride. For the structure of biodiesel is Alkyl ester R-(C= O)-O-R'. Hence, the product of biodiesel should have peak at 1195 cm^{-1} for O-CH_3. [47]

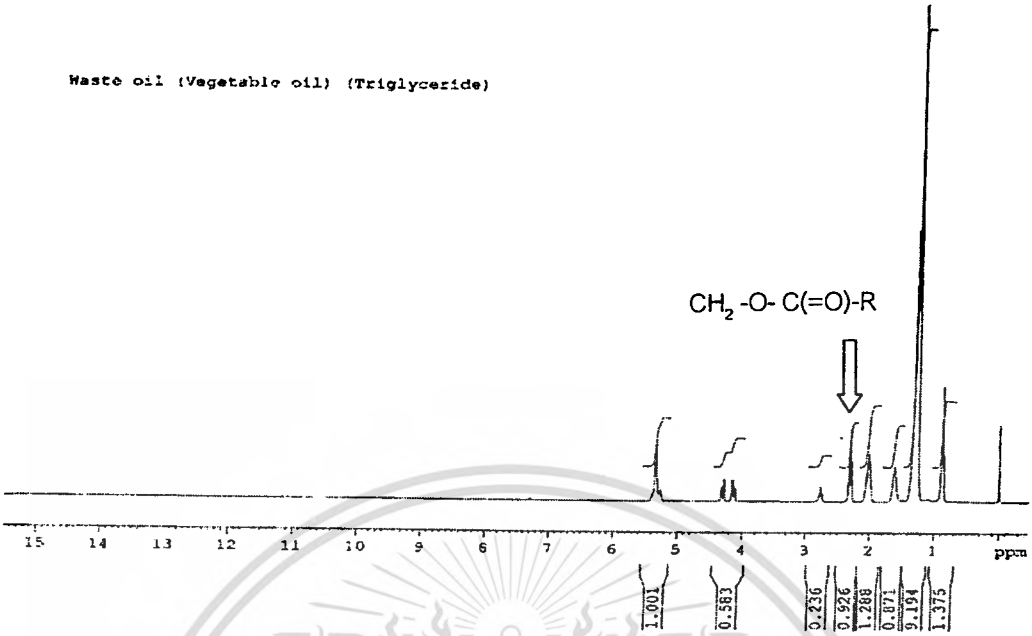


Figure 4.3 Waste vegetable oil, checked by Nuclear Magnetic Resonance Spectroscopy Instrument

From the Figure 4.3 has an important signal at 2.3 ppm which is corresponding to CH_2 -O- C(=O)-R but it is not appeared the signal at 3.7 ppm which is corresponding to CH_3-O. The signal at 4.1-4.4 ppm showed the proton signal from CH_2 of triglyceride. From this results, it was encouraged the results from FT-IR that the structure of raw material or WVO had only triglyceride.

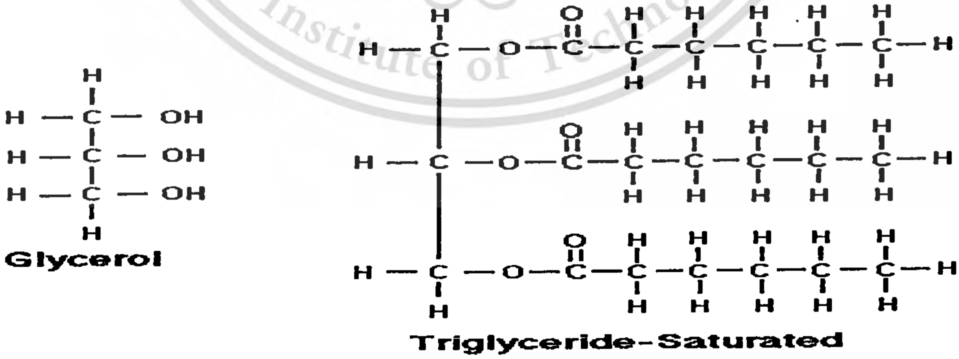


Figure 4.4 The structure of glycerol and triglyceride-saturated [8]

4.2 Analysis of the biodiesel with NaOH as a catalyst

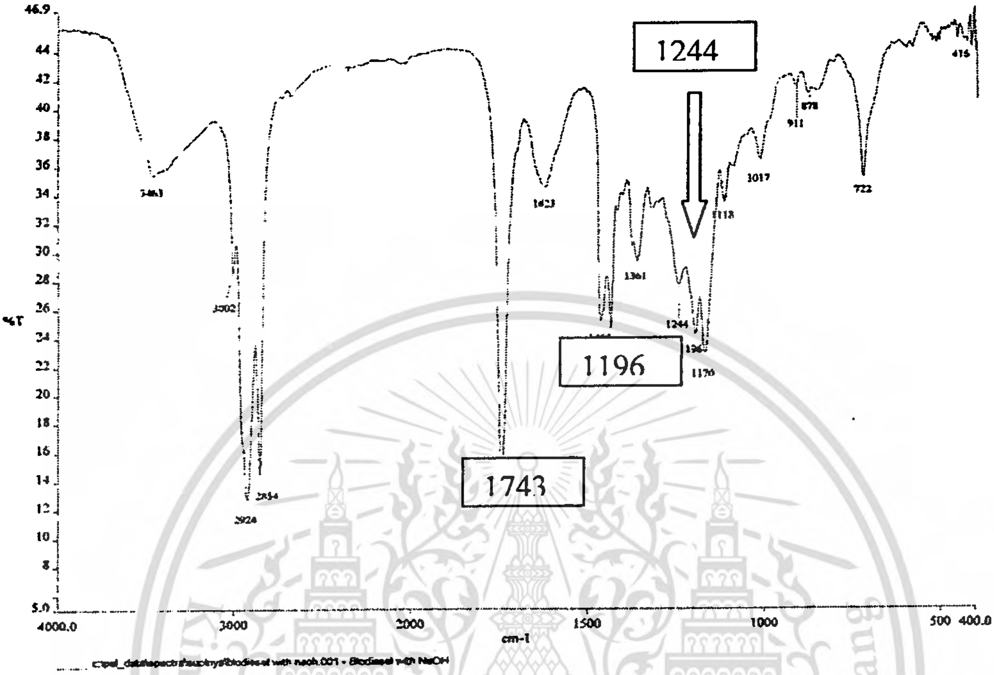


Figure 4.5 The product from biodiesel production with NaOH catalyst, checked by Fourier Transform Infrared Spectrometer.

From the Figure 4.5 the important peak at 1743 cm^{-1} is C=O and the peak at 2854 cm^{-1} is functional class of alkanes CH_3, CH_2 and CH stretching. The peak at 1464 cm^{-1} is functional class of CH_2 stretching and peek at1195 cm^{-1} for O-CH_3 functional. From the results, the structure of this sample was corresponding to R (C=O)-OCH_3. [47]

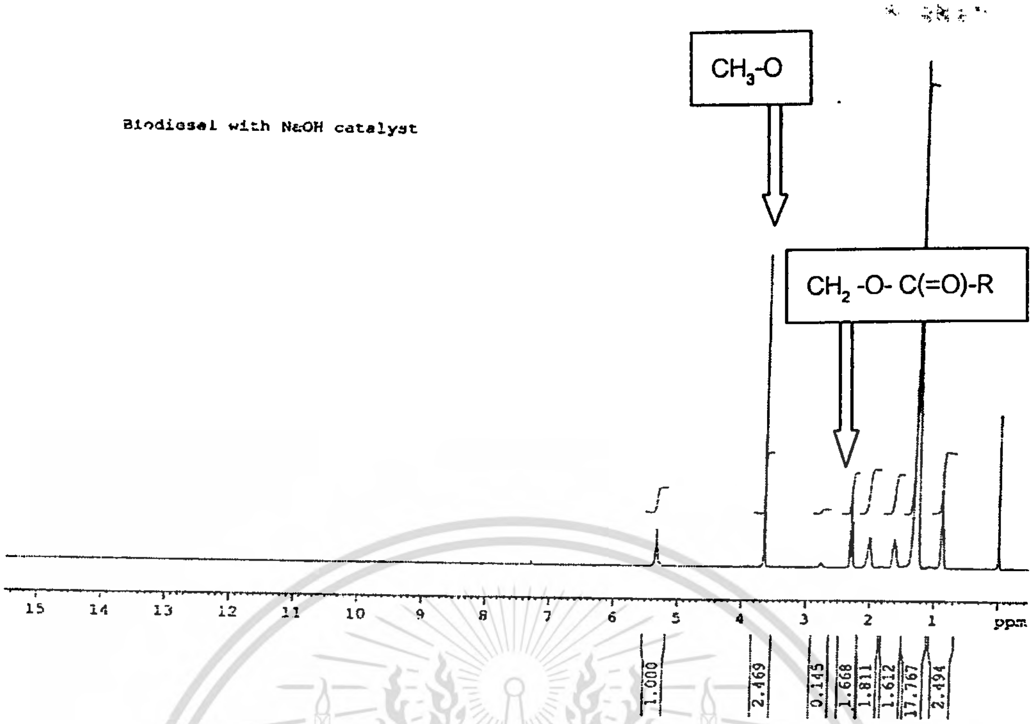


Figure 4.6 The product from biodiesel production with NaOH catalyst, checked by Nuclear Magnetic Resonance Spectrometer.

From the figure 4.6, the important peak at 2.3 ppm is CH_2 -O- C(=O)-R and the peak at 3.7 ppm is CH_3-O functional. Hence, the structure of this sample is R (C=O)-OCH_3 that shown in figure 4.7. From the results can verify that NaOH catalyst was accomplished for biodiesel production. [47]

Calculation % yield of Methyl Ester [47] = (2.469/1.668) (2/3) (100)

= 98.68 %

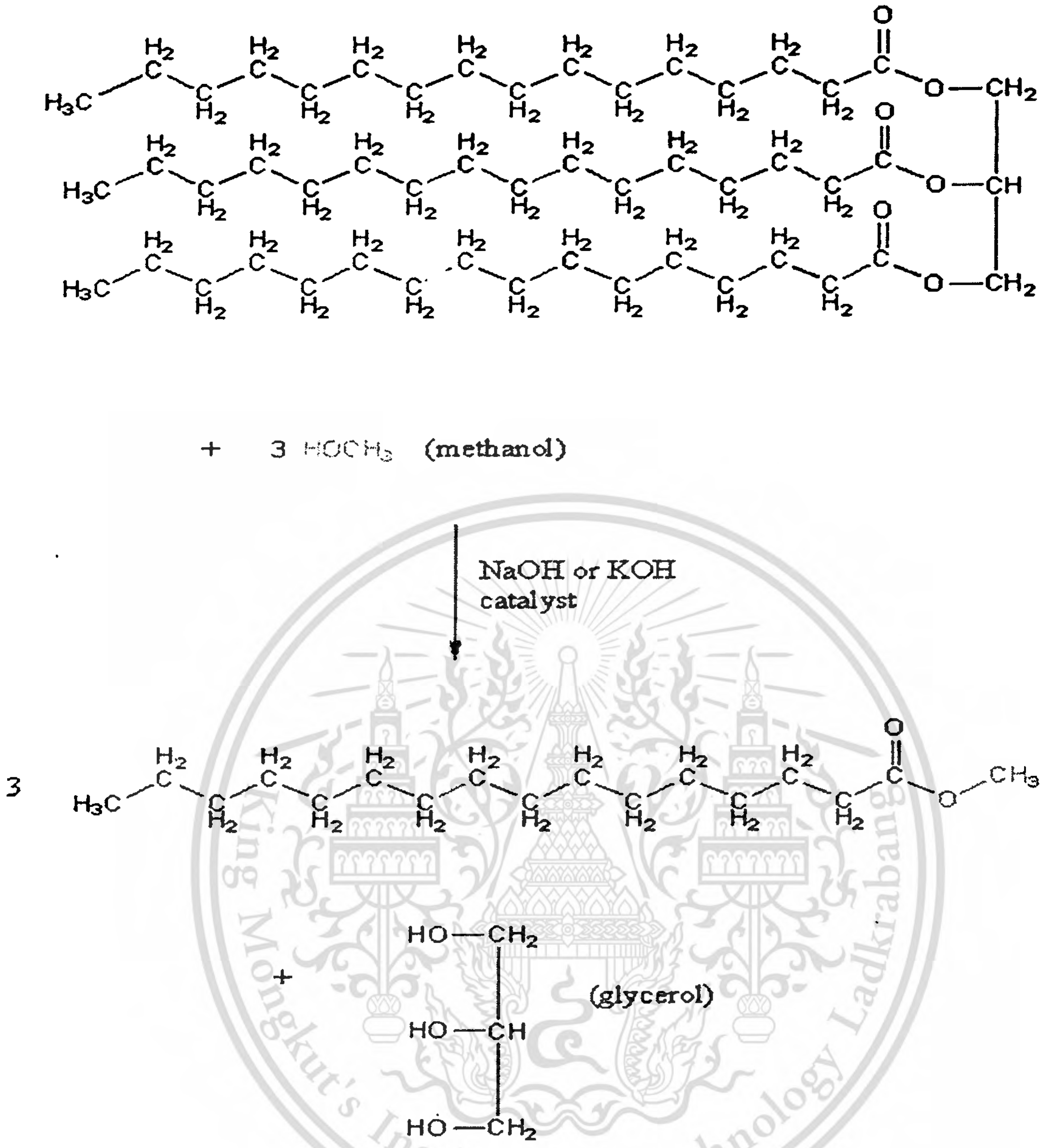


Figure 4.7 Transesterification reaction of triglyceride reacts with methanol which using NaOH as a catalyst to produce biodiesel product (methyl ester) and glycerol [47]

4.3 Analysis of the products from biodiesel production with TiO_2/Ag catalyst by heat treatment with various reaction times

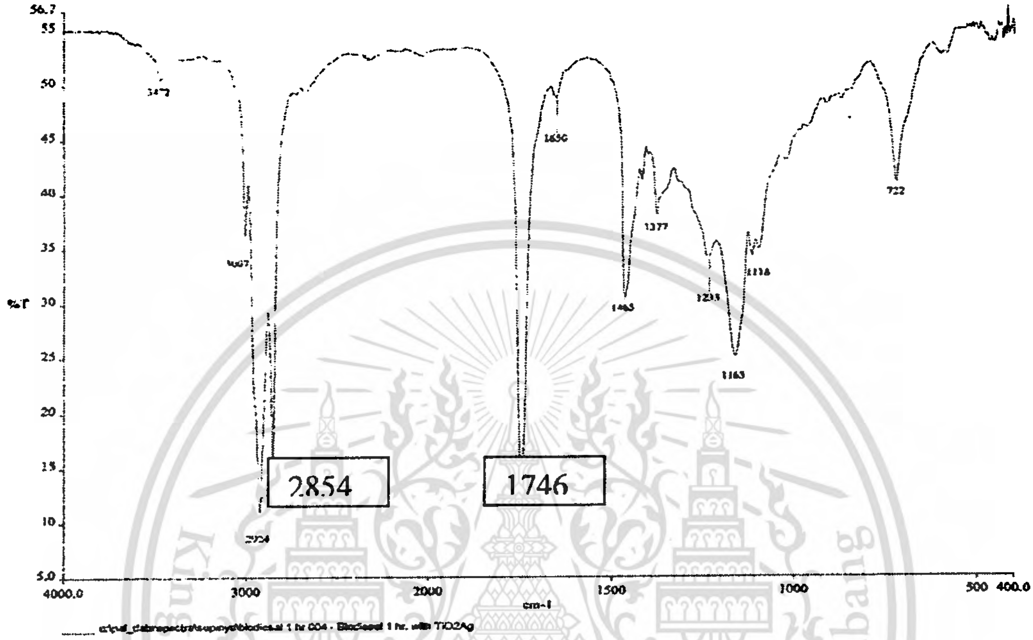


Figure 4.8 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 1 hour by hot plate (heat treatment) in protector laboratory hood (90°C), checked by Fourier Transform Infrared Spectrometer

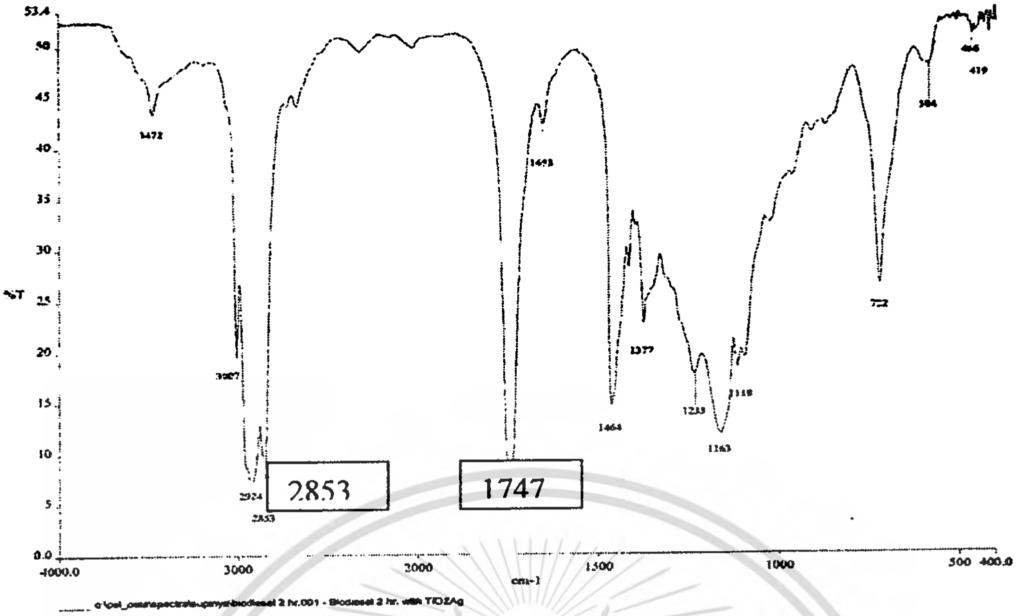


Figure 4.9 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 2 hours by hot plate (heat treatment) in protector laboratory hood (90°C), checked by Fourier Transform Infrared Spectrometer

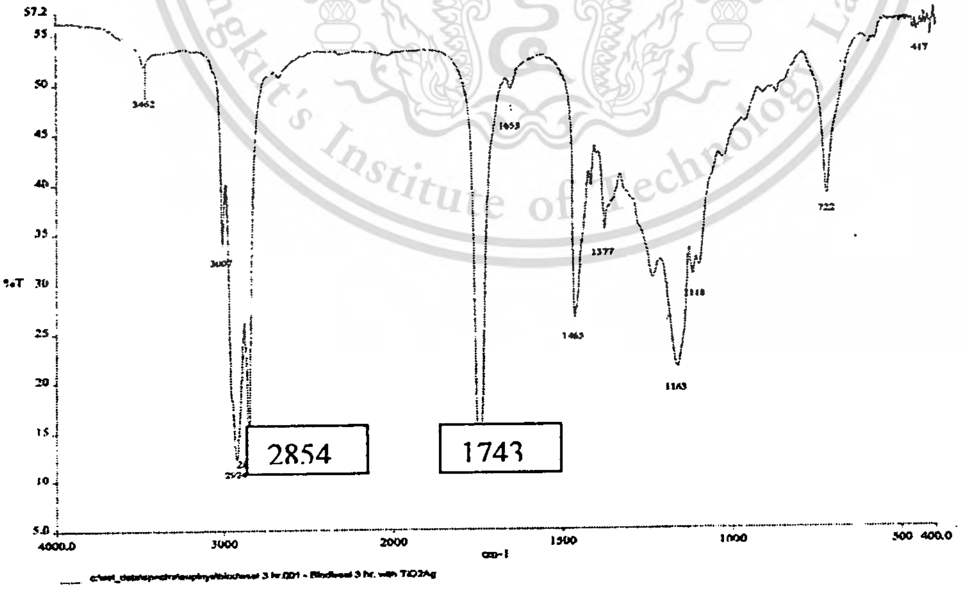


Figure 4.10 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 3 hours by hot plate (heat treatment) in protector laboratory hood (90°C), checked by Fourier Transform Infrared Spectroscopy

From Figures 4.8, 4.9 and 4.10, the reaction with TiO_2 doped silver catalyst in reflux system by hot plate or heat treatment for 1, 2 and 3 hours. The results were shown that the important peaks were appeared at 1743 cm^{-1} is C=O, at 2854 cm^{-1} as functional class of alkanes CH_3,CH_2 and CH stretching and 1464 cm^{-1} is functional class of CH_2 stretching, but they did not show the peek appeared at 1195 cm^{-1} for O-CH_3 . Hence, it can be concluded that the reaction did not change of reaction when compared with raw material (WVO). [47]

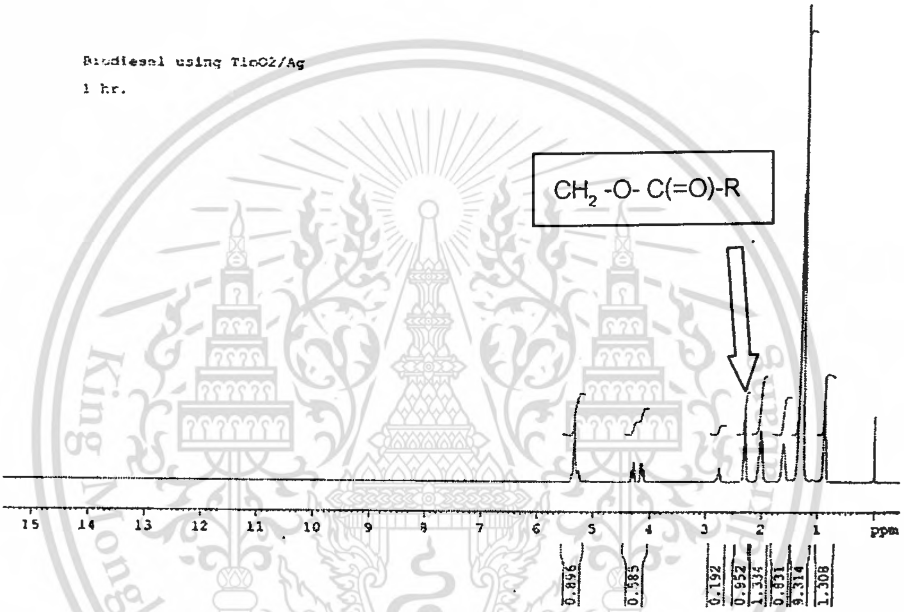


Figure 4.11 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 1 hour by hot plate (heat treatment) in protector laboratory hood (90°C), checked by Nuclear Magnetic Resonance Spectroscopy Instrument

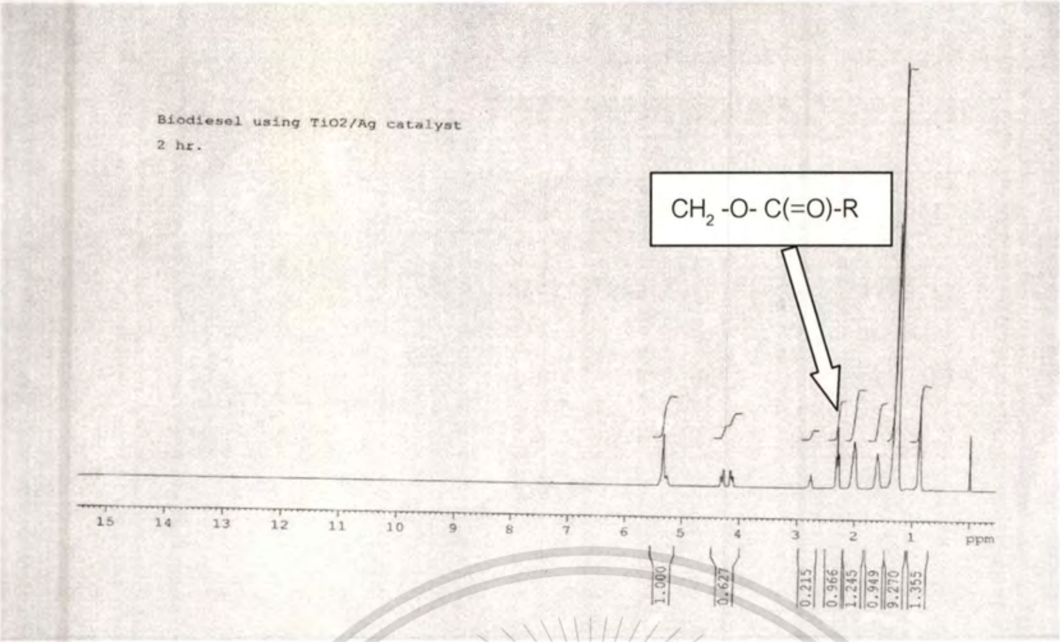


Figure 4.12 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 2 hours by hot plate (heat treatment) in protector laboratory hood (90°C), checked by Nuclear Magnetic Resonance Spectroscopy Instrument

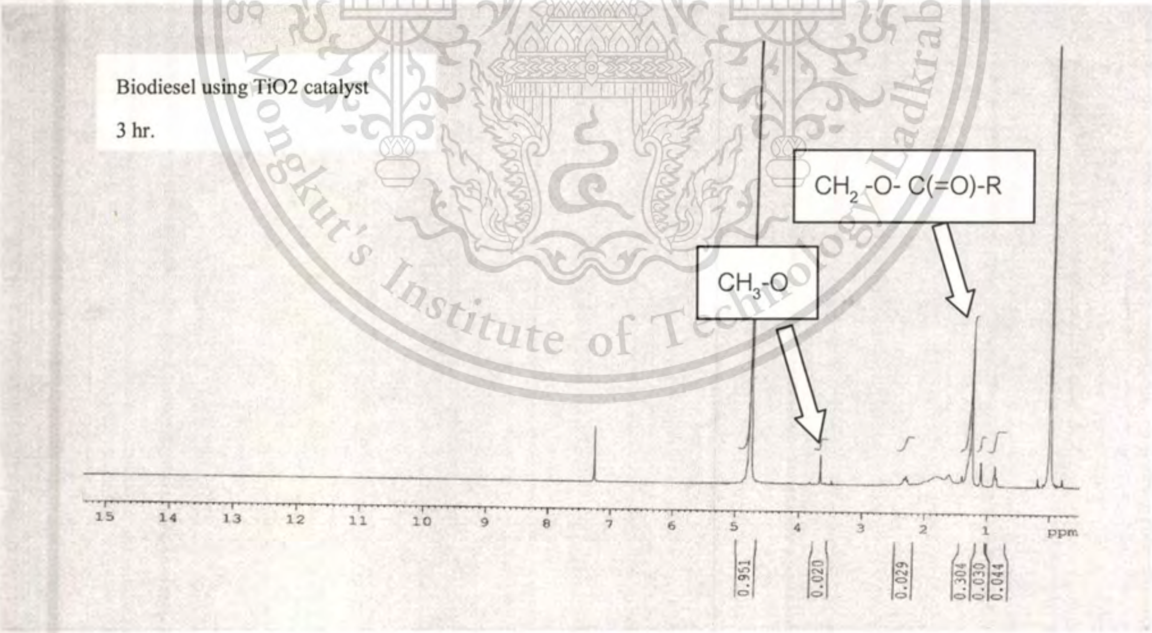


Figure 4.13 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 3 hours by hot plate (heat treatment) in protector laboratory hood (90°C), checked by Nuclear Magnetic Resonance Spectroscopy Instrument

From the Figures 4.11 and 4.12, we got the same results that the important signals were the signal at 2.3 ppm, is CH_2 -O-C(=O)-R and not shown the signal at 3.7 ppm. From these results was encouraged the results from FT-IR peaks, the structure of the sample was only triglyceride. From Figure 4.13 that was showed the two important signals at 2.3 ppm is CH_2 -O- C(=O)-R and the signal at 3.7 ppm is CH_3-O. [47] Hence, we can be concluded that the biodiesel production with TiO_2/Ag as catalyst using hot plate in protector laboratory hood for 1 and 2 hours that they did not occur the reaction. Whereas for 3 hours, it tend to occur the reaction and got the biodiesel.

4.4 Analysis of the results of the product from biodiesel production with TiO_2/Ag catalyst by UV-Visible reactor with various the weight of TiO_2/Ag catalyst for 10 hours

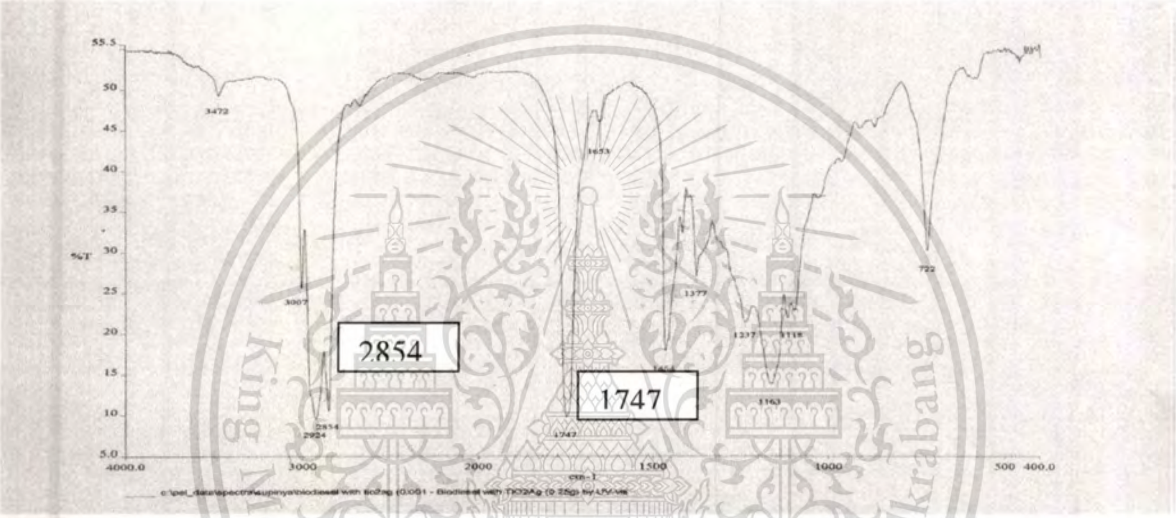


Figure 4.14 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 0.25 g. by UV- VIS reactor (40°C), checked by Fourier Transform Infrared Spectrometer

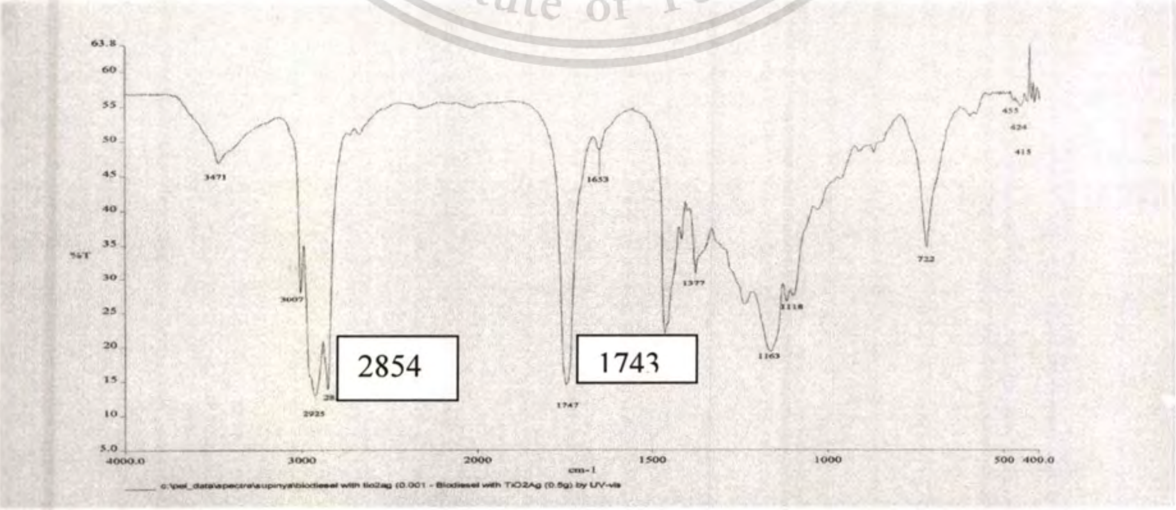


Figure 4.15 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 0.50 g. by UV-VIS reactor (40°C), checked by Fourier Transform Infrared Spectrometer

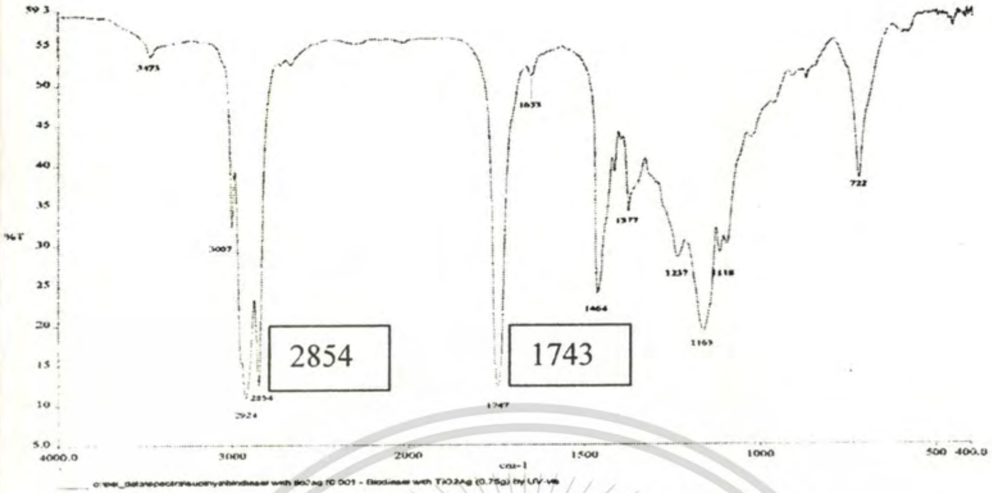


Figure 4.16 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 0.75 g. by UV-VIS reactor (40°C), checked by Fourier Transform Infrared Spectrometer

From Figures 4.14, 4.15 and 4.16, they have shown the same results that were not the reaction occurred in the process. The structure of sample as same as the raw material (WVO) that before the reaction and as same as the other reaction that is only triglyceride.

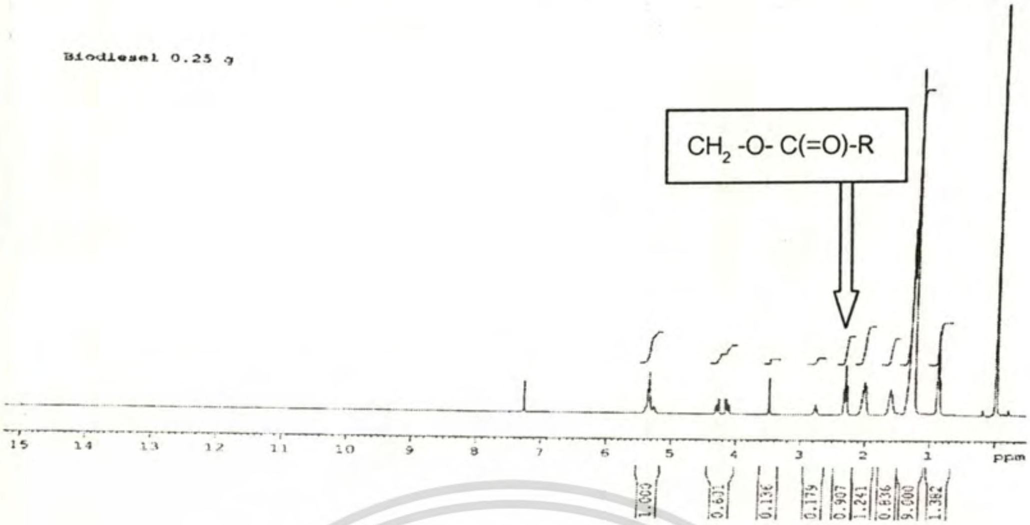


Figure 4.17 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 0.25 g. by UV-VIS reactor (40°C), checked by Nuclear Magnetic Resonance Spectroscopy Instrument

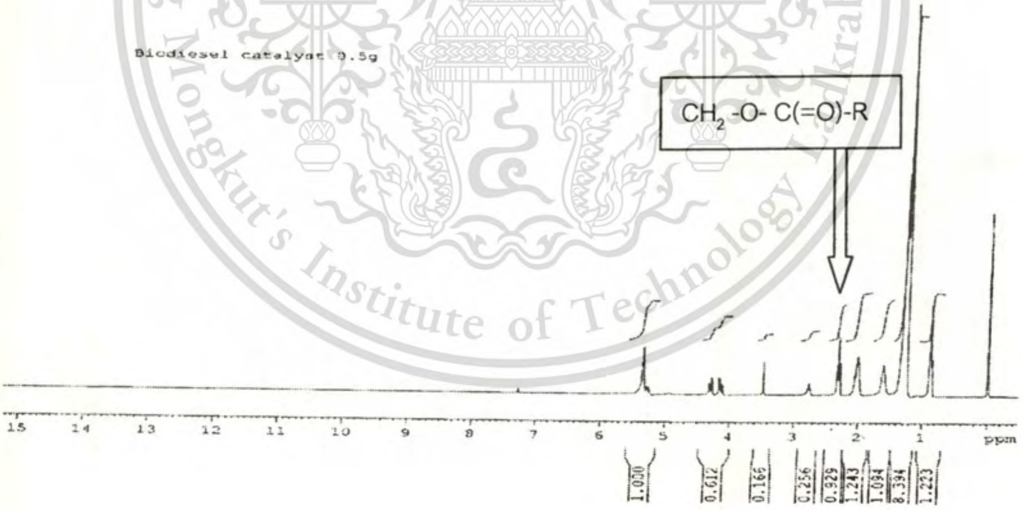


Figure 4.18 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 0.50 g. by UV-VIS reactor (40°C), checked by Nuclear Magnetic Resonance Spectroscopy Instrument

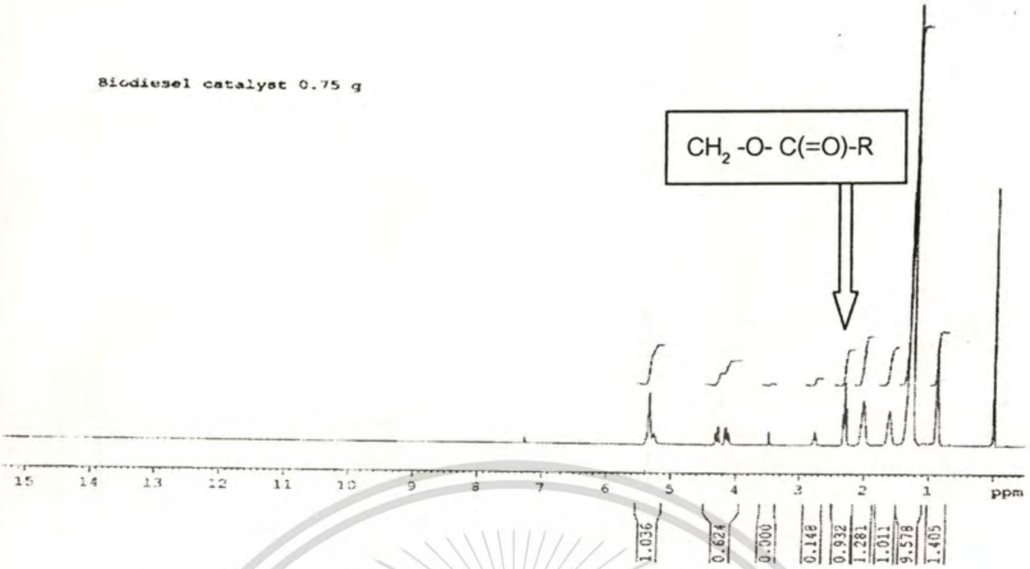


Figure 4.19 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 0.75 g. by UV-VIS reactor (40°C), checked by Nuclear Magnetic Resonance Spectroscopy Instrument

From Figures 4.17, 4.18 and 4.19 were shown the results with UV-VIS reactor, it was the same results that were not have reaction occurred.

No. of catalyst	% yield of biodiesel (methyl ester)
0.25	0.00
0.50	0.00
0.75	0.00

Table 4.1 The yield percentage of methyl ester from biodiesel production which using TiO_2/Ag by UV-Visible reactor with various the weight of TiO_2/Ag catalyst

Calculation % yield of Methyl Ester [47] = (0.00/0.00) (2/3)(100)

= 0 %

4.5 Analysis of the results of the product from biodiesel production with TiO_2/Ag catalyst in reflux system by heating mantle with various reaction times

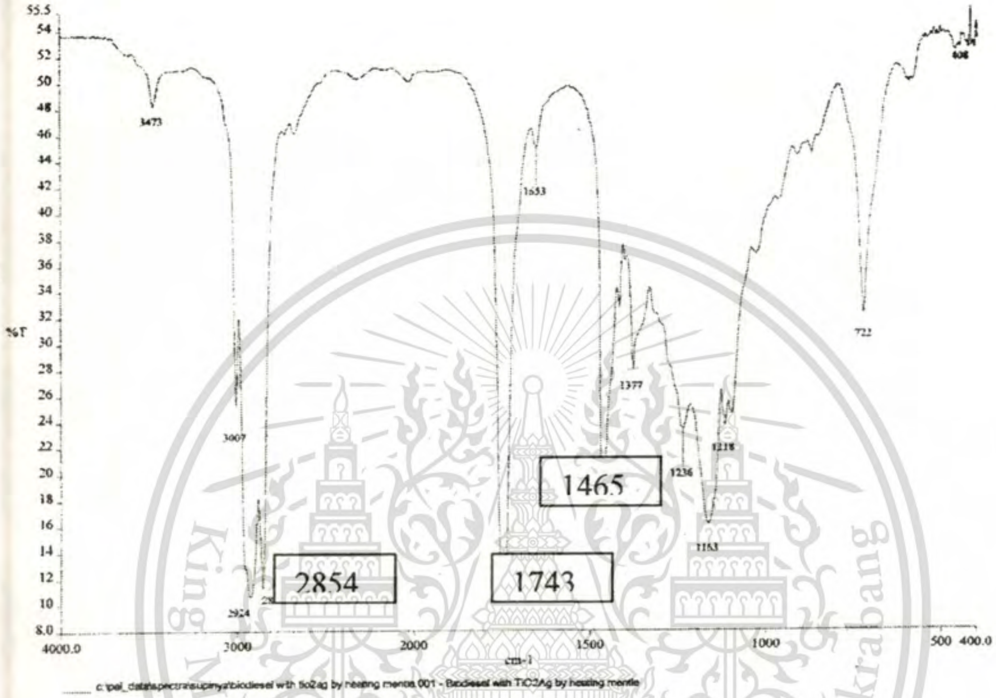


Figure 4.20 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 1 hour at 105°C by heating mantle in reflux system, checked by Fourier Transform Infrared Spectrometer

From the figure 4.20 shown the important peaks at 1743 cm^{-1} is C=O, the peak at 2854 cm^{-1} is functional class of alkanes CH_3,CH_2 and CH stretching and the peak at 1464 cm^{-1} is functional class of CH_2 stretching and it was not shown the peak at 1195 cm^{-1} for O-CH_3 [47]. Hence, the structure of this sample was the same with the other method that reaction was not occurred.

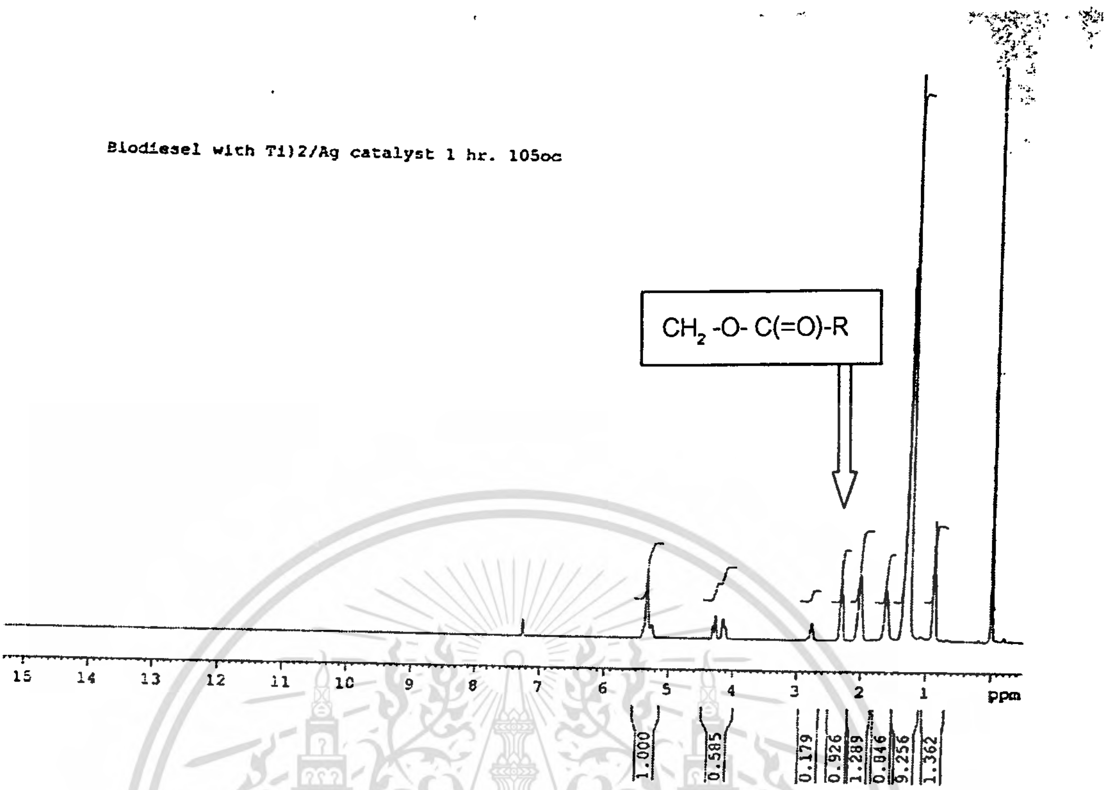


Figure 4.21 The product (top layer) from biodiesel production with TiO_2/Ag catalyst for 1 hour at 105°C by heating mantle in reflux system, checked by Nuclear Magnetic Resonance Spectroscopy Instrument

From the figure 4.21 shown the important signal was at 2.3 ppm , CH_2 -O- C(=O)-R and they did not shown the signal at 3.7 ppm, CH_3-O [47]. From this result, it did not have reaction occurred for this method.

Chapter V

Conclusions and Recommendations

5.1 Conclusions

Biodiesel production with NaOH catalyst can produced 98.68% yield of product at 90°C for 1 hour. The results of NMR peaks were shown two important peaks at 2.3 and 3.7 ppm of CH_2-C(=O)-O and CH_3-O-C(=O) respectively. The results of FT-IR spectrums were shown three peaks at 1744 cm^{-1}, 1242 $cm^{-1}$and 1195 cm^{-1} which are corresponding to C=O, C(=O)-O and CH_3-O, respectively.

Biodiesel production with TiO_2/Ag catalyst was prepared by sol-gel method, by using hot plate at 90°C for 1 hour and 2 hours but except for 3 hours, we got 45.51% yield of biodiesel which is characterized by NMR. The results from NMR, it was showed two important peaks which are 2.3 ppm and 3.7 ppm of CH_2-C(=O)-O and CH_3-O-C(=O) respectively and by using heating mantle at 105 °C for 1, 2, and 3 hours respectively. These were various the reaction times. Whereas, biodiesel production by using UV-VIS reactor at 40°C for 10 hours, it was various a weight of catalyst. The results of NMR peaks were not shown two important peaks at 2.3 and 3.7 ppm of CH_2-C(=O)-O and CH_3-O-C(=O), respectively. Also the results from FT-IR spectrums were not shown the spectra at 1744, 1242 and 1195 cm^{-1} are corresponding to C=O, C(=O)-O and CH_3-O, respectively.

We could be recovery the TiO_2/Ag catalyst after biodiesel production. It is characterized by XRD technique. The results from XRD technique, it was showed the peaks of anatase which is the same with the peak of anatase of TiO_2/Ag catalyst before using biodiesel production.

Using TiO_2/Ag catalyst may not be suitable for biodiesel production. Due to the results from two methods of biodiesel production, except for three hours of biodiesel production by using hot plate.

5.2 Recommendations

5.2.1 The type of catalyst and temperature should also be studied because it is the factors that affect the biodiesel production.

5.2.2 Increasing or decreasing the pressure for biodiesel production should be attempted.

5.2.3 Optimization of molar ratio in biodiesel production should be studied within wide range to determine the best molar ratio.

References

[1] Definition of Biodiesel. Available online at http://www.dede.go.th/dede/index.php?id=351, 3-10-08, 09.44 pm

[2] History of Biodiesel. Available online at http://www.biodiesel.com/index.php/biodiesel/history_of_biodiesel_fuel/, 3-10-08, 04.00 pm

[3] McDonnel K et al. JAOCS 1999, 76, 539

[4] Knothe G, Inform 2002, 13, 900

[5] J. Van Gerpen, B. Shanks, and R. Pruszko *Iowa State University*, D. Clements *Renewable Products Development Laboratory*, G. Knothe *USDA/NCAUR*: Biodiesel Analytical Methods August 2002–January 2004, page 1-95

[6] Leandro S. Oliveira a, Adriana S. Franca a, Rodrigo R.S. Camargos a, Vany P. Ferraz b : Bioresource Technology 99 (2008) 3244–3250

[7] Formation of Biodiesel. Available online at http://en.wikipedia.org/wiki/Biodiesel, 4-10-08, 08.08 am

[8] Biodiesel,Department of Alternative Energy Development and efficiency : Ministry of energy, Page 1-44,2007

[9] Formation of vegetable oils. Available online at http://en.wikipedia.org/wiki/Vegetable_oil, 04-10-08, 9.45 am

[10] Formation of pal oils. Available online at http://en.wikipedia.org/wiki/Palm_oil , 4-10-08 , 10.07 am

[11] Palm oil production. Available online at http://www.mareatech.com/product-palm.htm, 05-10-08, 5.33 am

[12] Bara scientific,Biodiesel. Available online at http://www.barascientific.com/bscnews/forum/Biodiesel2-eng/biodiesel.php, 05-10-08, 06.12 am

[13] Vegetable Oil used as Fuel. Available online at http://www.filterinternational.com/index.php?lay=show&ac=article&Id=560308&Ntype=3, 06-10-08, 11.00 am

[14] Formation of waste cooking oil. Available online at http://en.wikipedia.org/wiki/Cooking_oil#Waste_cooking_oil, 06-10-08 , 11.05 am

[15] Palm picture. Available online at www.bbznet.com, 06-10-08, 12.34 pm

[16] Picture of WVO. Available online at http://topicstock.pantip.com/food/topicstock/2006/02/D4141276/D4141276-71.jpg, 06-10-08, 03.55 pm

[17] Gerpen, J.V., Biodiesel processing and production, Fuel Processing Technology, 2005, 86, 1097-1107.

[18] Ma, F. & Hanna, M.A., Biodiesel production: a review, Bioresource Technology, 1999, 70, 1-15.

[19] Energy development and efficiency, Biodiesel production technology. Available online at http://www.dede.go.th/dede/index.php?id=595, 06-10-08, 05.24 pm

[20] Transesterification reaction. Available online at http://en.wikipedia.org/wiki/Biodiesel_production#Transesterification_chemistry, 06-10-08, 05.29 pm

[21] Journal of the Brazilian Chemical Society,J. Braz. Chem. Soc. v.9 n.3 São Paulo mayo/jun. 1998,transesterification of vegetable oils.Available online at http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0103-50531998000300002&lng=es&nrm=iso , 06-10-08 , 07.09 pm

[22] Formation of methanol. Available online at http://en.wikipedia.org/wiki/Methanol , 06-10-08, 07.33 pm

[23] Formation of sodium hydroxide. Available online at http://en.wikipedia.org/wiki/Sodium_hydroxide, 06-10-08, 08.24 pm

[24] Definition and history of titanium dioxide as a photocatalyst. Available online at http://www.noodor.net/id62.htm, 06-10-08, 10.30 pm

[25] Formation of titanium dioxide. Available online at http://en.wikipedia.org/wiki/Titanium_dioxide#Production, 06-10-08, 10.33 pm

[26] Structure and properties of titanium dioxide. Available online at http://ruby.colorado.edu/~smyth/min/tio2.html, 06-10-08, 10.35 pm

[27] Formation of silver compound. Available online at http://en.wikipedia.org/wiki/Silver, 06-10-08, 10.35 pm

[28] Geochemical Instrumentation and Analysis. Available online at http://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html, 06-10-08, 10.47 pm

[29] Nuclear Magnetic Resonance Spectrometer. Available online at www.chem.cmu.edu/cma/nmr.html, 10-03-08, 08.15 am

[30] Details of Nuclear Magnetic Resonance Spectrometer. Available online at http://en.wikipedia.org/wiki/Nuclear_magnetic_resonance, 10-03-08, 08.45 am

[31] Details of Fourier transform infrared (FTIR) spectroscopy. Available online at http://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy#Fourier_transform_infrared_spectroscopy, 10-03-08, 09.30 am

[32] Thiam Leng Chew, Subhash Bhatia , Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery , Bioresource Technology journal homepage: www.elsevier.com/locate/biortech , 06-10-08 , 10.35 pm

[33] Ayhan Demirbas, Comparison of transesterification methods for production of biodiesel from vegetable oils and fats, Energy Conversion and Management 49 (2008) 125–130

[34] Joelianingsiha,b,c,e, Hitoshi Maedaa,c, Shoji Hagiwaraa, Hiroshi Nabetania,_,Yasuyuki Sagarac, Tatang H. Soerawidjayad, Armansyah H. Tambunane, Kamaruddin Abdullahe , Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure: A kinetic study , Renewable Energy 33 (2008) 1629–1636

[35] Michael K. Seery a, Reenamole George, Patrick Floris , Suresh C. Pillai , Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis , Journal of Photochemistry and Photobiology A: Chemistry 189 (2007) 258–263

[36] Chia-Hsin Li , Yung-Hsu Hsich, Wan-Ting Chiu, Chin-Chuan Liu, Chao-Lang Kao , Study on preparation and photocatalytic performance of Ag/TiO2 and Pt/TiO2 photocatalysts , Separation and Purification Technology 58 (2007) 148–151

[37] L.A. Brook, P. Evans, H.A. Foster, M.E. Pemble 1, A. Steele, D.W. Sheel *, H.M. Yates , Highly bioactive silver and silver/titania composite films grown by chemical vapour deposition , Journal of Photochemistry and Photobiology A: Chemistry 187 (2007) 53–63

[38] Qilin Cheng a,b, Chunzhong Li a,*, Vladimir Pavlinek b,Petr Saha b, Huanbing Wang a , Surface-modified antibacterial TiO2/Ag+ nanoparticles. Preparation and properties , Applied Surface Science 252 (2006) 4154–4160

[39] Ayato Kawashima *, Koh Matsubara, Katsuhisa Honda, Development of heterogeneous base catalysts for biodiesel production, Bioresource Technology 99 (2008) 3439–3443

[40] Rusiene M. de Almeida a,*, Lu′ cia K. Noda b, Norberto S. Gonc,alves b,Simoni M.P. Meneghetti a, Mario R. Meneghetti a , Transesterification reaction of vegetable oils, using superacid sulfated TiO2–base catalysts, Applied Catalysis A: General 347 (2008) 100–105

[41] B. Bonelli a,b, M. Cozzolino c, R. Tesser c, M. Di Serioc, M. Piumetti a, E. Garrone a,b, E. Santacesaria c, Study of the surface acidity of TiO2/SiO2 catalysts by means of FTIR measurements of CO and NH3 adsorption, Journal of Catalysis 246 (2007) 293–300

[42] Bao-Xiang Peng, Qing Shu, Jin-Fu Wang*, Guang-Run Wang, De-Zheng Wang, Ming-Han Han, Biodiesel production from waste oil feedstocks by solid acid catalysis, process safety and environment protection 86 (2008) 441–447

[43] Simple flow diagram of biodiesel production. Available online at http://www.northeastbiofuels.com/biofuelsinfo/biodiesel_process.htm, 06-10-08 , 11.31 pm

[44] USA SUKKHA, Effect of thermal behavior and silver doping on crystal structure and physical properties of titanium dioxide,2551, Kmitl

[45] J. Van Gerpen, B. Shanks, and R. Pruszko Iowa State University Biodiesel Analytical Methods, August 2002–January 2004,

[46] Brady, John B., and Boardman, Shelby J., 1995, Introducing Mineralogy Students to X-ray Diffraction through Optical Diffraction Experiments Using Lasers. Jour. Geol. Education, v. 43 #5, 471-476.

[47] Calculation of the percentage of yield of methyl ester biodiesel. Available online at http://www.tiche.org, 15-03-09, 10.02 pm

Appendices

Appendix A: Calculation for biodiesel production

Appendix A.1 Calculation the free fatty acids of waste vegetable oil for biodiesel production

$$\%\text{ free fatty acid [8]} = \frac{\text{Volume of NaOH (ml)} \times \text{Concentration of NaOH in molar} \times 25.6}{\text{Weight of waste vegetable oil (g)}}$$

$$= \frac{3.0 \times 0.135 \times 25.6}{10}$$

$$= 1.03 \quad (< 2.5)$$

Note ; Palmitic acid is 25.6 % of palm oil.

Appendix A.2 Calculation the molar ratio for biodiesel production

The molar ratio → Methanol / oil / NaOH catalyst

40 / 90 / 0.6

Solution :

1.) Methanol;

$$\frac{40 \times 0.7918}{32} = 0.98975 \text{ mole}$$

So,

$$\frac{0.98975 \times 1000}{130} = 7.61346 \text{ molar}$$

2.) Waste vegetable oil (WVO) ;

$$\frac{90 \times 0.88}{267.874} = 0.295 \text{ mole}$$

So,

$$\frac{0.295 \times 1000}{130} = 2.269 \text{ molar}$$

3.) NaOH catalyst ;

$$\frac{0.6}{39.99} = 0.0176 \text{ mole}$$

So, $$\frac{0.0176 \times 1000}{130} = 0.135 \text{ molar}$$

The molar ratio → Methanol / oil / TiO_2/Ag catalyst

120 / 20 / 1

Solution :

1.) Methanol; $$\frac{120 \times 0.7918}{32} = 2.96925 \text{ mole}$$

So, $$\frac{2.96925 \times 1000}{140} = 21.2089 \text{ molar}$$

2.) Waste vegetable oil (WVO) ;

$$\frac{20 \times 0.88}{267.874} = 0.065 \text{ mole}$$

So, $$\frac{0.065 \times 1000}{140} = 0.469 \text{ molar}$$

3.) TiO_2/Ag catalyst ;

$$\frac{1}{79.88} = 0.0125 \text{ mole}$$

So, $$\frac{0.0125 \times 1000}{140} = 0.0892 \text{ molar}$$

The molar ratio → Methanol / oil / TiO_2/Ag catalyst

60 / 10 / 0.5

Solution :

1.) Methanol; $$\frac{60 \times 0.7918}{32} = 1.4846 \text{ mole}$$

So, $$\frac{1.4846 \times 1000}{140} = 21.2085 \text{ molar}$$

2.) **Waste vegetable oil (WVO) ;**

$$\frac{10 \times 0.88}{267.874} = 0.0328 \text{ mole}$$

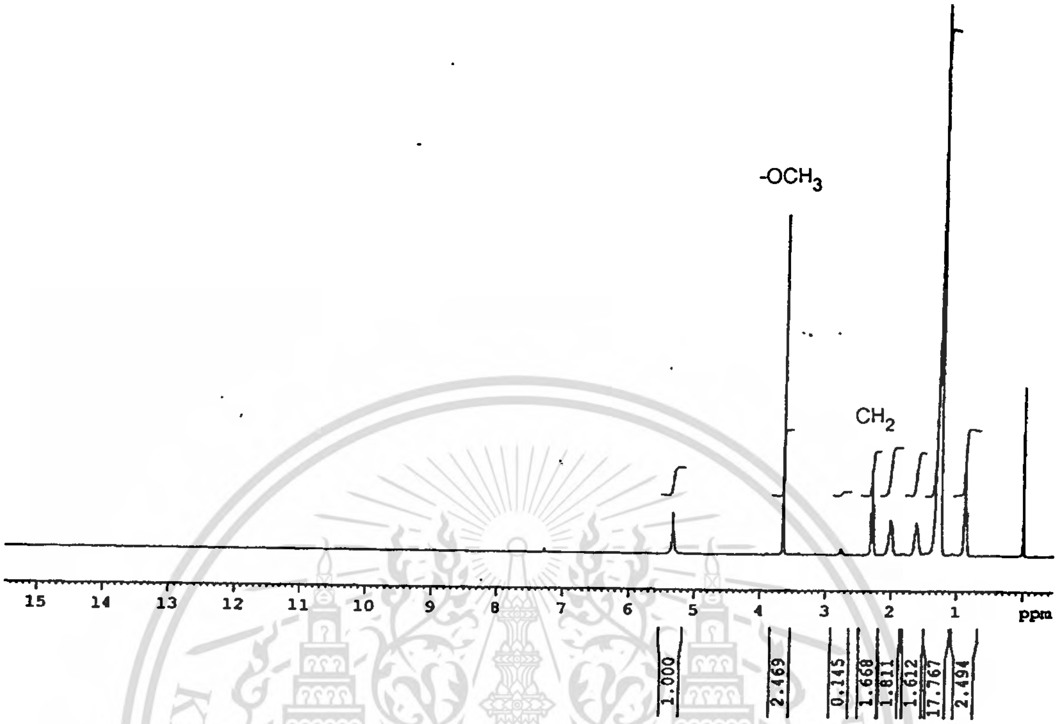
So, $$\frac{0.0328 \times 1000}{140} = 0.469 \text{ molar}$$

3.) TiO$_2$/Ag catalyst ;

$$\frac{0.5}{79.88} = 0.00625 \text{ mole}$$

So, $$\frac{0.00625 \times 1000}{140} = 0.0892 \text{ molar}$$

Appendix A.3 Calculation of yield percentage of methyl ester by ^{1}H-NMR [47]



% Methyl ester [47]

$$= \frac{100 \times (2 \times \text{Integration value of -OCH}_3)}{3 \times \text{Integration value of } \alpha\text{- CH}_2}$$

$$= \frac{100 \times (2 \times 2.469)}{3 \times 1.668}$$

$$= 98.68\ \%$$

Appendix B: Analysis the results of TiO_2/Ag catalyst

Figure B.1 TiO_2/Ag catalyst which checked by X-ray powder diffraction (before using in biodiesel production)

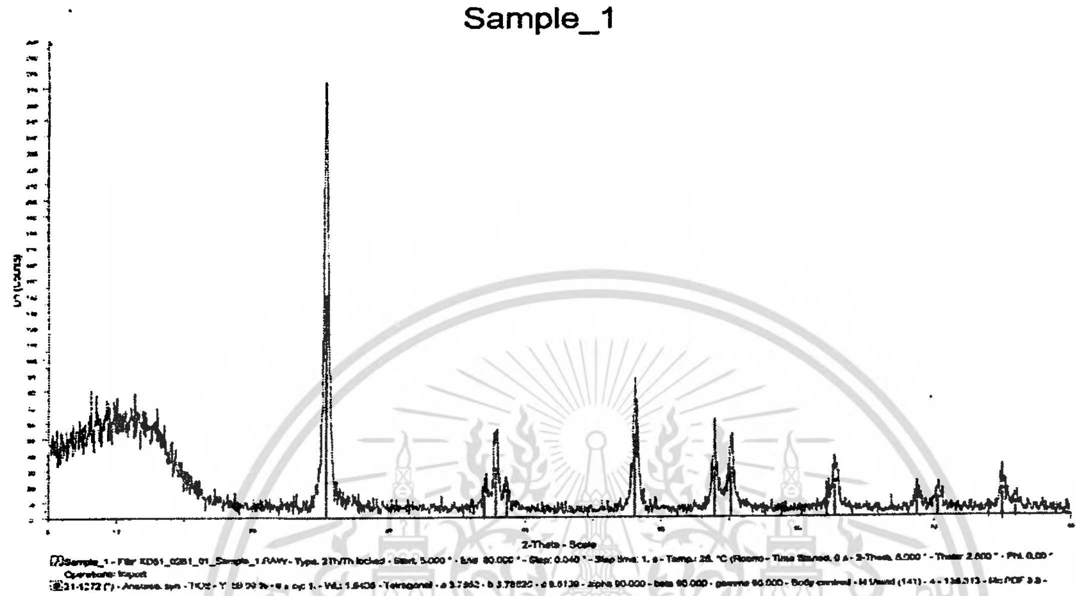
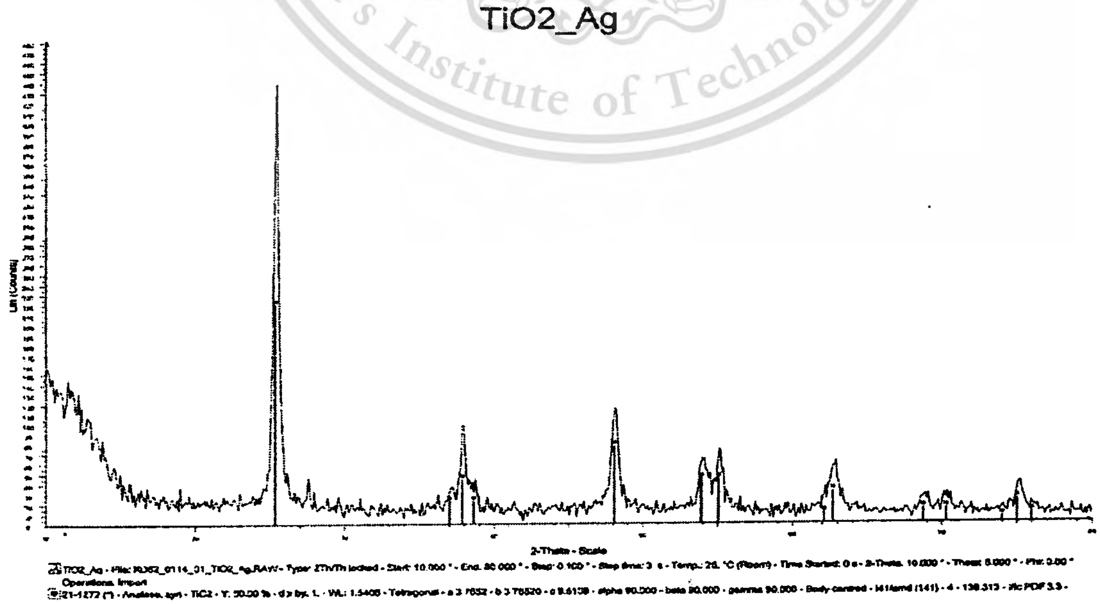


Figure B.2 TiO_2/Ag catalyst which checked by X-ray powder diffraction (after using in biodiesel production)



Appendix C: Analysis of the results of product from biodiesel production

Figure C.1 The product (top layer) from biodiesel production with TiO$_2$/Ag catalyst for 1 hour (1sttime) by hot plate (heat treatment) in protector laboratory hood, checked by Nuclear Magnetic Resonance Spectroscopy Instrument

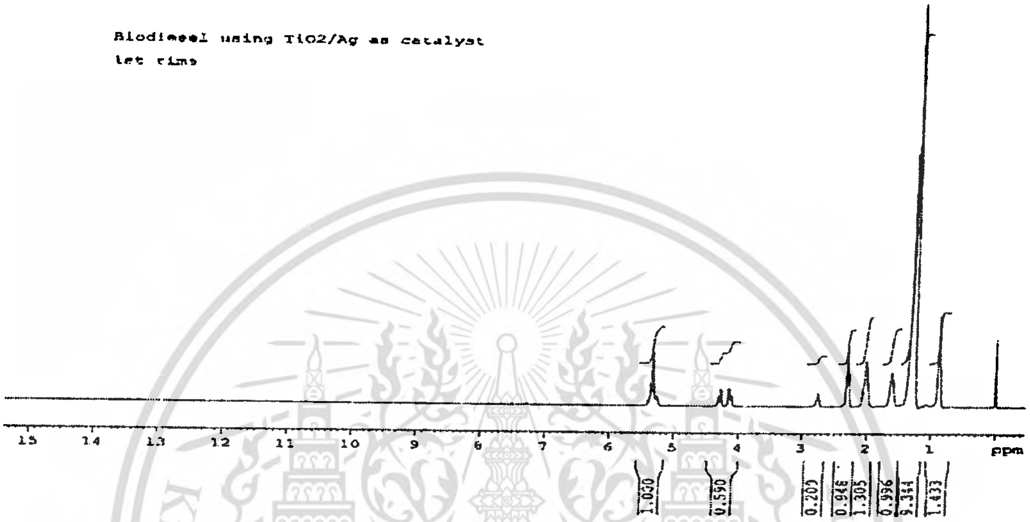


Figure C.2 The product (bottom layer) from biodiesel production with TiO$_2$/Ag catalyst for 1 hour by hot plate (heat treatment)in protector laboratory hood, checked by Nuclear Magnetic Resonance Spectroscopy Instrument

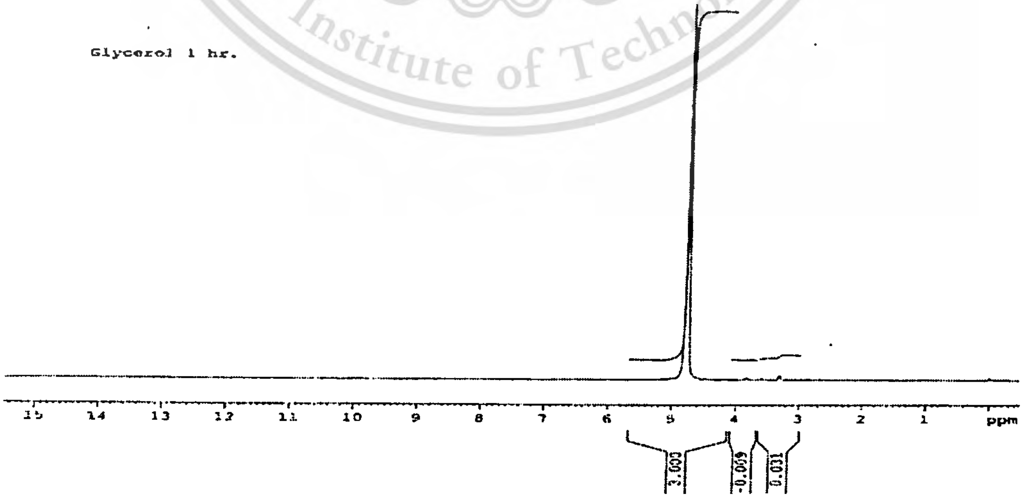


Figure C.3 The product (bottom layer) from biodiesel production with TiO_2/Ag catalyst for 2 hours by hot plate (heat treatment) in protector laboratory hood, checked by Nuclear Magnetic Resonance Spectroscopy Instrument

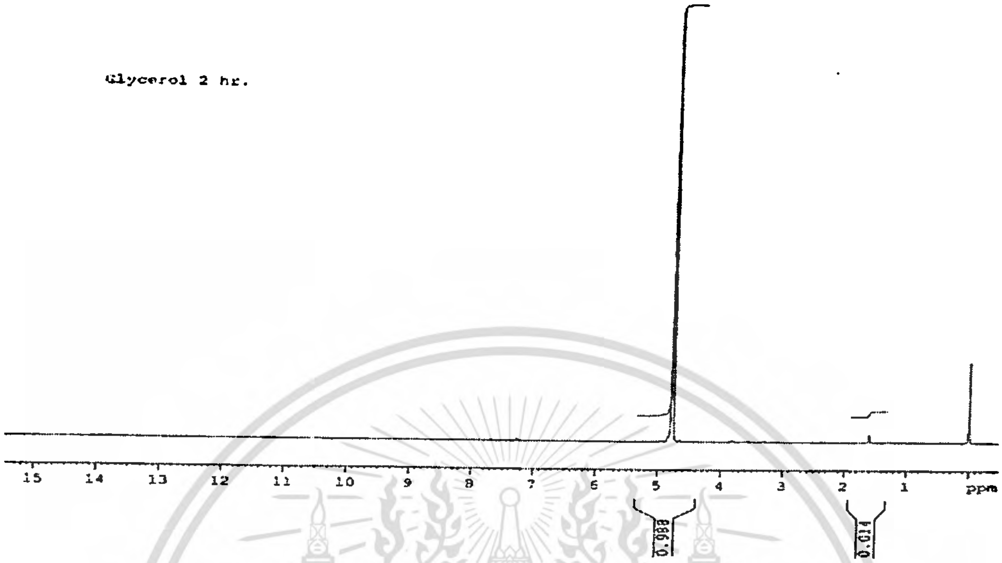


Figure C.4 The product (bottom layer) from biodiesel production with TiO_2/Ag catalyst for 3 hours by hot plate (heat treatment) in protector laboratory hood, checked by Nuclear Magnetic Resonance Spectroscopy Instrument

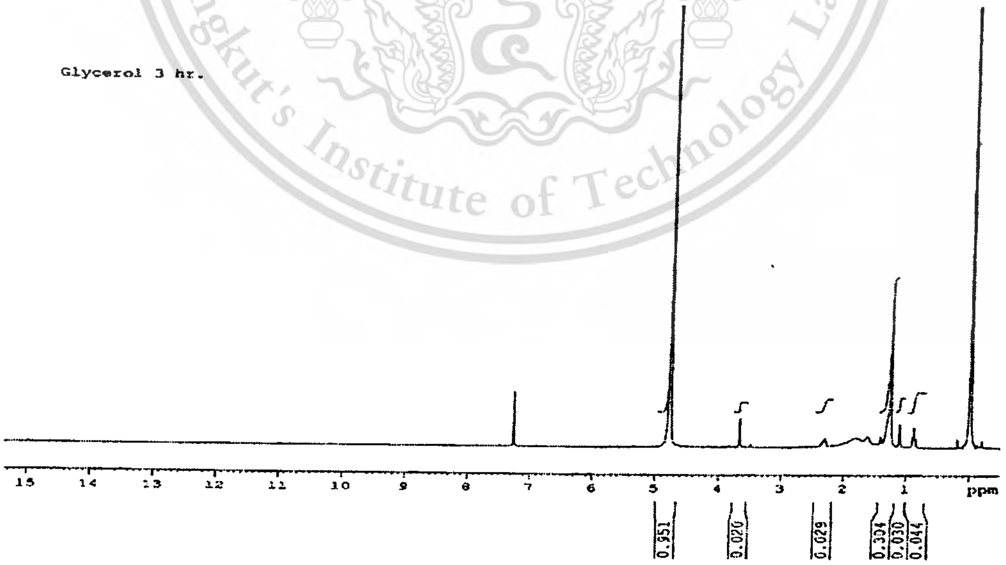


Figure C.5 The product (top layer) from biodiesel production with TiO$_2$/Ag catalyst for 1 hour (1st time) by hot plate (heat treatment) in protector laboratory hood, checked by Fourier Transform Infrared Spectrometer

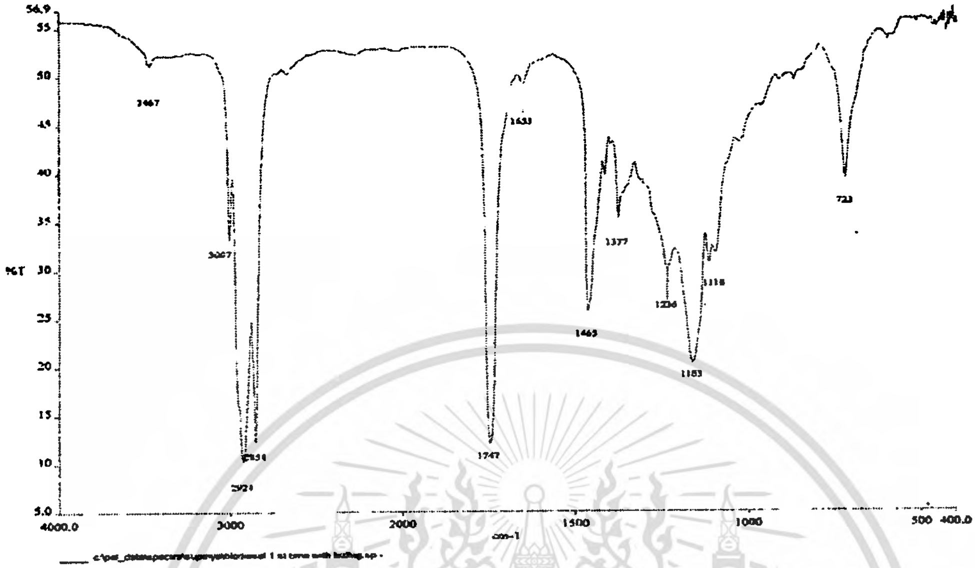


Figure C.6 The product (bottom layer) from biodiesel production with TiO$_2$/Ag catalyst for 1 hour by hot plate (heat treatment) in protector laboratory hood, checked by Fourier Transform Infrared Spectrometer

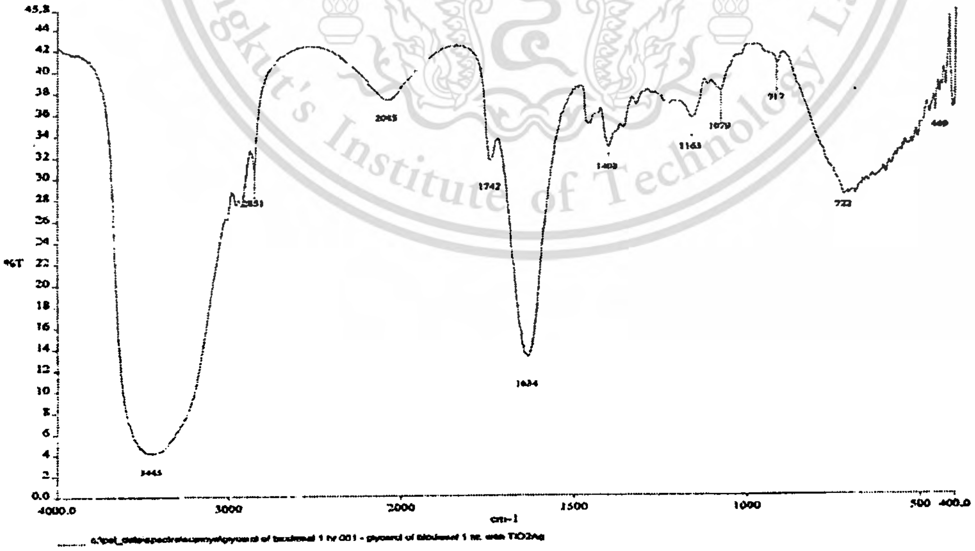


Figure C.7 The product (bottom layer) from biodiesel production with TiO$_2$/Ag catalyst for 2 hours by hot plate (heat treatment) in protector laboratory hood, checked by Fourier Transform Infrared Spectrometer

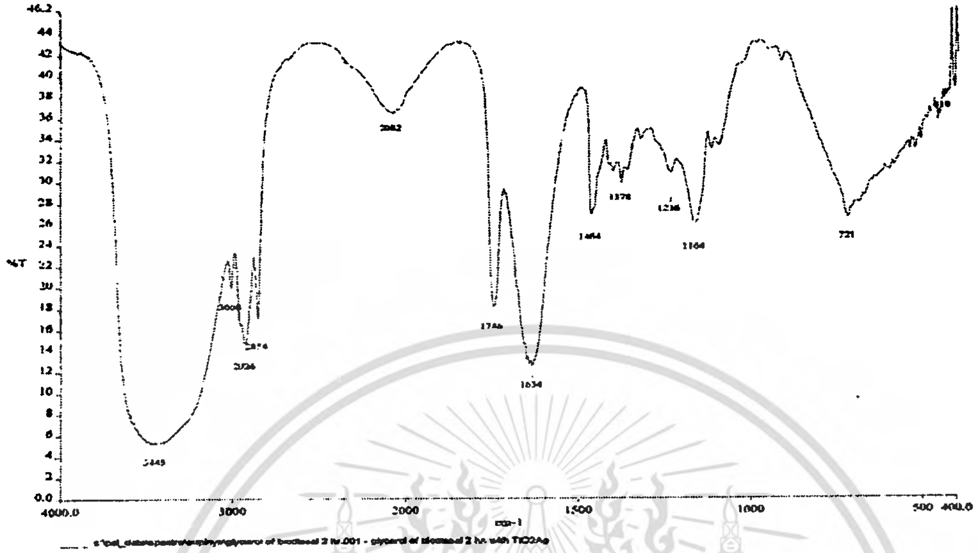


Figure C.8 The product (bottom layer) from biodiesel production with TiO$_2$/Ag catalyst for 3 hours by hot plate (heat treatment) in protector laboratory hood, checked by Fourier Transform Infrared Spectrometer