# EFFECT OF TITANIUM DIOXIDE POWDERS AS BASE CATALYSTS ON BIODIESEL PROCESSING

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# ABSTRACT

In this study, titanium dioxide powders ($TiO_2$) were used as novel heterogeneous base-catalyst for biodiesel production. $TiO_2$ nano-powder were prepared by Sol-gel method. Crystal structure and purity of $TiO_2$ were characterized by XRD technique. Its show anatase structure and high purity of $TiO_2$ powders. The selected $TiO_2$ concentrations are 2, 4 and 6 % w/v. The reaction conditions are 60 °C for 90 minutes in 500 ml. reactor and 40 °C under UV lamp for 6 hours, and 200 °C for 4 hours of hydrothermal using auto clave. NMR technique was used to characterized quantity of alkyl ester (3.7 ppm) and triglyceride (2.3 ppm). Peak area of methylene protons and methoxy protons were used to calculate % yield of biodiesel production. From the NMR result, Its shown that $TiO_2$ catalysts can not produce methyl ester from palm oil under this condition. However, It could be alternative research to develop new solid acid catalyst for biodiesel production.

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**Figures** **Page**

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# Chapter 1

# Introduction

## 1.1 Motivation

Biodiesel has become more attractive recently because of increases in crude oil prices, limited resources of fossil oil and environmental [1]. Biodiesel, as an alternative diesel fuel, is a promising non-toxic and biodegradable renewable fuel comprised of mono-alkyl esters of long chain fatty acids, which are derived from vegetable oils or animal fats [2]. Biodiesel is characterized by excellent properties as diesel engine fuels and, thus, biodiesel can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression–ignition (diesel) engines with little or no modifications. Biodiesel not only has proper viscosity, boiling point, and high cetane number, but biodiesel has more biodegradable, has lower $CO_2$ and sulfur emissions and almost none particulate pollutants [3], so, biodiesel fuel has the potential to reduce the level of pollutants and the level of potential or probable carcinogens [1]. Biodiesel has been produced by transesterification of triglyceride to methyl esters with methanol using sodium or potassium hydroxide dissolved in methanol as catalyst [3].

Biodiesel has around 9% less heating value in volume than conventional diesel fuel. Thus, if engine efficiency is the same, engine fuel consumption should be proportionally higher, and consequently vehicle autonomy proportionally lower, when using biodiesel. Biodiesel fuels have higher lubricity than conventional fuels, but they can contribute to the formation of deposits, the degradation of materials or the plugging of filters, depending mainly on their degradability, their glycerol (and other impurities) content, their cold flow properties, and on other quality specifications.

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Biodiesel fuels also have an interesting potential to reduce chemical emissions. However, the effect of biodiesel is specific for each of the different pollutant species, and depends on the type of engine, on the engine speed and load conditions, on the ambient conditions, on the origin and quality of biodiesel, etc [4]

Biodiesel have the main advantage in its usage is attributed to lesser exhaust emissions in terms of carbon monoxide, hydrocarbons, particulate matter, polycyclic aromatic hydrocarbon compounds and nitrited polycyclic aromatic hydrocarbon compounds. Biodiesel is said to be carbon neutral as more of carbon dioxide is absorbed by the biodiesel yielding plants than what is added to the atmosphere when used as fuel. Exhaust emissions of NOx can be controlled by adopting certain strategies such as change in composition of feedstock, addition of cetane improvers, retardation of injection timing, exhaust gas recirculation, etc. Transesterification is the process that to reduce the viscosity of biodiesel and improve other characteristics. Methanol being cheaper is the commonly used alcohol during transesterification reaction. Among the catalysts, homogeneous catalysts such as sulphuric acid, sodium hydroxide, potassium hydroxide are commonly used at industrial level production of biodiesel. Heterogeneous catalysts such as calcium oxide, magnesium oxide and others are also being tried to decrease the catalyst amount and production cost of biodiesel [5]. Due to some advantages the majority of industrial processes are based on heterogeneous catalytic systems. In comparison with homogenous systems, the heterogeneous one allow: (i) easy separation of the catalyst from the reaction medium, resulting in lower product contamination levels; (ii) regeneration and recycling of catalyst; and (iii) to reduce corrosion problems, even if acid species are involved. Indeed, the development of heterogeneous catalytic systems, for biodiesel production, can be an important factor to help the design of continuous processes [6], thus ,the heterogeneous catalyst process is expected to be an effective biodiesel production process with low cost and minimal environmental impact because of the possibility of simplifying the production and purification processes under mild conditions. Therefore, many heterogeneous catalysts for the transesterification of oils have been developed [15].

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In this project, Aim to study as a potential $TiO_2$ catalyst for biodiesel production. In generally, the synthesis of $TiO_2$ produced via a single-step sol–gel technique. Several studies have shown that $TiO_2$ obtained via the sol–gel technique presented high surface area and homogeneous structure. The quantity of $TiO_2$ by weigh of palm oil have investigated for maximum yield of biodiesel and compared with NaOH bsae catalyst. $TiO_2$ catalysts have been prepared by sol–gel technique and tested purity with XRD. Then, take $TiO_2$ catalyst in the methanolysis reaction of palm oils at 60 °C, for 90 min [6]

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## 1.2 Objectives

1. Study the method to prepare $TiO_2$ by Sol-gel.

2. Study the purity of $TiO_2$ with X-Ray diffraction (XRD).

3. Study the effect of $TiO_2$ as catalyst in biodiesel production.

4. Comparative the production quantity of the $TiO_2$ and NaOH as catalysts in biodiesel production.

## 1.3 Scopes of study

1. Preparation the sol solution by Sol-gel method.

2. Evaporate and calcined the sol solution form of powder at 500 °C with for 2 hours.

3. Study the purity and crystalline of $TiO_2$ powder with XRD.

4. Study the properties of NaOH catalyst in biodiesel oil.

5. Study the applications of $TiO_2$ catalyst compare with NaOH catalyst in biodiesel oil.

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## 1.4 Expected results

1. Develop $TiO_2$ catalyst for quality biodiesel from palm oil when compare with usually catalyst, Sodium Hydroxide.

2. Obtain the best quantity ratio of $TiO_2$ and methanol for maximum the yield of biodiesel from palm oil production.

3. Develop an inexpensive process and lower capital cost which can recover $TiO_2$ catalyst.

4. Reduction of the environmental impact.

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# Chapter 2

# Theoretical Background and Literature Reviews

## 2.1 Vegetable Oils [7]

Vegetable oils are lipid materials derived from plants. Physically, oils are liquid at room temperature. Chemically, 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. 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.

Vegetable oils may be edible or inedible. Examples of inedible vegetable 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 di-glycerides. Vegetable oils are also used to make biodiesel, which can be used like conventional diesel. Some vegetable oil blends are used in unmodified vehicles but straight vegetable oil, also known as pure plant oil, needs specially prepared vehicles which have a method of heating the oil to reduce its viscosity. The vegetable oil economy is growing and the availability of biodiesel around the world is increasing.

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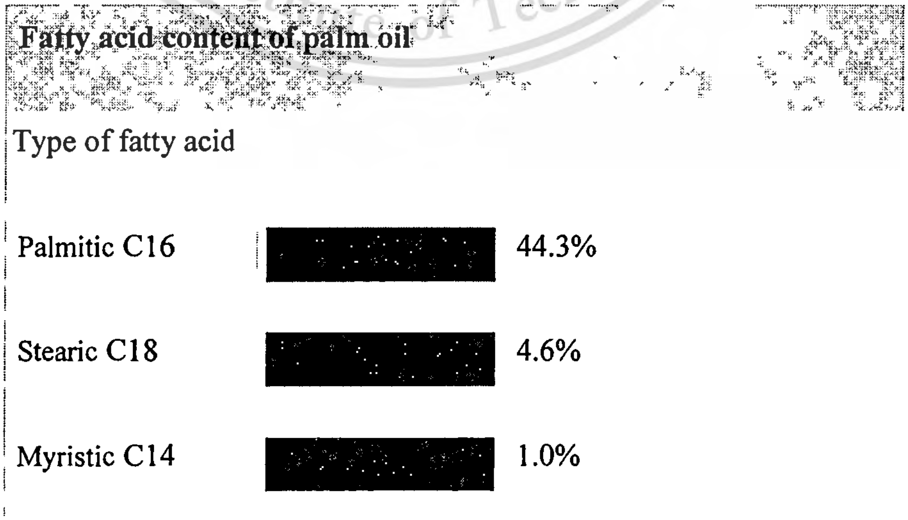
## 2.2 Palm Oils [8]

Palm oil is an edible plant oil derived from the fruit of the Arecaceae Elaeis oil palm. It is an important component of many soaps, washing powders and personal care products, is used to treat wounds, and has controversially found a new use as a feedstock for biofuel. Palm oil is one of the few vegetable oils relatively high in saturated fats (like coconut oil) and thus semi-solid at room temperature.

Chemistry and processing

Palm oil is 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. 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.

**Table 2.1** The approximate concentration of fatty acids (FAs) in palm oil [8]



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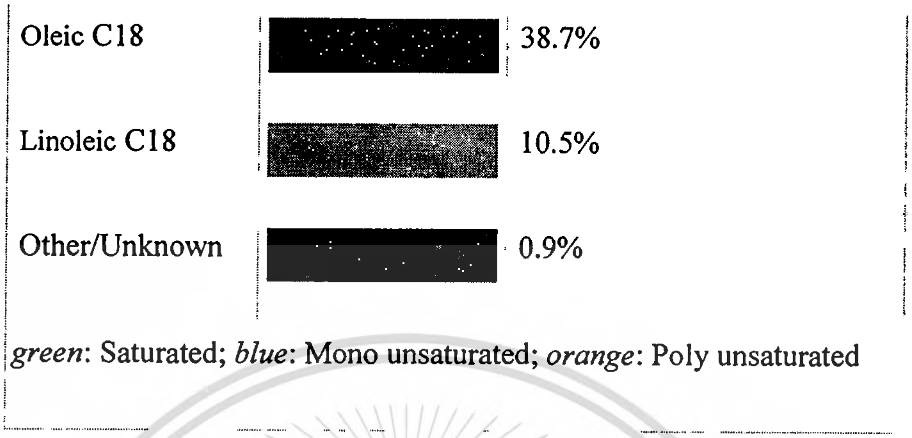

Fatty acids are saturated and unsaturated aliphatic carboxylic acids with carbon chain length in the range of $C_6$ up to $C_{24}$. An example of a fatty acid is palmitic acid [ $CH_3 - (CH_2)_{14} - COOH$ ]. Palm is also used in biodiesel production, as either a simply-processed palm oil mixed with petrodiesel, or processed through transesterification to create a palm oil methyl ester blend, with glycerin as a by-product.

## 2.3 Biodiesel [8]

Biodiesel is the common denomination of the product obtained from the reaction of transesterification of triglycerides, found in vegetable oils or animal fats, with short-chain alcohols. Catalysts are normally used for this reaction, most of which are based on alkaline hydroxides under homogeneous conditions.

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### 2.3.1 Transesterification [9]

The transesterification reaction proceeds with or without any catalyst by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms as follows by

$$\text{Triglycerides} + \text{Monohydric} \rightleftharpoons \text{Glycerin} + \text{Monoalkylesters}$$

Transesterification means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerin and creating an alcohol ester. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. A catalyst is usually used to improve the reaction rate and yield. Theoretically, the transesterification reaction is an equilibrium reaction. In this reaction, however, a larger amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters as the proposed product.

#### 2.3.1.1 Transesterification of Vegetable Oils [10]

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation

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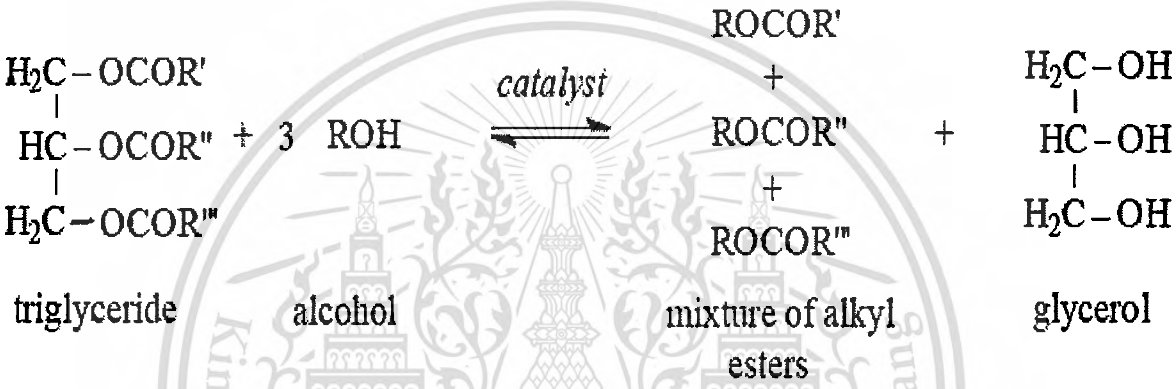
from the glycerol formed. Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification , based on the type of catalyst used.



$$\begin{array}{c} H_2C-OCOR' \\ | \\ HC-OCOR'' \\ | \\ H_2C-OCOR''' \end{array} + 3\ ROH \underset{}{\overset{catalyst}{\rightleftharpoons}} \begin{array}{c} ROCOR' \\ + \\ ROCOR'' \\ + \\ ROCOR''' \end{array} + \begin{array}{c} H_2C-OH \\ | \\ HC-OH \\ | \\ H_2C-OH \end{array}$$

**Eq. 2.1** Transesterification of vegetable oils

## 2.4 Catalyst [10]

Catalyst is the process in which the rate of a chemical reaction is increased by means of a chemical substance known as a catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed. Thus, the catalyst may participate in multiple chemical transformations, although in practice catalysts are sometimes consumed in secondary processes.

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### 2.4.1 Acid and Base catalyst [10]

In acid catalyst and base catalyst a chemical reaction is catalyzed by an acid or a base. The acid is often the proton and the base is often a hydroxyl ion. Typical reactions catalysed by proton transfer are esterfications and aldol reactions. In these reactions the conjugate acid of the carbonyl group is a better electrophile than the neutral carbonyl group itself. Catalyst by either acid or base can occur in two different ways: specific catalyst and general catalyst. Acid catalyst is mainly used for organic chemical reactions. There are many possible chemical compounds that can act as sources for the protons to be transferred in an acid-catalyzed process. A compound such as sulphuric acid ($H_2SO_4$) can be used. Usually this is done to create a more likely leaving group, such as converting an OH group to a $H_2O^+$ group. With carbonyl compounds such as esters, synthesis and hydrolysis go through a tetrahedral transition state, where the central carbon has an oxygen, an alcohol group, and the original alkyl group. Strong acids protonate the carbonyl, which makes the oxygen positively charged, so that it can easily receive the double bond electrons when the alcohol attacks the carbonyl carbon. This enables ester synthesis and hydrolysis. The reaction is an equilibrium between the ester and its cleavage to carboxylic acid and alcohol. On the contrary, strong bases deprotonate the attacking alcohol or amine, which also promotes the reaction. However, bases also deprotonate the acid, which is irreversible. Therefore, in a strongly basic, aqueous environment, esters only hydrolyze.

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### 2.4.1.1 Acid-Catalyzed Processes [10]

The transesterification process is catalyzed by Bronsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 h to reach complete conversion. The alcohol /vegetable oil molar ratio is one of the main factors that influences the transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Eq. 2.2, for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H+. According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

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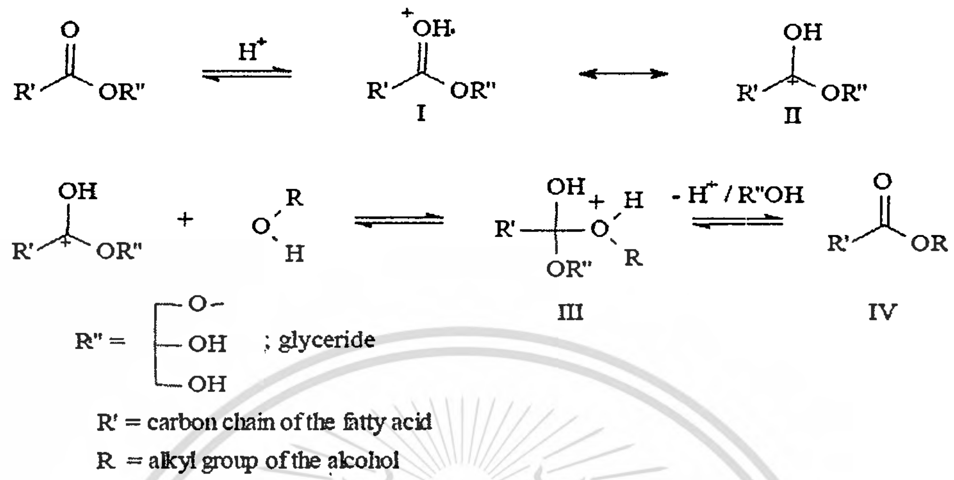

Mechanism of the acid-catalyzed transesterification of vegetable oils.

**Eq. 2.2** The mechanism of the acid-catalyzed transesterification of vegetable oil

### 2.4.1.2 Base-Catalyzed Processes [10]

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 corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

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The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Scheme. The first step (Eq. 2.3) 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. 2.4), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 2.5). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 2.6), 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.

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 (See the Eq. 2.7 and Eq. 2.8). This undesirable saponification reaction reduces the ester yields and considerably difficult the recovery of the glycerol due to the formation of emulsions.

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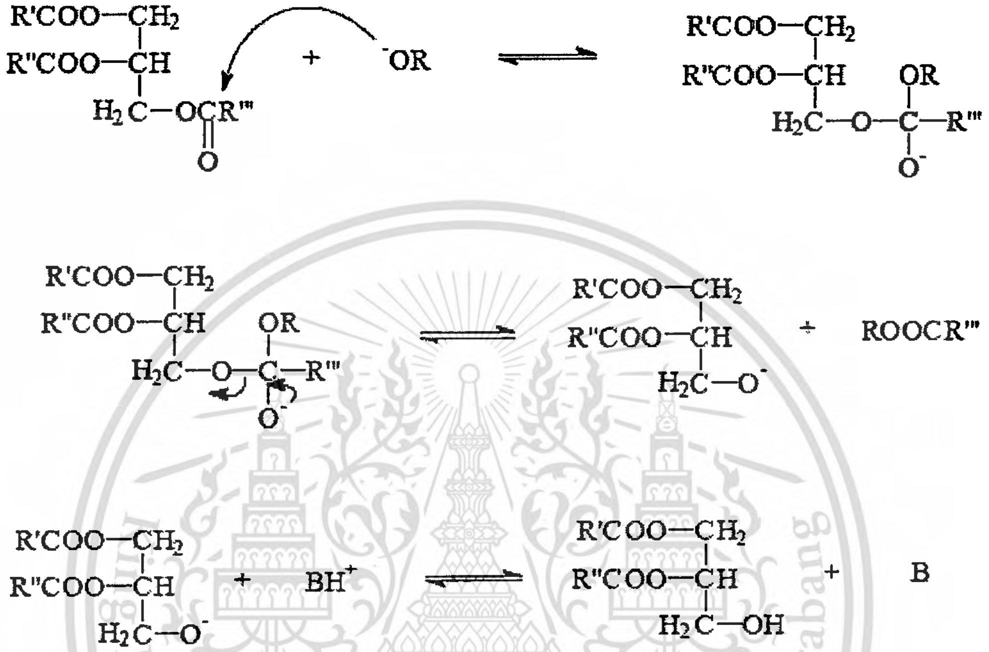
$$ROH + B \rightleftharpoons RO^- + BH^+$$ **Eq. 2.3**

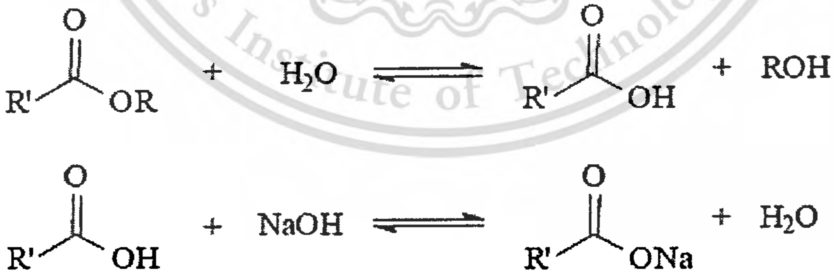


**Eq. 2.4**

**Eq. 2.5**

**Eq. 2.6**

Mechanism of the base-catalyzed transesterification of vegetable oils.



**Eq. 2.7**

**Eq. 2.8**

R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Saponification reaction of the produced fatty acid alkyl esters.

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## 2.4.2 Heterogeneous and Homogeneous catalyst [11]

### 2.4.2.1 Heterogeneous catalysts [11]

Heterogeneous catalysts are present in different phases from the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place (Langmuir-Hinshelwood and Eley-Rideal). Most examples of heterogeneous catalyst go through the same stages: One or more of the reactants are adsorbed on to the surface of the catalyst at active sites. There is some sort of interaction between the surface of the catalyst and the reactant molecules which makes them more reactive .The reaction happens. The product molecules are desorbed. A good catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not so strongly that the product molecules stick more or less permanently to the surface. Metals like platinum and nickel make good catalysts because they adsorb strongly enough to hold and activate the reactants, but not so strongly that the products cannot break away.

For example, in the Haber process, finely divided iron serves as a catalyst for the synthesis of ammonia from nitrogen and hydrogen. The reacting gases adsorb onto "active sites" on the iron particles. Once adsorbed, the bonds within the reacting molecules are weakened, and new bonds between the resulting fragments form in part due to their close proximity. In this way the particularly strong triple bond in nitrogen is weakened and the hydrogen and nitrogen atoms combine faster than would be the case in the gas phase, so the rate of reaction increases.

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Heterogeneous catalysts are typically "supported," which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Sometimes the support is merely a surface upon which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction.

#### 2.4.2.2 Homogeneous catalysts [11]

Homogeneous catalysts function in the same phase as the reactants, but the mechanistic principles involved in heterogeneous catalysis are generally applicable. Typically homogeneous catalysts are dissolved in a solvent with the substrates. One example of homogeneous catalysis involves the influence of $H^+$ on the esterification of esters, e.g. methyl acetate from acetic acid and methanol.

## 2.5 Titanium dioxide ($TiO_2$)

### 2.5.1 Introduction [12]

Common name : Titanium dioxide : Titanium (IV) oxide

Other names : Titania
Rutile
Anatase
Brookite

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Molecular formula : $TiO_2$

Appearance : White solid

Density : 4.23 $g/cm^3$

Melting point : 1870 °C (3398 °F)

Boiling point : 2972 °C (5381.6 °F)

Solubility : Insoluble

Std. enthalpy of : −944 kJ/mol

Titanium dioxide ($TiO_2$) belongs to the family of transition metal oxides and it is heterogeneous base catalyst . In the beginning of the 20th century, industrial production started with titanium dioxide replacing toxic lead oxides as pigments for white paint, textiles, food, leather, pharmaceuticals Titanium metal is not found unbound to other elements that are present in various, igneous rocks and sediments. It occurs primarily in minerals like rutile, ilmenite, leucoxene, anatase, brookite, perovskite, and sphene, and it is found in titanates and many iron ores. Titanium is also found in coal, ash, plants, and even in the human body. Mineral sources are rutile, ilmenite, and leucoxene (a weathering product of ilmenite). In addition, a high-$TiO_2$ slag is produced from ilmenite that contains 75–85% $TiO_2$. $TiO_2$ is also used in catalytic reactions acting as a promoter, a carrier for metals and metal oxides, an additive, or as a catalyst.

Titanium dioxide may be manufactured by either the sulfate or the chlorine process. In the sulfate process, ilmenite is transformed into iron- and titanium sulfates by reaction with sulfuric acid. Titanium hydroxide is precipitated by hydrolysis, filtered, and calcinated at 900 °C . This sulfate process yields a substantial amount of waste iron sulfides and a poor quality $TiO_2$. Therefore, the chlorine process has now become the dominant method. This process uses rutile, which is either excavated or produced in a

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crude quality from ilmenite using the Becher process. which is purified and reoxidized, yielding very pure $TiO_2$.

$TiO_2$ has received a great deal of attention due to its chemical stability, non-toxicity, low cost, and other advantageous properties.

### 2.5.2 Crystal structure and properties [14]

The structures of rutile, anatase and brookite can be discussed in terms of ($TiO_2^{-6}$) octahedrals. The three crystal structures differ by the distortion of each octahedral and by the assembly patterns of the octahedral chains. Anatase can be regarded to be built up from octahedrals that are connected by their vertices, in rutile, the edges are connected, and in brookite, both vertices and edges are connected. (Fig. 2.1) $TiO_2$ offers great potential as an industrial technology for detoxification.

The process can occurs under ambient conditions very slowly, direct UV light exposure increases the rate of reaction and $TiO_2$ has band gap energy about 3.2 ev. which has the frequency in the period of UV light.

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**Table 2.2** The properties of $TiO_2$ [14]

| Properties | Rutile | Anatase | Brookite |
|---|---|---|---|
| Crystal system | Tetragonal | Tetragonal | Orthorhombic |
| Density, $g/cm^3$ | 4.24 | 3.83 | 4.17 |
| Harness, Mohs scale | 5.5 - 6 | 5.5 - 6 | 7 – 7.5 |
| Refractive index | 2.71 | 2.52 | - |
| Melting point | 1858 °C | Changes to rutile at high temperature | - |

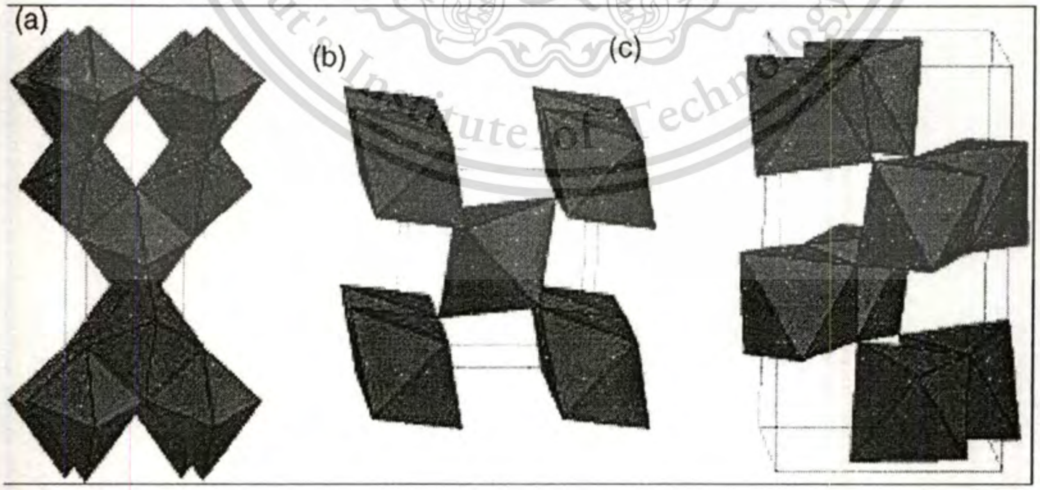

**Fig. 2.1** Crystal structures of anatase (a), rutile (b), and brookite (c) [12]

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### 2.5.3 $TiO_2$ catalyst in biodiesel production

The mechanism of the $TiO_2$-catalyzed transesterification of Plam oils is shown in Scheme. The first step (Eq. 2.9) is the reaction of the $TiO_2$ with the methanol, producing an methoxide and the protonated catalyst. The nucleophilic attack of the methoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq.2.10), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 2.11). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 2.12), which is now able to react with a second molecule of the methanol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

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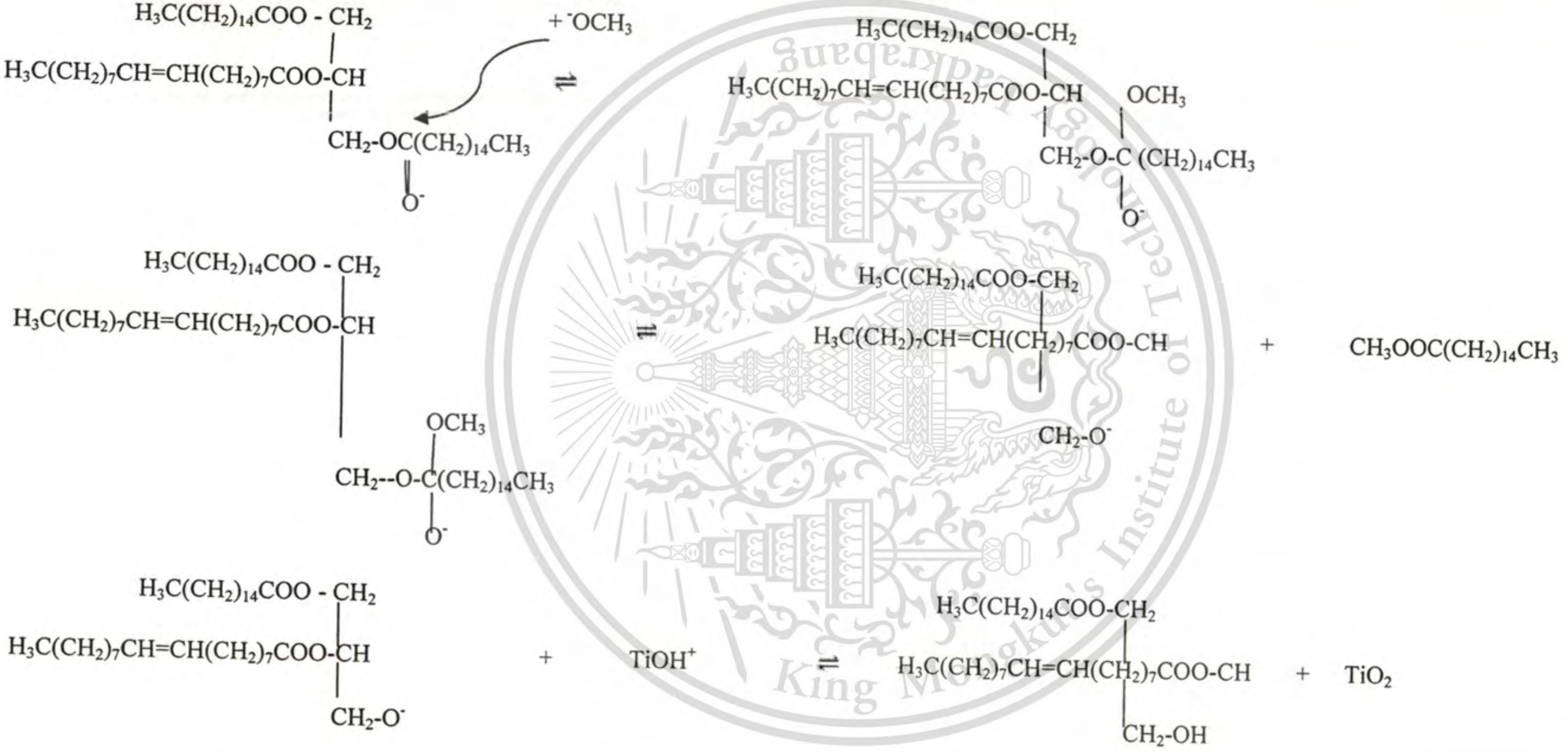
$$CH_3OH + TiO_2 \rightleftharpoons CH_3O^- + TiOH^+$$ Eq. 2.9



Eq. 2.10

Eq. 2.11

Eq. 2.12

**Mechanism of the heterogeneous base catalyst transesterification of palm oils.**

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## 2.6 Sol–gel methods [13]

$TiO_2$ can be prepared in the form of powder, crystals, or thin films. Both powders and films can be built up from crystallites ranging from a few nanometers to several micrometers. [Fig. 2.2] It should be noted that nanosized crystallites tend to agglomerate. If separate nanosized particles are desired, often a deagglomeration step is necessary. Many novel method.

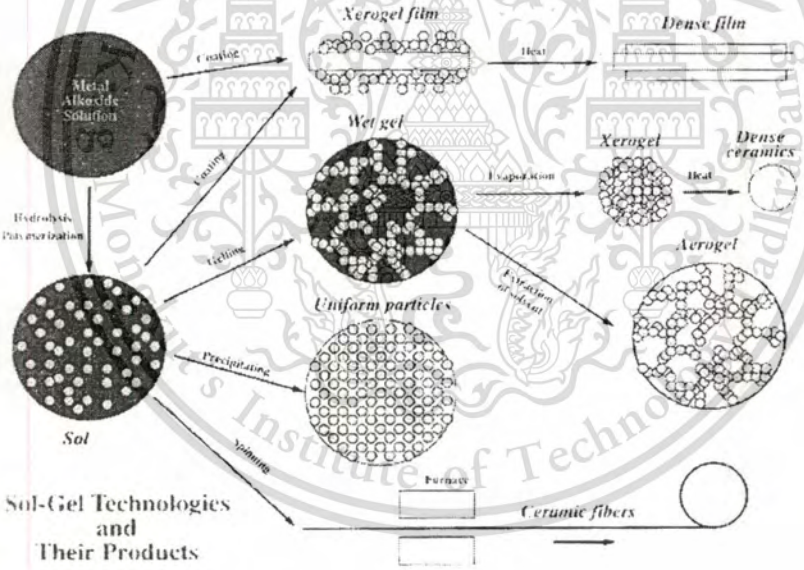

Fig. 2.2. Sol-Gel Technologies and their Products [13]

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Sol–gel methods are used for the synthesis of thin films, powders, and membranes. Two types are known: the non-alkoxide and the alkoxide route. Depending on the synthetic approach used, oxides with different physical and chemical properties may be obtained. The sol–gel method has many advantages over other fabrication techniques such as purity, homogeneity, felicity, and flexibility in introducing dopants in large concentrations, stoichiometry control, ease of processing, control over the composition, and the ability to coat large and complex areas.

This method involves the formation of a $TiO_2$ sol or gel or precipitation by hydrolysis and condensation (with polymer formation) of titanium alkoxides. In order to exhibit better control over the evolution of the microstructure, it is desirable to separate and temper the steps of hydrolysis and condensation.

Hydrolysis:

$M(OR)_X + H2O \rightarrow M(OR)_{X-1}(OH) + R\text{-}OH$ **Eq. 2.13**

Water condensation:

$(OR)_{X-1}\text{-}M\text{-}(OH) + (OR)_{X-1}\text{-}M\text{-}(OH) \rightarrow (OR)_{X-1}\text{-}M\text{-}O\text{-}M\text{-}(OR)_{X-1} + H_2O$ **Eq. 2.14**

Alcohol condensation:

$M(OR)_X + (OH)\text{-}M\text{-}(OR)_{X-1} \rightarrow (OR)_{X-1}\text{-}M\text{-}O\text{-}M\text{-}(OR)_{X-1} + R\text{-}(OH)$ **Eq. 2.15**

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Additionally, the preferred coordination mode of these ligands can be exploited to control the evolution of the structure.

Acid–base catalysis can also be used to enable separation of hydrolysis and condensation steps It has been demonstrated that acid catalysis increases hydrolysis rates and ultimately crystalline powders are formed from fully hydrolyzed precursors. Base catalysis is thought to promote condensation with the result that amorphous powders are obtained containing unhydrolyzed alkoxide ligands.

On the other hand, acetic acid may be used in order to initiate hydrolysis via an esterification reaction, and alcoholic sols prepared from titanium alkoxide using amino alcohols have been shown to stabilize the sol, reducing or preventing the condensation and the precipitation of titania. These reactions are followed by a thermal treatment (450–600 °C) to remove the organic part and to crystallize either anatase or rutile $TiO_2$.

The solvent is evaporated and the particles are interconnected by a sintering process, normally at air temperatures around 450 °C. Sol–gel methods coupled with hydrothermal routes for mesoporous structures lead to large surface area even after heating at temperatures up to 500 °C. This may be explained as follows: generally, mesopores collapse during calcination due to crystallization of the wall. When a hydrothermal treatment induces the crystallization of amorphous powders, the obtained powders can effectively sustain the local strain during calcination and prevent the mesopores from collapsing.

The sol–gel method has been widely studied particularly for multicomponent oxides where intimate mixing is required to form a homogeneous phase at the molecular level. Very recently, sol–gel and templating synthetic methods were applied to prepare very large surface area titania phases, which exhibit a mesoporous structure.

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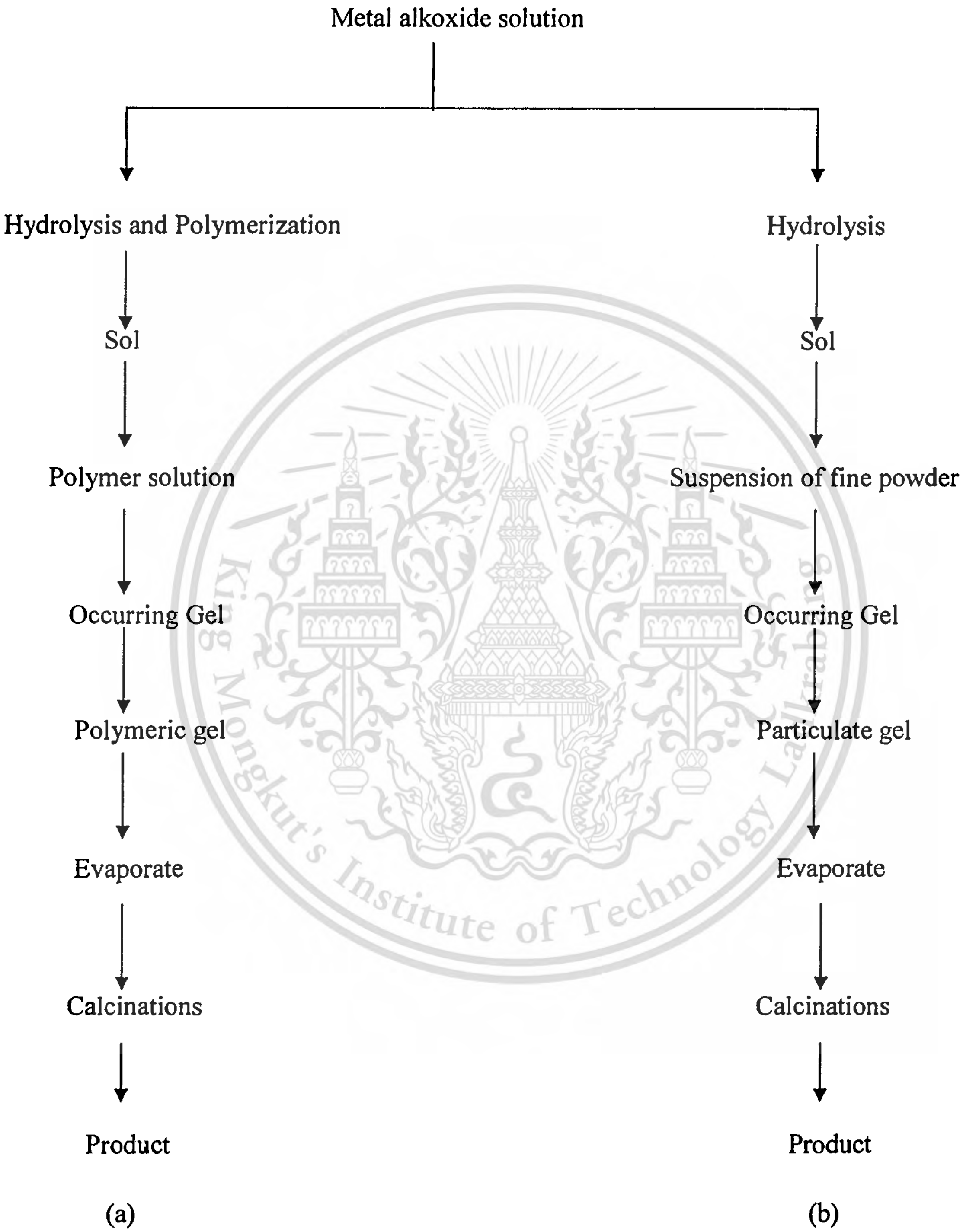

**Fig. 2.3** Sol-gel method a) Polymer and b) colloid [13]

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## 2.7 Literature reviews

**Ayato Kawashima, Koh Matsubara and Katsuhisa Honda [15]** 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, $Ca_2Fe_2O_5$, $CaZrO_3$, and CaO–$CeO_2$ – 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 $CaZrO_3$ and CaO–$CeO_2$ show high durability and have the potential to be used in biodiesel production processes as heterogeneous base catalysts.

**Hak-Joo Kim, Bo-Seung Kang, Min-Ju Kim, Young Moo Park , Deog-Keun Kim, Jin-Suk Lee and Kwan-Young Lee [3]** Biodiesel produced by the transesterification of vegetable oils (VOs) is a promising alternative fuel to diesel regarding the limited resources of fossil fuel and the environmental concerns. In this work, an environmentally benign process for the production of biodiesel from VOs using heterogeneous catalyst was developed. Na/NaOH/γ-Al2O3 heterogeneous base catalyst was firstly adopted for the production of biodiesel. A study for optimizing the reaction conditions such as the reaction time, the stirring speed, the use of co-solvent, the oil to methanol ratio, and the amount of catalyst, was performed. The Na/NaOH/ γ -Al2O3 heterogeneous base catalyst showed almost the same activity under the optimized reaction conditions compared to conventional homogeneous NaOH catalyst. The basic

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strength of Na/NaOH/ γ -Al2O3 catalyst was estimated and the correlation with the activity towards transesterification was proposed.

**Wenlei Xie , Hong Peng and Ligong Chen [2]** Transesterification of soybean oil with methanol was carried out at 60, 120, and 150 °C in the presence of a series NaX faujasite zeolite, ETS-10 zeolite, and metal catalysts. The stock zeolites were exchanged with potassium and cesium; NaX containing occluded sodium oxide (NaO*x*/NaX) and occluded sodium azide (NaO*x*/NaX). The catalysts were calcined at 500 °C prior to use in order to increase activity. The ETS-10 catalysts provided higher conversions than the Zeolite-X type catalysts. The increased conversions were attributed to the higher basicity of ETS-10 zeolites and larger pore structures that improved intra-particle diffusion. Methyl ester yield increased with an increase in temperature from 60 to 150 °C. The metal catalysts increased conversion by one to over two orders of magnitude over the homogeneous reaction with several of the zeolite catalysts performing better than the metal catalysts. The catalyst was reused without observed loss of activity. A preliminary design assessment shows that these catalysts are sufficiently active to be commercially viable contingent upon the costs of the catalysts achieving conversions in excess of 90% at temperatures below 125 °C.

**Fangrui Ma and Milford A. Hanna [1]** Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. The cost of biodiesel, however, is the main hurdle to commercialization of the product. The used cooking oils are used as raw material, adaption of continuous transesterification process and recovery of high quality glycerol from biodiesel by-product (glycerol) are primary options to be considered to lower the cost of biodiesel. There are four primary ways to make biodiesel, direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification. The most commonly used method is

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transesterification of vegetable oils and animal fats. The transesterification reaction is affected by molar ratio of glycerides to alcohol, catalysts, reaction temperature, reaction time and free fatty acids and water content of oils or fats. The mechanism and kinetics of the transesterification show how the reaction occurs and progresses. The processes of transesterification and its downstream operations are also addressed.

**Y.C. Sharma, B. Singh and S.N. Upadhyay [5]** An ever increasing demand of fuels has been a challenge for today's scientific workers. The fossil fuel resources are dwindling day by day. Biodiesel seems to be a solution for future. Biodiesel is an environmentally viable fuel. Out of the four ways viz. direct use and blending, micro-emulsions, thermal cracking and transesterification, most commonly used method is transesterification of vegetable oils, fats, waste oils, etc. Latest aspects of development of biodiesel have been discussed in this work. Yield of biodiesel is affected by molar ratio, moisture and water content, reaction temperature, stirring, specific gravity, etc. Biodegradability, kinetics involved in the process of biodiesel production, and its stability have been critically reviewed. Emissions and performance of biodiesel has also been reported.

**Fernando Gordillo Delgado, Katherine Villa Gomez and Claudia Meja Morales [16]** Titanium dioxide thin films were grown by sol –gel technique in order to obtain films to be used in photocatalytic reactions. We present results on the structural and optical characterization measured for series of films in which number of layers and sintering temperature were changed. Using X-ray diffraction we have characterized the crystalline phase in the films depending on the growth conditions and by using the spectrophotometer we characterized the resulting bandgap energy. The results on the photocatalytic activity were obtained by immersing these films in a methylene blue solution with the presence of ultraviolet light, which is a standard used to

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characterize the efciency of the reaction. High bactericidal activity with these films in wastewater samples was observed subtracting the action of used ultraviolet light, through gas evolution measurements using photoacoustic (PA) technique. The analysis of $TiO_2$ films bactericidal action using PA technique showed high efficiency for applying to elimination of microorganisms that cause contamination of river water for processing coffee seeds.

**Rusiene M. de Almeida, Lucia K. Noda, Norber to S. Goncalves, Simoni M.P. Meneghetti and Mario R. Meneghetti [17]** have been prepared the Superacid sulfated titania catalyst, $TiO_2$ /SO (TS-series), via the sol gel technique with different sulfate concentrations. The relation of structure and catalytic activity of the prepared material have been evaluated. The catalyst that exhibits the highest analyses and obtention of $N_2$ catalytic activity in the methanolysis of soybean and castor oil sat 120 °C, 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(TS5). From thermal analyses, it was verified that the catalytic systems that are active in biodiesel production presented two peak sin regions corresponding to loss of sulfate mass, featured higher specific surface area, higher mean pore volume and higher Bronsted / Lewis acid sites ratio. The methanolysis reaction of castor oil was less effective than that of soybean oil, which may be a reaction of the presence of an OH group in the molecular structure of ricin oleic acid, the main constituent of castor oil. The hydroxyl moiety may interact with the Lewis acid sites and/or act as Bronsted base, decreasing the system activity.

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**G. Arzamendi, I. Campoa, E. Argui˜narena, M. S´anchez, M. Montes, L.M. Gand´ıa [18]** The activity and selectivity of a series of NaOH catalysts supported on alumina for the transesterification with methanol of refined sunflower oil have been investigated compared with that of homogeneous NaOH. The results have shown that the transesterification rate largely depends on the catalyst/methanol ratio, whereas the reaction selectivity seems to be governed by the methanol/oil molar ratio. Calcination of the NaOH/_-Al2O3 catalysts had a negative effect on their activity. On the other hand, the performance of the NaOH/alumina catalysts just dried at 393 K was not far of that of homogeneous NaOH dried at 323 K. The molar methanol/oil ratios considered were 6:1 and 12:1. The initial rate of transesterification is controlled by the catalyst/methanol ratio. The concentration of NaOH in the alcohol phase: 0.45 wt% (0.3 g NaOH, methanol/oil 6:1 show oil conversion about 86% and 0.6 g NaOH, methanol/oil 12:1 show oil conversion about 70%) or 0.23 wt.% (0.15 g. NaOH, methanol/oil 6:1 show oil conversion about 58% and 0.3 g. NaOH, methanol/oil 12:1 show oil conversion about 72%).

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## 2.8 Instruments

### 2.8.1 X-Ray Diffraction (XRD) [19]

This method used to prove the reaction of $TiO_2$ which complete or not complete reaction and observe crystalline structure of $TiO_2$ catalyst.

The diffraction of x-rays is of great analytical interest as applied to the study of the crystalline material producing the diffraction. No two chemical substances would be expected to form crystals in which the spacing of the planes is identical in all analogous direction, and so a complete study in which the sample assumes all possible angular positions in the path of the x-rays should give a unique result for each substances.

Equipment for x-ray diffraction is essentially comparable to an optical grating spectrometer, but since lenses and mirrors cannot be used with x-rays, the instrument is quite different in appearance from its optical analog. A reasonably collimated beam can be obtained from the output of an x-ray source with an extended target by passage through a bundle of metal tubes, or if collimation in one plane only is required, through the spaces between a stack of parallel metal sheets.

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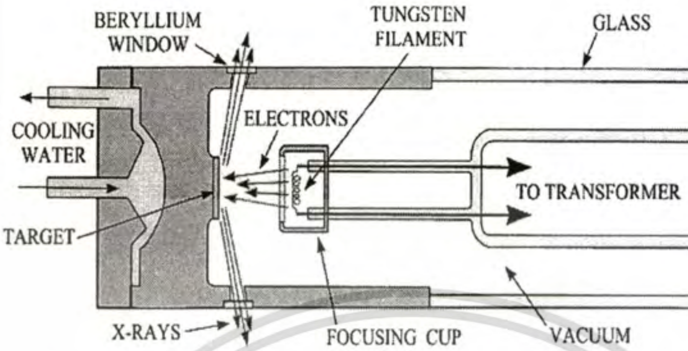

**Fig. 2.4** The electrodes of a x-ray tube, schematic cross section from U. S. Geological Survey Open-File Report 01-041 [19]

For diffraction apparatus, the diffracted beam of x-rays can be detected photographically elements which give its own particular pattern, and the appearance of a certain pattern proves the presence of that particular compounds. The photographic method is typified by an apparatus know as Debye-scherrer powder camera. The sample is prepared in the form of a fine homogeneous powder, and a thin layer of it is inserted in the path of the x-ray. The powder can be mounted on any noncrystalline material, such as paper, with an organic mucilage or glue as adhesive. The powdered sample contains so many particles that some are oriented in every possible direction relative to the beam of radiation. There will therefore be diffracted rays corresponding to all sets of planes in the crystals.

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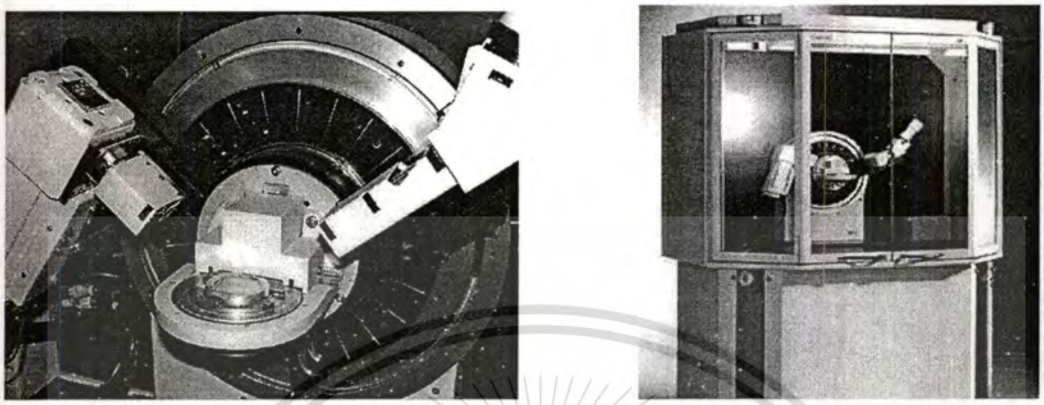

**Fig. 2.5** X-Ray Diffraction Instruments from Bruker AG Thailand [18]

### 2.8.2 Nuclear Magnetic Resonance (NMR) [20]

NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about molecules due to either the chemical shift Zeeman effect, or the Knight shift effect, or a combination of both, on the resonant frequencies of the nuclei present in the sample. It is a powerful technique that can provide detailed information on the topology, dynamics and three-dimensional structure of molecules in solution and the solid state. Thus, structural and dynamic information is obtainable (with or without "magic angle" spinning (MAS)) from NMR studies of quadrupolar nuclei (that is, those nuclei with spin $S > \frac{1}{2}$) even in the presence of magnetic dipole-dipole interaction broadening (or simply, dipolar broadening) which is always much smaller than the quadrupolar interaction strength because it is a magnetic vs. an electric interaction effect.

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Additional structural and chemical information may be obtained by performing double-quantum NMR experiments for quadrupolar nuclei such as 2H. Also, nuclear magnetic resonance is one of the techniques that has been used to design quantum automata, and also build elementary quantum computers [4][5]. This shift in the NMR frequency due to the electrons' molecular orbital coupling to the external magnetic field is called chemical shift, and it explains why NMR is able to probe the chemical structure of molecules which depends on the electron density distribution in the corresponding molecular orbitals. If a nucleus in a specific chemical group is shielded to a higher degree by a higher electron density of its surrounding molecular orbital, then its NMR frequency will be shifted "upfield" (that is, a lower chemical shift), whereas if it is less shielded by such surrounding electron density, then its NMR frequency will be shifted "downfield" (that is, a higher chemical shift).

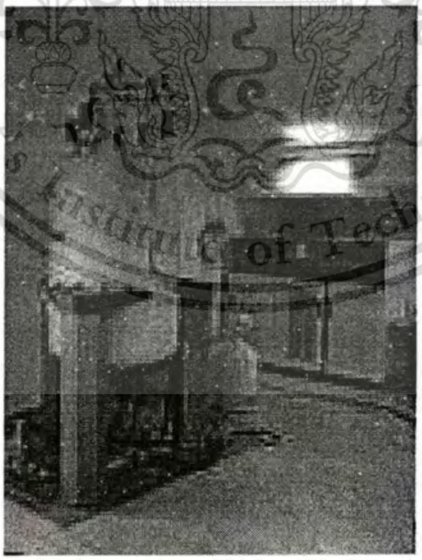

**Fig. 2.6** Nuclear Magnetic Resonance (NMR) [20]

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# Chapter 3

# Experimental Details

## 3.1 Chemicals

1. Refine palm olein from pericarp, Morrakot Industry company limited.
2. Toluene, Analytical grade, Apex Company Limited.
3. Potassium hydroxide, Analytical grade, Labscan Company Limited.
4. Phenolphthalein, Analytical grade, Apex Company Limited.
5. Methanol, Analytical grade, Apex Company Limited.
6. Sodium hydroxide, Analytical grade, Italma Company Limited.
7. Propanol,Analytical grade, Merck Company Limited.
8. Isopropanol, Analytical grade, Apex Company Limited.
9. Acetic acid, Analytical grade, Lab System Company Limited.
10. Acetyl acetone, Analytical grade, Laboratory Rasayan Company Limited.
11. Titanium (IV) isopropoxide, Analytical grade, Aldrich Company Limited.

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## 3.2 Equipments

1. Laboratory glassware
    - Volumetric flask
    - Pipet
    - Beaker
    - Distillation set
    - Separate funnel
    - Cylinder
    - Round bottom flask
    - Erlenmeyer Flask
2. Hot pate, Fisher Scientific Company.
3. Thermometer
4. Oven dry, Isotemp model, Fisher Scientific Company.
5. Burner, Furnace 6000 model, Thermolyne Company.
6. Crucible
7. Magnetic bar
8. Autoclave

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## 3.3 Instruments

1. X-Ray Diffractometer (XRD), D8 advance model, Bruker AXS GmbH Company Limited.

2. Nuclear Magnetic Resonance spectroscopy (NMR), AVANCE DPX 300, Bruker AXS GmbH Company Limited.

3. Small bench centrifuge, Varispeed model, Centurion Scientific Company Limited

4. UV lamp box, λ max 239 nm, 125 w.

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## 3.4 Experiment procedures

### 3.4.1 Prepare $TiO_2$ catalyst [13]

1. Mix isopropanol 50 ml., acetic acid 10 ml. and acetyl acetone 2 ml. into 100 ml. of volumetric flask.

2. Pipet titanium (IV) isopropoxide ($C_{12}H_2O_4Ti$) 0.1 M for 3.0686 ml.

3. Adjust the volume of solution with isopropanol to 100 ml.

4. Stir at 50 °C with hot plate for 30 minutes.

5. Leave the solution 6 hours.

6. Pour the solution into beaker and cover with aluminum foil.

7. Oven dry at 130 °C for 12 hours.

8. Grind and calcine with burner at 500 °C with heating rate at 3 °C/min, burn for 2 hours and cool down at 1 °C/min until room temperature for purify catalyst.

9. Test the characteristic of $TiO_2$ catalyst with XRD.

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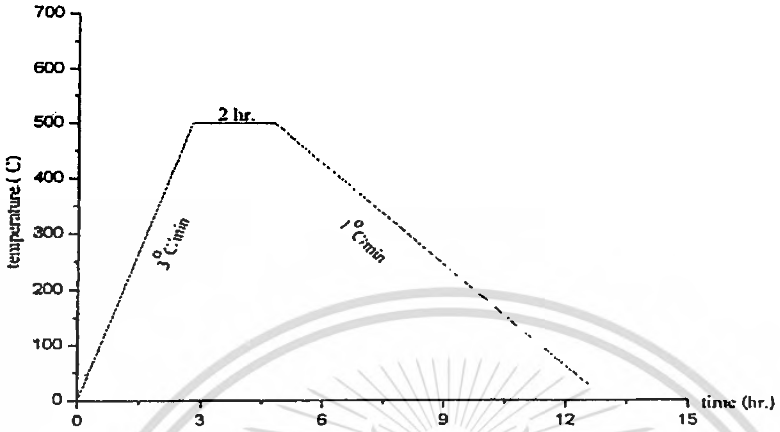

**Fig 3.1** Show the relationship between temperature and time of calcining [13]

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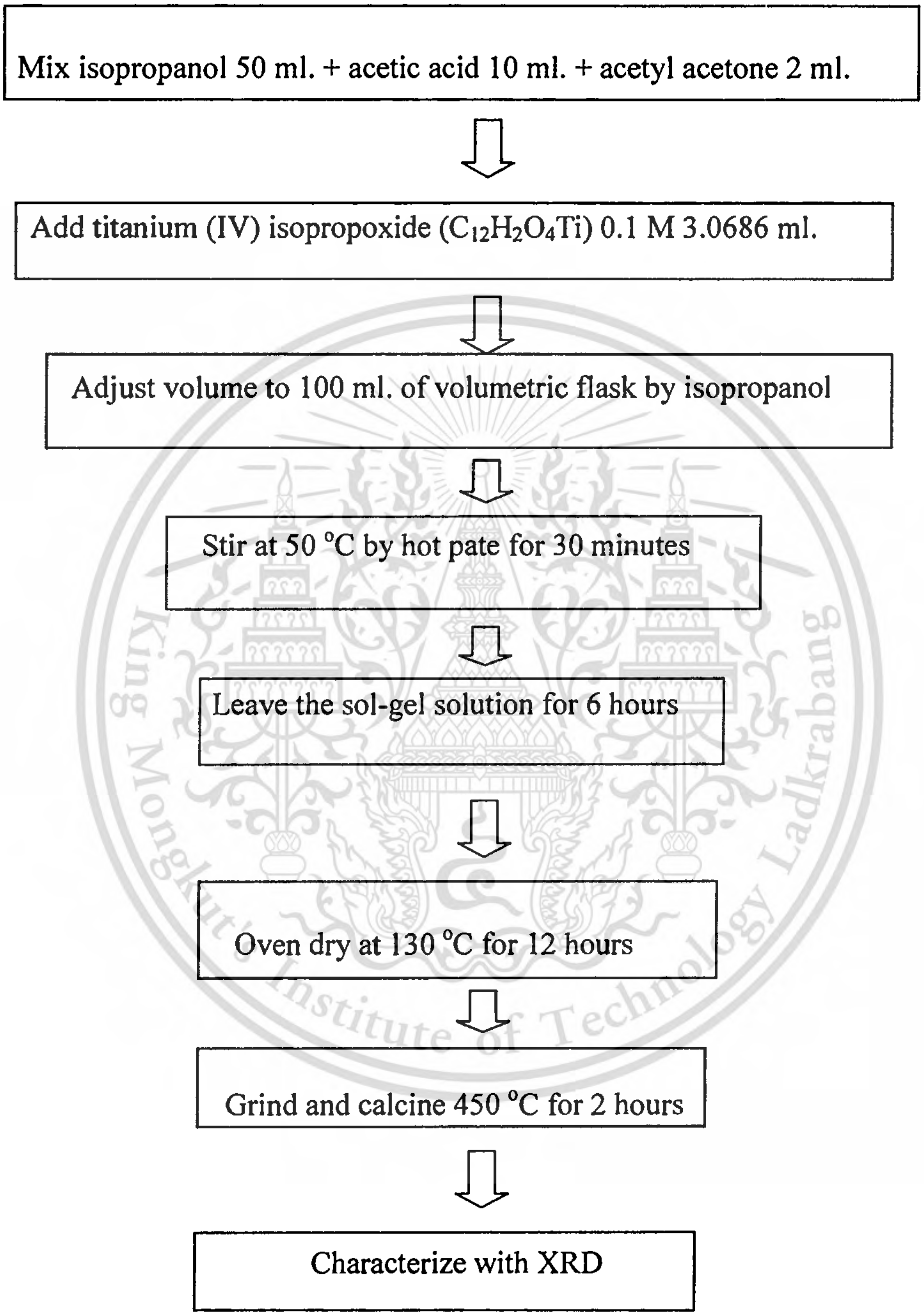

**Flow diagram 3.1** Preparation of $TiO_2$ catalyst.

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### 3.4.2 Biodiesel production

**Part 1** Biodiesel production for reference with sodium hydroxide catalyst with reflux

1. Weigh of palm oil 100 g.

2. Weigh of methanol 45 g. (12:1 weight of oil) [18]

3. Weigh solid sodium hydroxide 1.46 g.

4. Set the distillation set and warm to temperature 60 °C.

5. Dissolve sodium hydroxide 1.46 g. into methanol until clearly solution.

6. Pour the mixture of alcohol/catalyst into palm oil which is in distillation set which already have warmed to temperature about 60 °C then stir for complete the reaction for 90 minutes.

7. Pour the solution into separate funnel, the glycerin phase can be gravity separation with glycerin simply drawn off at the bottom of separate funnel.

8. After separate from the glycerin, the biodiesel is purified by washing gently with 50 ml. of water to remove residual catalyst or soaps.

9. Wash biodiesel with water until biodiesel is neutralized by testing pH of washed water with universal indicator.

10. Test the quantity of biodiesel with NMR.

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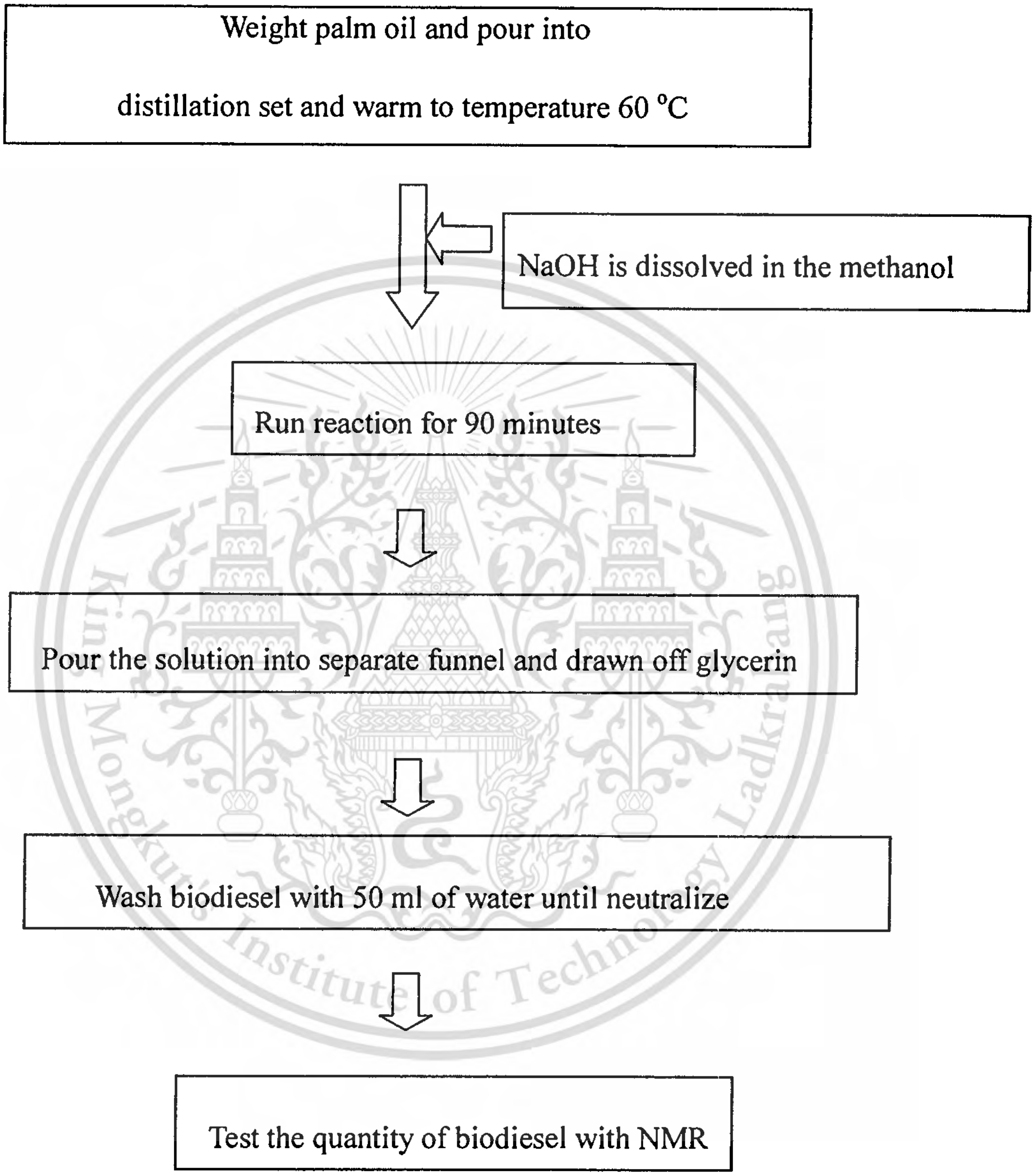

**Flow diagram 3.2** Biodiesel production with NaOH by reflux

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**Part 2** Biodiesel production as $TiO_2$ catalyst with reflux.

1. Weigh palm oil and set distillation column set.

2. 2, 4, and 6 % w/v of $TiO_2$ are dissolved in mixer with methanol.

3. The mixture of alcohol/catalyst are poured into the palm oil in distillation set which already have warmed to temperature about 60 °C and then stir it for complete the reaction for 90 minutes.

4. Catalysts are separated from reaction mixture with centrifugation 6,000 rpm for 20 minutes and catalysts are washed with hexane and dry at 60 °C for recovery.

5. Test the quantity of biodiesel with NMR.

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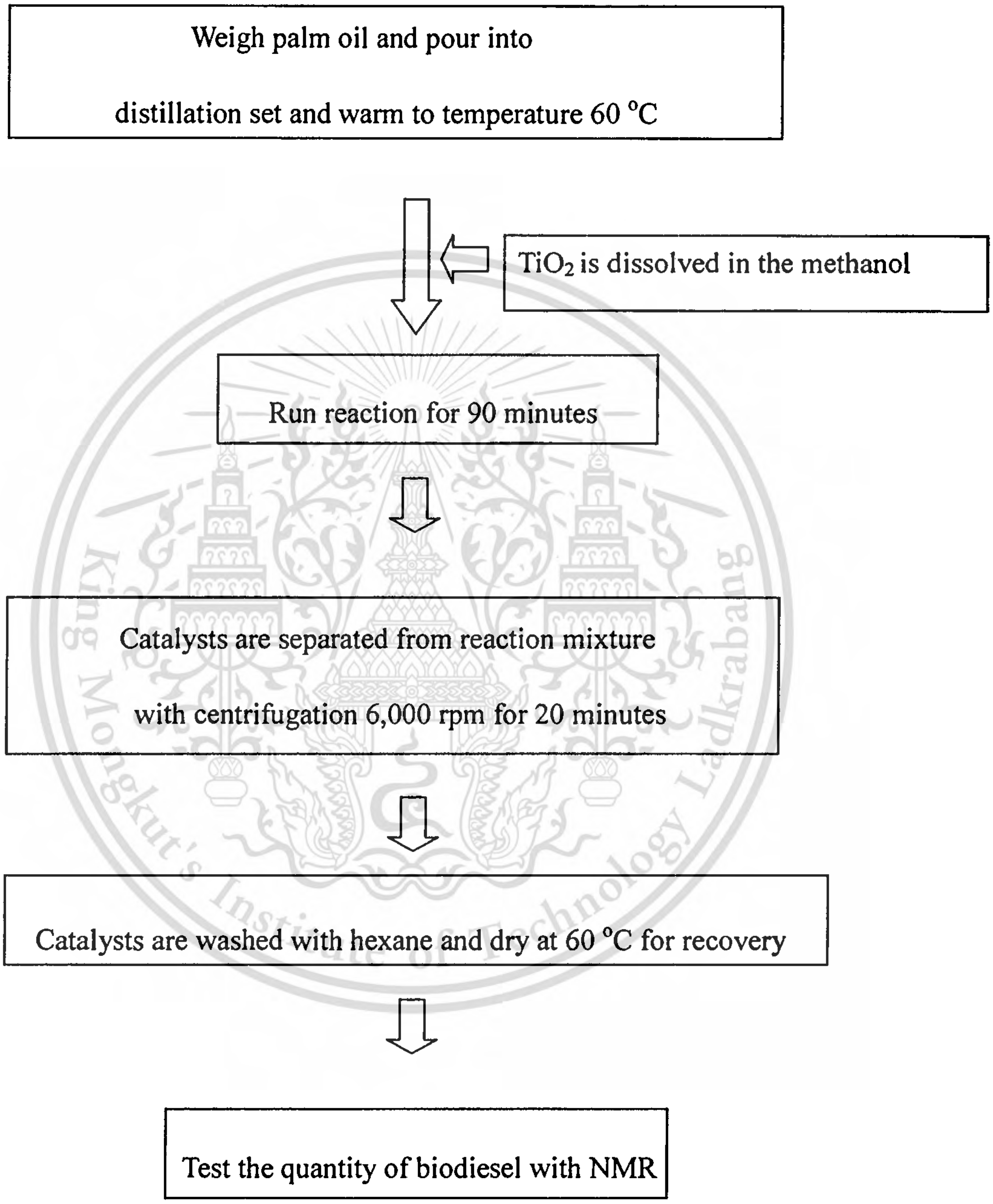

**Flow diagram 3.3** Biodiesel production with $TiO_2$ by reflux

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**Part 3** Biodiesel production as $TiO_2$ catalyst under UV lamp condition

1. Weigh palm oil 50 g. into volumetric flask.

2. Weigh methanol 23 g. (12:1 weight of oil).

3. 2, 4, and 6 % w/v of $TiO_2$ are dissolved in mixer with methanol and palm oil.

4. Stir and leave mixtures under UV lamp condition for 6 hours.

5. Catalysts are separated from reaction mixture with centrifugation 6,000 rpm for 20 minutes and catalysts are washed with hexane and dry at 60 °C for recovery.

6. Test the quantity of biodiesel with NMR.

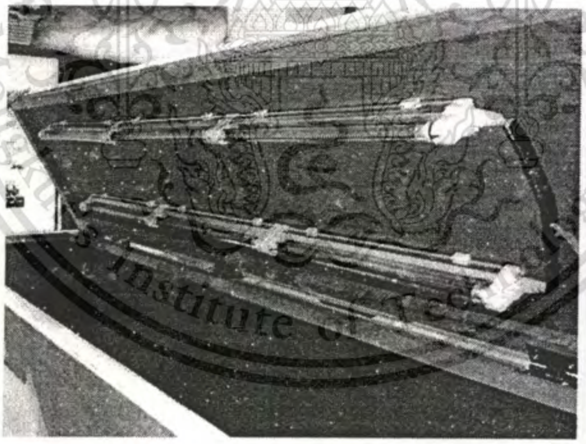

**Fig 3.2** UV lamp box

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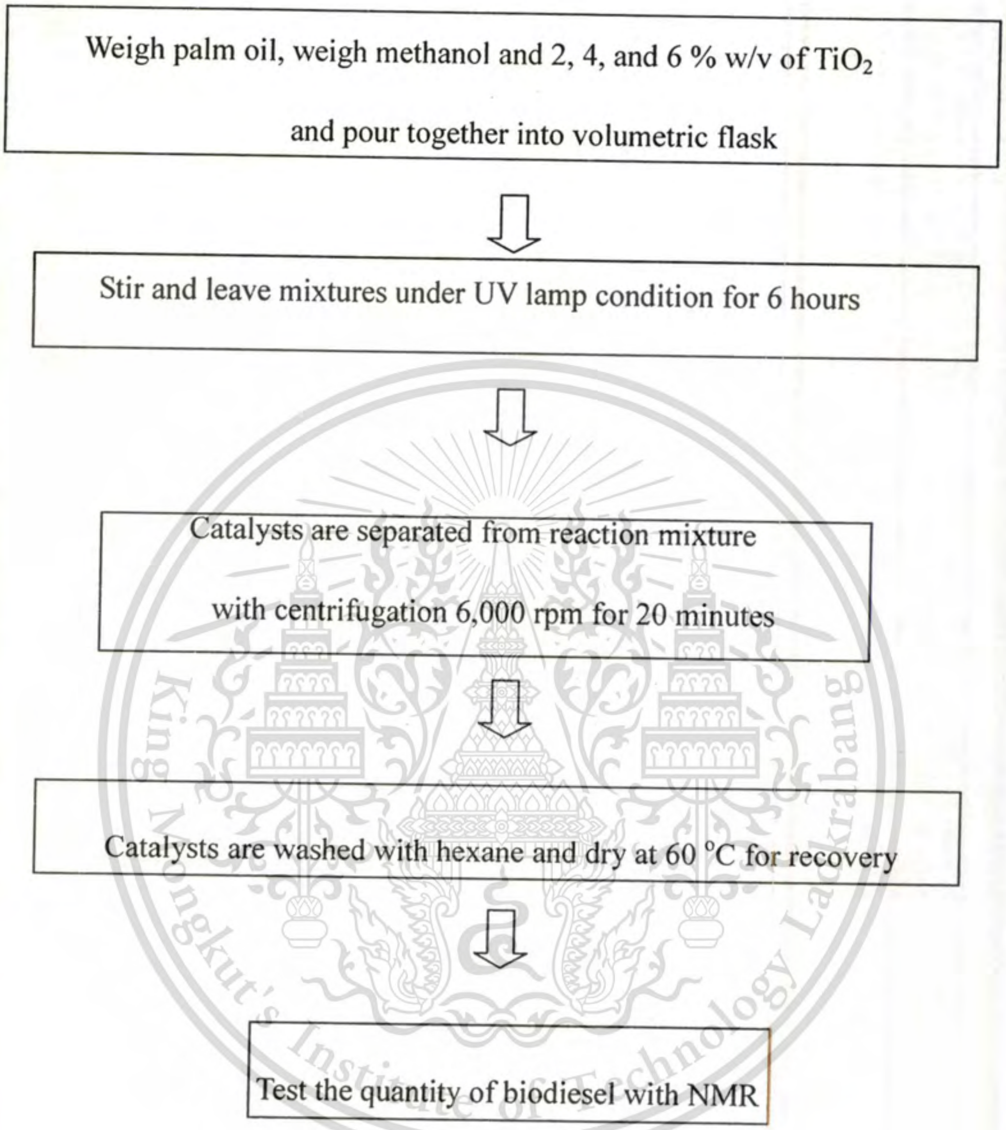

**Flow diagram 3.4** Biodiesel production with $TiO_2$ under UV lamp condition

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**Part4** Biodiesel production as $TiO_2$ catalyst with hydrothermal using autoclave [23]

1. Weigh palm oil 5 g. and methanol 2.24 g. into autoclave.

2. 2, 4, and 6 % w/v of $TiO_2$ are dissolved in mixer with methanol and palm oil.

3. Set the autoclave and heat with oven dry for 4 hours.

4. Catalysts are separated from reaction mixture with centrifugation 6,000 rpm for 20 minutes and catalysts are washed with hexane and dry at 60 °C for recovery.

5. Test the quantity of biodiesel with NMR.

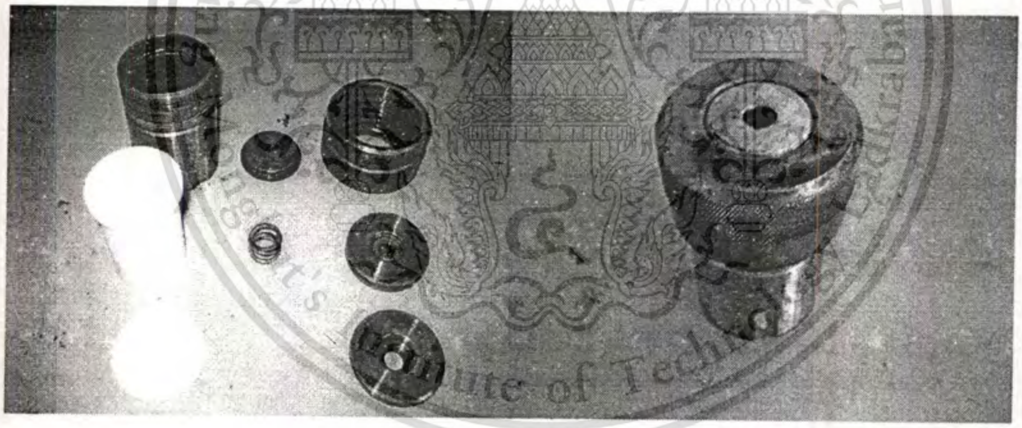

**Fig 3.3** Teflon-line auto clave

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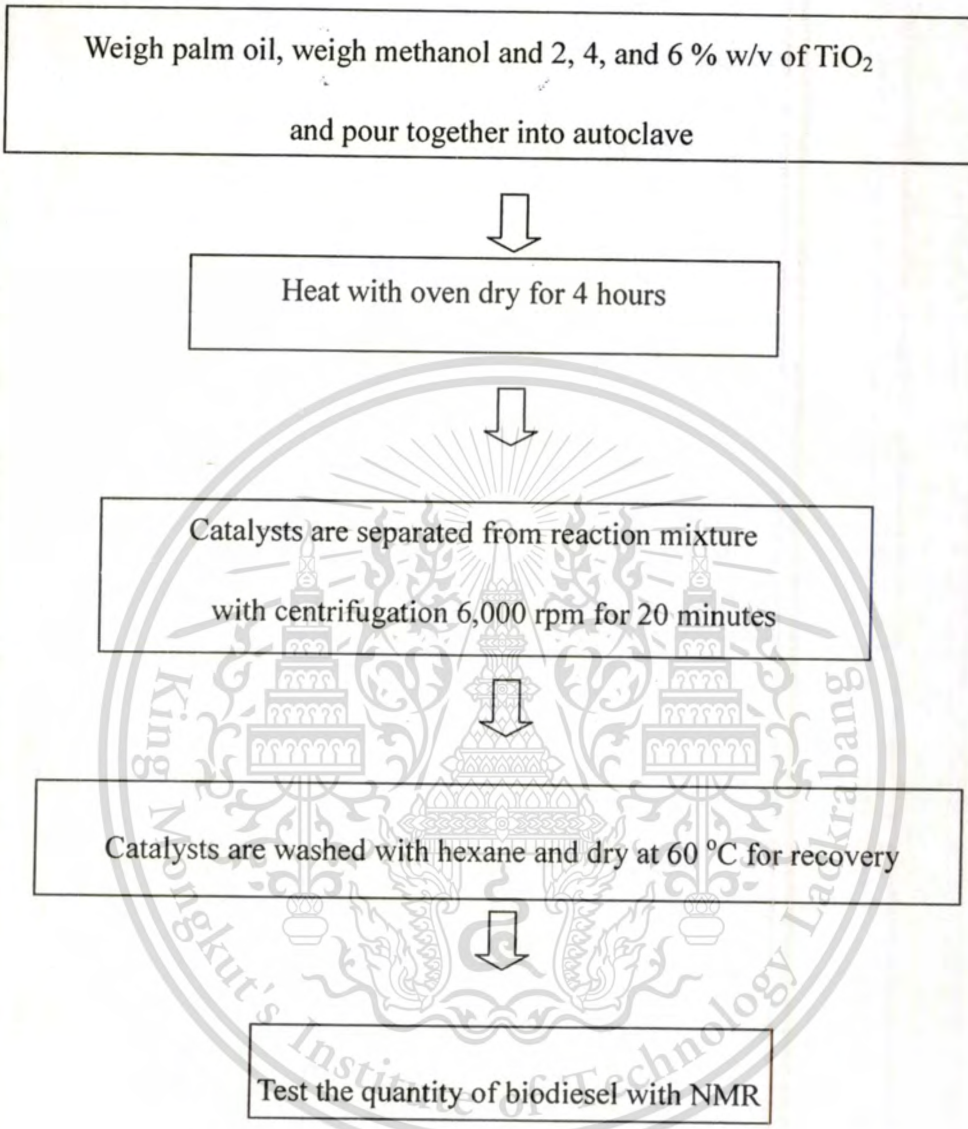

**Flow diagram 3.5** Biodiesel production with $TiO_2$ catalyst using autoclave

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# Chapter 4

# Results and Discussion

The objective of this project were to study the effect of $TiO_2$ as catalyst in biodiesel production and comparative the production quantity of the $TiO_2$ and NaOH as catalysts in biodiesel production with palm oil to methanol ratio was 12:1[18]. The structure of $TiO_2$ was analysis by XRD and the percentage of methyl ester of biodiesel by using $TiO_2$ as catalyst was analysis by NMR which these results were also determined.

## 4.1 Characterization technique of $TiO_2$ by the x-ray diffraction (XRD)

The first part of this work,The anatase $TiO_2$ nano powder were prepared by sol-gel because of anatase $TiO_2$ structure are more stable than others structure. We prepared 0.1 M $TiO_2$ by mix isopropanol 50 ml., acetic acid 10 ml., and acetyl acetone 2 ml. then adjust volume to 100 ml. of volumetric flask by isopropanal. After that stir at 50 °C for 30 minutes. Sol-gel solution was left at room temperature for 6 hours and dried at 103 °C for 12 hours. Dried sol-gel was calcined at 500 °C with heating rate at 3 °C per minutes for 2 hours. Crystal structural calcined gel are characterized by x-ray diffraction technique[13].

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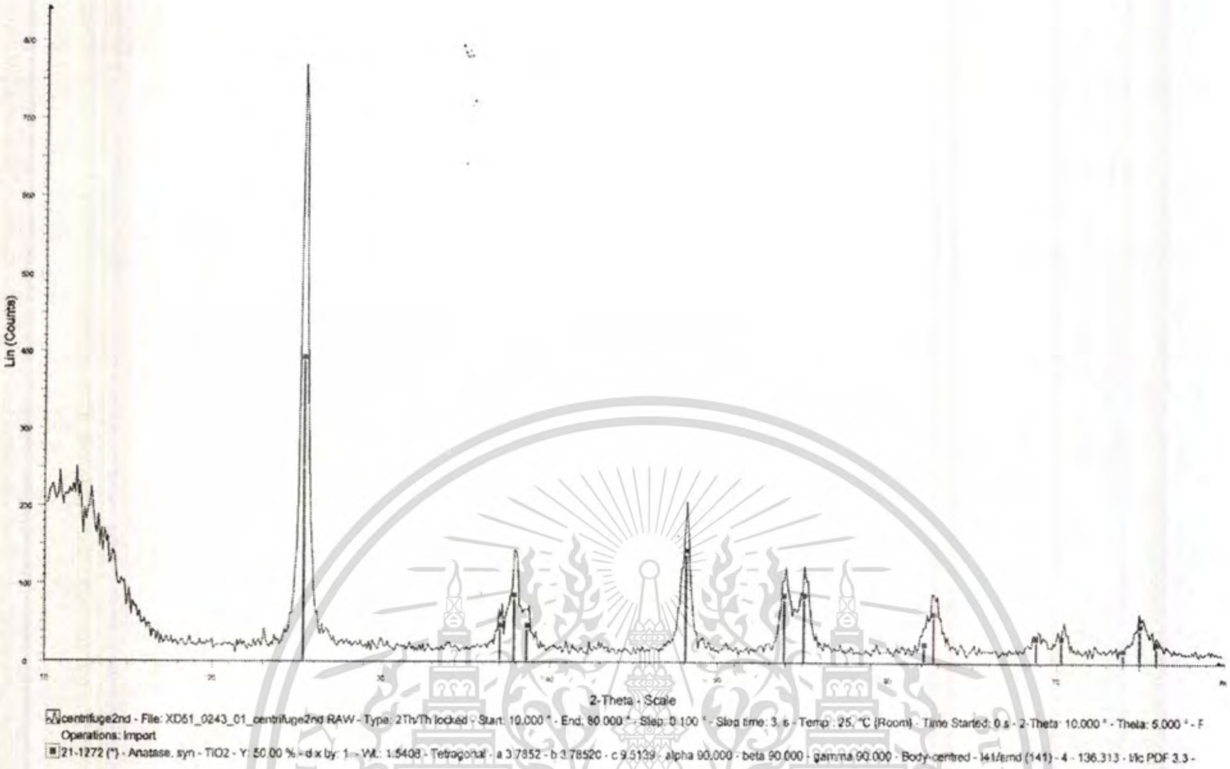

**Fig 4.1** Shows the x-ray diffraction pattern of 0.1 M $TiO_2$

Fig 4.1 shows the x-ray diffraction pattern of 0.1 M $TiO_2$ which match with JCPDS Standard numbers 21-1272 by consider main peak at plane 101 with 2Θ be equal to 25.32° which specific only anatase structure. From previous research [13], $TiO_2$ with others concentration will give the lower composition of anatase structure.

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## 4.2 Physical characterization of $TiO_2$ before and after calcining

**Fig 4.2** Physical characterization of $TiO_2$ before calcining

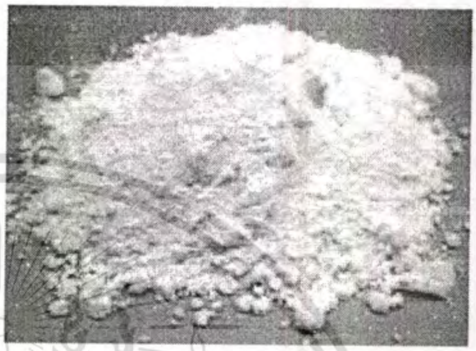

**Fig 4.3** Physical characterization of $TiO_2$ after calcining

The powder of $TiO_2$ before calcining has red color by a thermal treatment (450-600 °C) to remove the organic parts and solvent is evaporated. When a hydrothermal treatment, crystallization of powders has white color.

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## 4.3 Analysis functional group of biodiesel [21]

The functional groups of biodiesel production are observed by $^1$H–Nuclear Magnetic Resonance ($^1$H-NMR) technique. The first report on spectroscopic determination of the yield of transesterification reaction utilized $^1$H-NMR depicting its progressing spectrum. The signal due to methylene protons adjacent to the ester group in triglycerides appear at 2.3 ppm. and after the reaction the methoxy protons of the methyl esters appear at 3.7 ppm. (Fig. 4.4). These authors have used the areas of the signals of methylene and methoxy protons to monitor the yield of transesterification.

A simple equation is given:

$$C = 100 \times \left(\frac{2A_{ME}}{3A_{CH_2}}\right)$$

where C, percentage conversion of triglycerides to corresponding methyl ester

$A_{ME}$, integration value of the protons of the methyl esters (the strong singlet)

$A_{CH_2}$, integration value of the methylene protons

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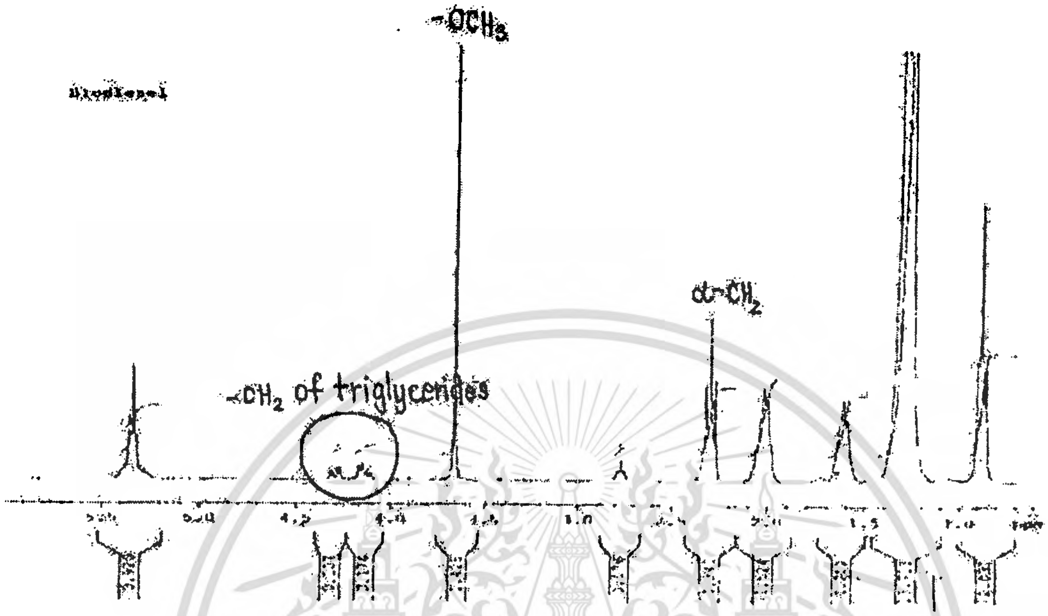
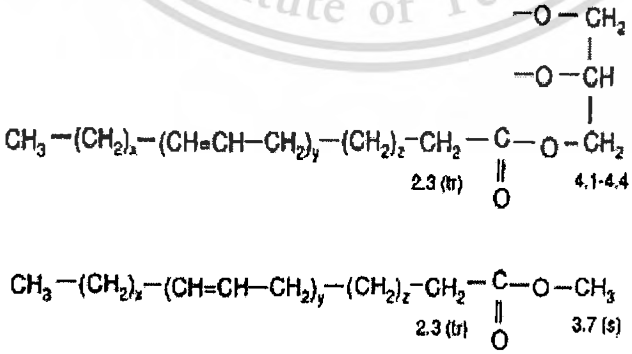


Fig 4.4 Show the signal of biodiesel production [22]



Triglycerides

$$CH_3-(CH_2)_x-(CH{=}CH-CH_2)_y-(CH_2)_z-\underset{2.3\,(tr)}{CH_2}-\underset{O}{\overset{\|}{C}}-O-\underset{4.1\text{-}4.4}{CH_2}$$

$$\begin{array}{l} -O-CH_2 \\ \quad\;\; | \\ -O-CH \\ \quad\;\; | \end{array}$$

Biodiesel

$$CH_3-(CH_2)_x-(CH{=}CH-CH_2)_y-(CH_2)_z-\underset{2.3\,(tr)}{CH_2}-\underset{O}{\overset{\|}{C}}-O-\underset{3.7\,(s)}{CH_3}$$

Fig 4.5 Assignment of chemical shifts of protons in transesterification reaction [21]

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## 4.4 Performance of homogeneous NaOH

In this experiment, a 1.46 g of catalyst was used to 100 g of oil and use 45 g of methanol. The molar methanol/oil ratios considered was 12:1. The initial rate of transesterification is controlled by the catalyst/methanol ratio. NaOH is soluble in methanol according to the following reaction leading to the formation of sodium methoxide :

$$NaOH + CH_3OH \longleftrightarrow NaOCH_3 + H_2O \qquad \textbf{Eq. 4.1}$$

The process of oil methanolysis involves three stepwise reversible reactions. First, the triglycerides (TG) present in the oil are converted to diglycerides (DG). The second step is the conversion of diglycerides to monoglycerides (MG), which are finally converted to glycerol (GLY). A molecule of methyl ester (ME) is produced from each acylglycerol ( TG, DG or MG) at each step:

$$TG + CH_3OH \longleftrightarrow DG + ME \qquad \textbf{Eq. 4.2}$$

$$DG + CH_3OH \longleftrightarrow MG + ME \qquad \textbf{Eq. 4.3}$$

$$MG + CH_3OH \longleftrightarrow GLY + ME \qquad \textbf{Eq. 4.4}$$

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The reaction proceeds via the nucleophilic attack of the methoxide species on a carbon atom of the carbonyl groups of the aclyglycerols resulting in the formation of a methyl ester. Taking into account that the methoxide according to Eq. 4.1, this mechanism justifies the important role found for the NaOH concentration in determining the initial rate of transesterification.

However, reactions (Eq. 4.2 – Eq. 4.4) are reversible. This fact implies that the final extent to which the oil is converted mainly depends on the methanol/oil ratio, that is, the amount of methanol used in excess with respect to the stoichiometric relation (12:1), which helps to shift the reaction towards the methyl esters formation.

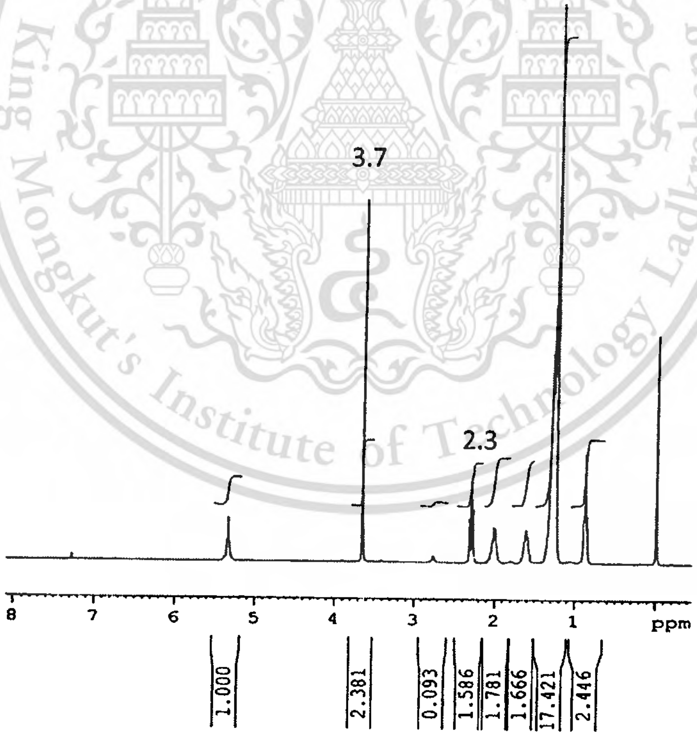

**Fig 4.6** Shows the NMR patterns of biodiesel production by use NaOH as catalyst

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From experiment, Fig 4.6 shows the NMR patterns of biodiesel production by use NaOH as catalyst. The report on $^1$H-NMR determination of the yield of transesterification.The signal due to methylene protons ($CH_2$-C (=O)-O) adjacent to the ester group in triglycerides appear at 2.3 ppm, the reaction of the methoxy protons ($CH_3$-O-C-(=O)) of the methyl ester appear at 3.7 ppm.

So, this result indicated that is methyl ester by transesterification reaction of palm oil and can calculation for find percentage of yield of methyl ester by following this formula:

$$\%\ \text{methyl ester} = \frac{100\times(2\times\text{area of peak} -OCH_3)}{3\times\text{area of peak } \alpha\text{-}CH_2}$$

$$= \frac{100\times(2\times2.381)}{3\times1.586}$$

$$=100.08\ \%$$

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## 4.5 Performance of $TiO_2$ as catalyst by reflux method

The evolution with reaction time of palm oil conversion at 60°C . Catalyst ($TiO_2$) ranged from 2, 4 and 6 % w/v of $TiO_2$ referred to the amount of oil (100 g.) changed initially into the reflux condenser. The molar methanol/oil ratios considered was 12:1

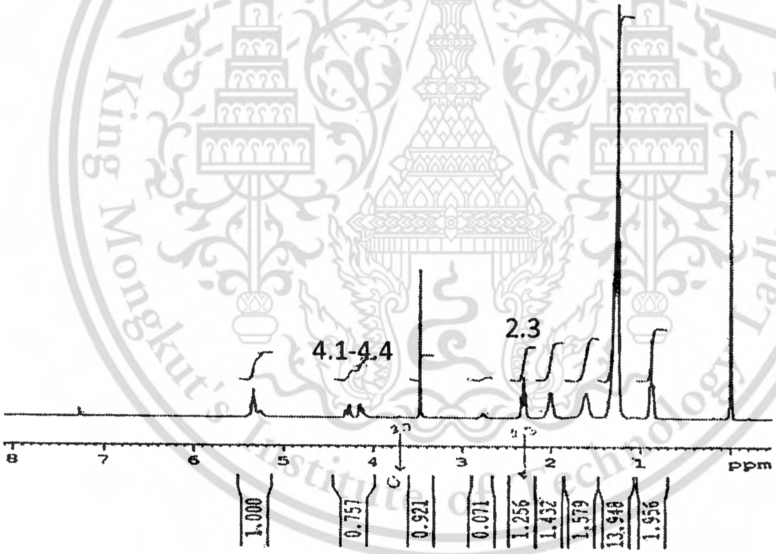

Fig 4.7 Shows the NMR patterns of biodiesel production by use 2% $TiO_2$ as catalyst

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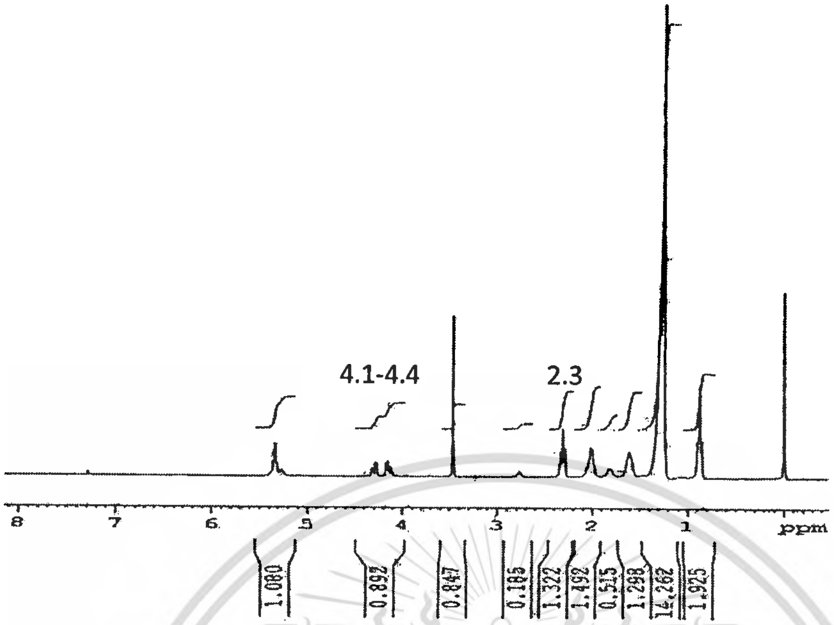

**Fig 4.8** Shows the NMR patterns of biodiesel production by use 4% $TiO_2$ as catalyst

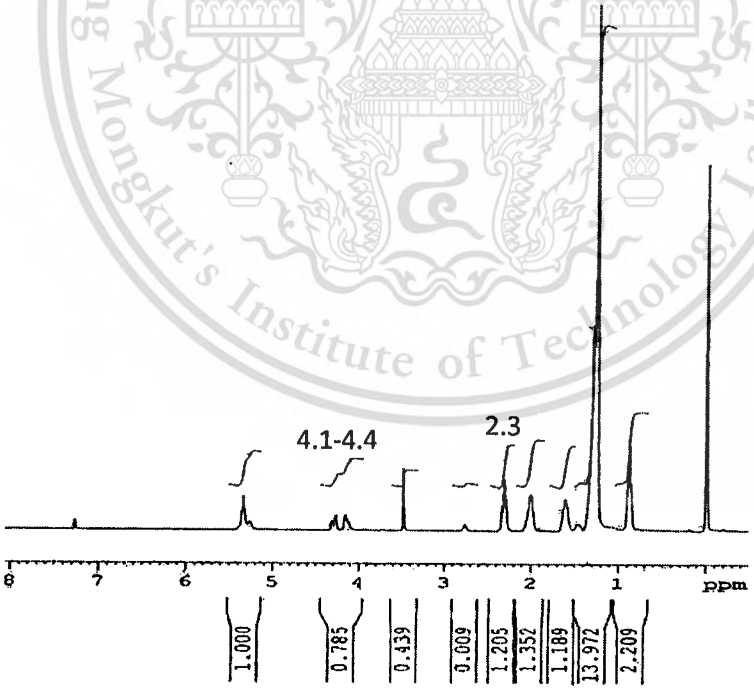

**Fig 4.9** Shows the NMR patterns of biodiesel production by use 6% $TiO_2$ as catalyst

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From Fig 4.7 – 4.9, We can consider that the signal of methylene protons ($CH_2$-C(=O)-O) in triglycerides appear at 2.3 ppm and the signal of $CH_2$ of triglycerides appear at 4.1-4.4 ppm which still be palm oil. Signal of methoxy protons ($CH_3$-O-C(=O) of the methyl ester is not appear at 3.7 ppm. So, this result of $TiO_2$ for this condition is unaffected catalyst and can not occur the methyl ester.

## 4.6 Performance of $TiO_2$ as a catalyst by UV lamp

We conducted the catalytic activity tests for the $TiO_2$ catalysts at 40°C with a 12:1 molar ratio of the methanol to oil. It will occur transesterification reaction for 6 h. Catalyst ($TiO_2$) ranged from 2, 4 and 6 % w/v of $TiO_2$ referred to the amount of oil (100 g.) react into the UV lamp.

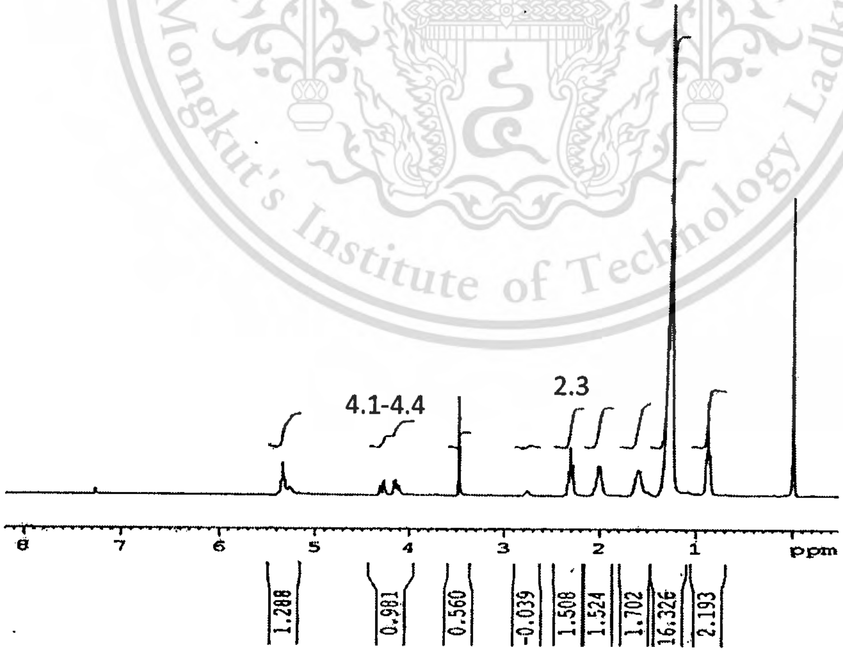

**Fig 4.10** Show the NMR patterns of biodiesel production by use 2% $TiO_2$ by UV lamp

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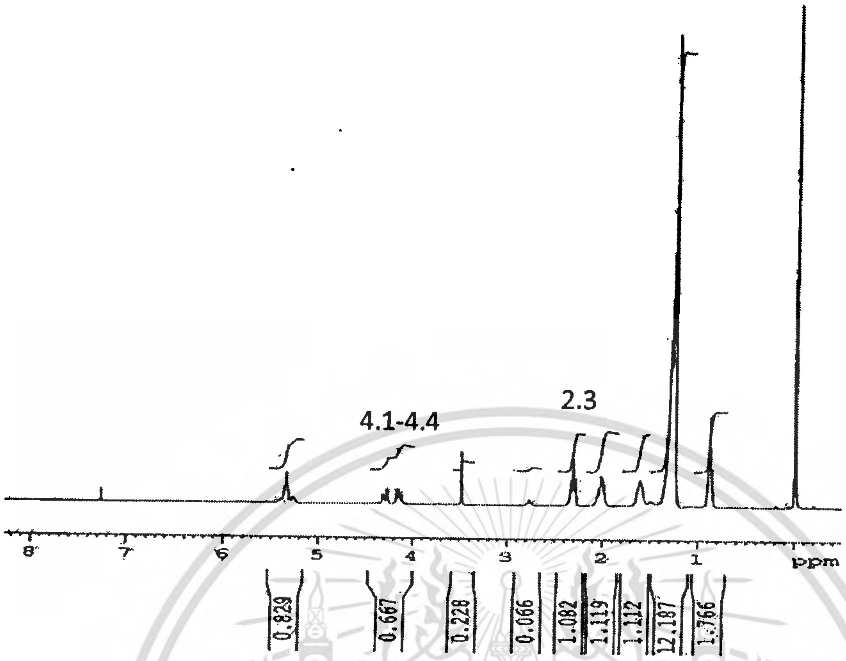

**Fig 4.11** Show the NMR patterns of biodiesel production by use 4% $TiO_2$ by UV lamp

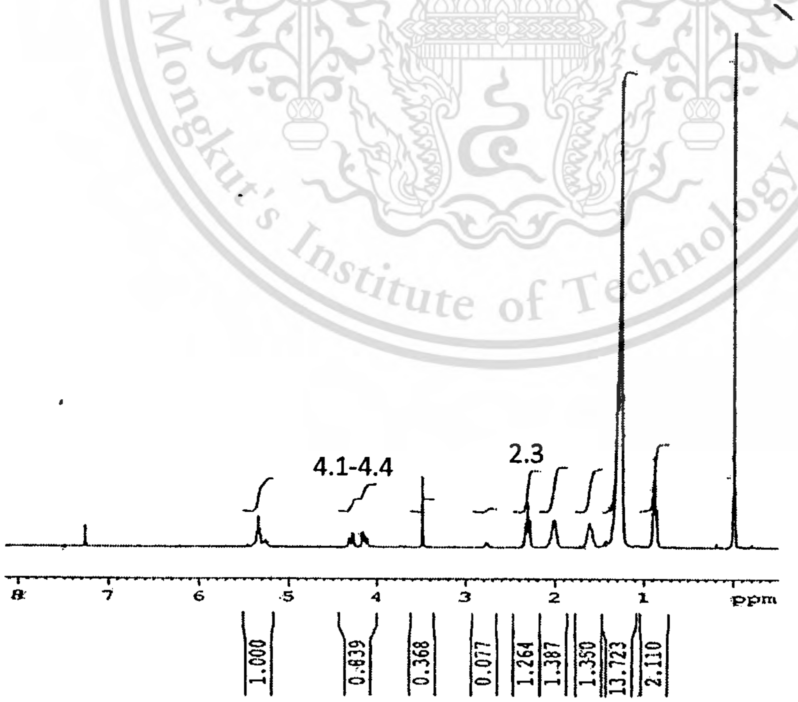

**Fig 4.12** Show the NMR patterns of biodiesel production by use 6% $TiO_2$ by UV lamp

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From Fig 4.10 – 4.12, We can consider that the signal of methylene protons ($CH_2$-C(=O)-O) in triglycerides appear at 2.3 ppm and the signal of $CH_2$ of triglycerides appear at 4.1-4.4 ppm But, it don't find signal of methoxy protons ($CH_3$-O-C(=O) of the methyl ester appear at 3.7 ppm

The result for the $TiO_2$ by UVlamp, show that palm oil did not turn into methyl ester. One of the reasons of this seem to be the possible obstruction of not sufficient energy to stimulate the catalyst.

## 4.7 Performance of $TiO_2$ as a catalyst by Hydrothermal [23]

In this experiment, we use 5 g of oil and use 2.25 g of methanol. The initial rate of transesterification is controlled by the catalyst/methanol ratio. We conducted the catalytic activity tests for the $TiO_2$ catalysts at 200°C with a 12:1 molar ratio of the methanol to oil. It will occur transesterification reaction for 4 h. Catalyst ($TiO_2$) ranged from 2, 4 and 6 % w/v of $TiO_2$ referred to the amount of oil (5 g.) react into the hydrothermal.

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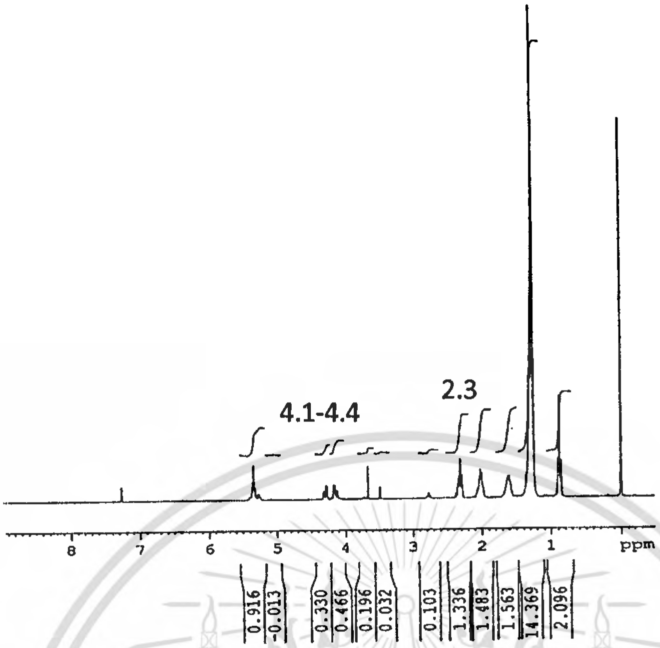

**Fig 4.13** Show the NMR patterns of biodiesel production by use 2% $TiO_2$ by hydrothermal

This result indicated that is methyl ester by transesterification reaction of palm oil and can calculation for find percentage of yield of methyl ester by following this formula:

$$\%\ \text{methyl ester} = \frac{100\times(2\times\text{area of peak -}OCH_3)}{3\times\text{area of peak }\alpha\text{-}CH_2}$$

$$= \frac{100\times(2\times0.196)}{3\times1.336}$$

$$= 9.78\ \%$$

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**Fig 4.14** Show the NMR patterns of biodiesel production by use 4% $TiO_2$ by hydrothermal

This result indicated that is methyl ester by transesterification reaction of palm oil and can calculation for find percentage of yield of methyl ester by following this formula:

$$\% \text{ methyl ester} = \frac{100\times(2\times\text{area of peak} -OCH_3)}{3\times\text{area of peak } \alpha\text{-}CH_2}$$

$$= \frac{100\times(2\times0.204)}{3\times1.380}$$

$$=9.85\ \%$$

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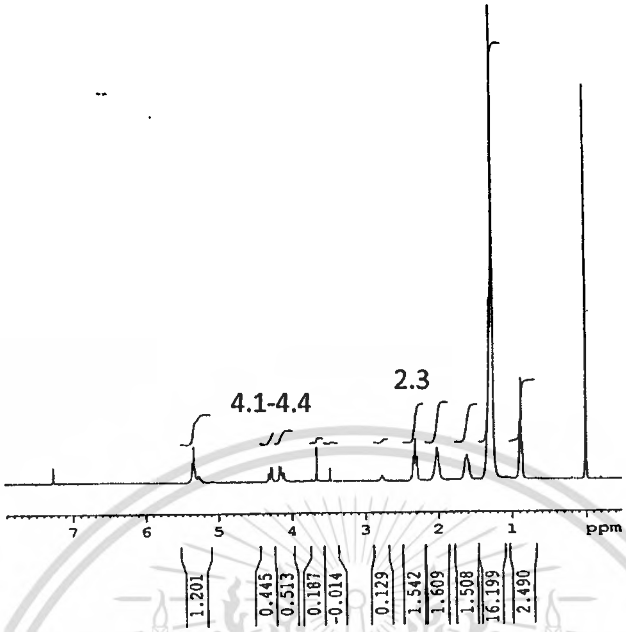

**Fig 4.15** Show the NMR patterns of biodiesel production by use 6% $TiO_2$ by hydrothermal

This result indicated that is methyl ester by transesterification reaction of palm oil and can calculation for find percentage of yield of methyl ester by following this formula:

$$\% \text{ methyl ester} = \frac{100\times(2\times\text{area of peak }-OCH_3)}{3\times\text{area of peak }\alpha\text{-}CH_2}$$

$$= \frac{100\times(2\times0.187)}{3\times1.542}$$

$$=8.08\ \%$$

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From Fig 4.13 – 4.15, The signal due to methylene protons ($CH_2$-C (=O)-O) adjacent to the ester group in triglycerides appear at 2.3 ppm, the reaction of the methoxy protons ($CH_3$-O-C-(=O)) of the methyl ester appear at 3.7 ppm. So, this result indicated that is methyl ester by transesterification reaction of palm oil.

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# Chapter 5

# Conclusions and recommendations

## 5.1 Conclusions

Biodiesel has become more attractive for an alternative diesel fuel because of increases in crude oil price, limited resources of fossil oil and environmental problem. In this work, $TiO_2$ catalyst is developed for biodiesel production from palm oil when compare with usually catalyst, NaOH to decrease the catalyst amount and production cost of biodiesel.

In the case of reference NaOH, it found that NaOH is effective catalyst by the reflux method while give the condition at 60 °C with 12:1 molar ratio of methanol per oil for a reaction time of 90 minutes and atmospheric pressure. NaOH give 100.08% of methyl ester.

As concerns about $TiO_2$, We performed three method. Both reflux method and UV light bulb method are unaffected by the 2, 4, and 6 % w/v of $TiO_2$ catalyst in the condition at 60 °C with 12:1 molar ratio of methanol per oil for a reaction time of 90 minutes with atmospheric pressure in case of reflux method and 40 °C with 12:1 molar ratio of methanol per oil for a reaction time of 6 hours with atmospheric pressure in case of UV lamp method.

For hydrothermal using autoclave method has an effected by the 2, 4, and 6 % w/v of $TiO_2$ catalyst in the condition at 200 °C with 12:1 molar ratio of methanol per oil for reaction time 4 hours. 2% w/v of $TiO_2$ give 9.98% of methyl ester, 4% w/v of $TiO_2$ give 9.85% of methyl ester and 6% of $TiO_2$ give 8.08% of methyl ester.

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We found that percentage of $TiO_2$ did not significant cause of are not different in percentage of methyl ester for the autoclave method. Moreover, $TiO_2$ are unaffected when compared with NaOH because at the reaction of $TiO_2$ with methanol or initial step, they can not produce an methoxide which is protonated catalyst for complete the biodiesel reaction, from electron potential of hole and electron in the valance and conduct state have not enough energy to oxidize methanol or the recombination rate between electron and hole are very fast, maybe faster than oxidize reaction rate. $TiO_2$ catalyst must use the higher in pressure for higher temperature and more time to stimulate $TiO_2$ to reach the reaction while NaOH have the higher activity. Furthermore, the other disadvantage of $TiO_2$ are complicated to separate $TiO_2$ for recover catalyst.

## 5.2 Recommendations

1. The most possible method is hydrothermal using autoclave, we recommence strongly condition such as higher pressure for higher temperature, more time.
2. The nano particle catalyst can be reused and more economize which resulting in reduce the cost for biodiesel production.
3. We expect to apply this experiment to produce more efficiency of biodiesel.

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# References

[1] Fangrui Ma, Milford A. Hanna, *Biodiesel production: a review*, Bioresource Technology 70 (1999) 1-15

[2] Wenlei Xie, Hong Peng, Ligong Chen, *Transesterification of soybean oil catalyzed by potassiumloaded on alumina as a solid-base catalyst* , Applied Catalysis A: General 300 (2006) 67–74

[3] Hak-Joo Kim, Bo-Seung Kang, Min-Ju Kim, Young Moo Park, Deog-Keun Kim, Jin-Suk Lee, Kwan-Young Lee, *Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst*, Catalysis Today 93–95 (2004) 315–320

[4] Magın Lapuerta, Octavio Armas, Jose Rodrı guez-Ferna ndez , *Effect of biodiesel fuels on diesel engine emissions*, Progress in Energy and Combustion Science 34 (2008) 198–223

[5] Y.C. Sharma, B. Singh, S.N. Upadhyay, *Advancements in development and characterization of biodiesel: A review*, Fuel 87 (2008) 2355–2373

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

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

[7] http://en.wikipedia.org/wiki/Vegetable_oils, 05-10-08, 09:46pm

[8] http://en.wikipedia.org/wiki/Palm_oil, 05-10-08, 01:05pm

[9] Ayhan Demirbas, *Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics*, Energy Conversion and Management 47 (2006) 2271–2282

[10] Ulf Schuchardta, Ricardo Serchelia, and Rogério Matheus Vargas, *Transesterification of Vegetable Oils: a Review*, J. Braz. Chem. Soc., Vol. 9, No. 1, 199-210, 1998.

[11] http://en.wikipedia.org/wiki/Catalysis, 05-10-08, 01:27pm

[12] http://ruby.colorado.edu/~smyth/min/tio2.html., 04-10-08, 11:18pm

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

[13] Usa Sukkha, *The effect of thermal behavior and silver doping on crystal structure and physical properties of titanium dioxide,* King Mongkut's Institute of Technology Ladkrabang. , page 5-6, 2008

[14] O.Carp, C.L. Huisman and A. Reller, *Photoinduced reactivity of titanium dioxide*, Progress in Solid State Chemistry (2004)33-177

[15] Ayato Kawashima, Koh Matsubara and Katsuhisa Honda, *Development of heterogeneous base catalysts for biodiesel production*, Bioresource Technology (2008)

[16] Fernando Gordillo Delgado, Katherine Villa Gomez, Claudia Mejıa a Morales, " *Titanium dioxide nanocrystalline bactericidal thin films grown by sol–gel technique* ", Microelectronics Journal (2008)

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

[18] G. Arzamendi, I. Campoa, E. Argui˜narena, M. S´anchez, M. Montes, L.M. Gand´ıa, "*Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts:Comparison with homogeneous NaOH*",Chemical Engineering Journal (2007)

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Forbidden to modify the content, and cite the document when use.

[19] Pungor Erno, *A practical guide to instrument analysis*, CRC press, 1995

[20] http://en.wikipedia.org/wiki/NMR#Theory_of_nuclear_magnetic_resonance

[21] L.C. Meher, D. Vidya Sagar and S.N. Naik, *Technical aspects of biodiesel production by transesterification*—a review, Renewable and Sustainable Energy Reviews (2006)

[22] Kanita Singthaisomboon, Jiranan Rompoyen and Naruemol Passayawan , *Production of Biodiesel from Waste Vegetable oil by Solar Energy,* King Mongkut's Institute of Technology Ladkrabang. (2007)

[23] Zull Ilham and Shiro Saka, *Dimethyl carbonate as potential reactant in non-catalytic biodiesel production by supercritical method*, Bioresource Technology (2009)

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# Appendix

## Calculation

### 1. Calculation for $TiO_2$ catalyst with reflux and UV lamp

1.1. Methanol per oil ratio (12:1)

methanol : oil

$$\frac{X}{32} = \frac{100}{854}$$

$$x = 3.747$$

So, methanol is 3.747(12) = 44.96 g.

1.2. The concentration of titanium dioxide ($TiO_2$)

2 % of $TiO_2$; $$\frac{X}{144.96+X} = \frac{2}{100} \quad \therefore X = 2.958 \text{ g.}$$

4 % of $TiO_2$; $$\frac{X}{144.96+X} = \frac{4}{100} \quad \therefore X = 6.040 \text{ g.}$$

6 % of $TiO_2$; $$\frac{X}{144.96+X} = \frac{6}{100} \quad \therefore X = 9.253 \text{ g.}$$

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2. Calculation of $TiO_2$ as catalyst with hydrothermal using autoclave

2.1. Methanol per oil ratio (12:1)

methanol : oil

$$\frac{X}{32}=\frac{5}{854}$$

x = 0.187

So, methanol is 0.187(12) = 2.24 g.

2.2. The concentration of titanium dioxide ($TiO_2$)

2 % of $TiO_2$; $$\frac{X}{7.2+X}=\frac{2}{100} \qquad \therefore X = 0.147 \text{ g.}$$

4 % of $TiO_2$; $$\frac{X}{7.2+X}=\frac{4}{100} \qquad \therefore X = 0.300 \text{ g.}$$

6 % of $TiO_2$; $$\frac{X}{7.2+X}=\frac{6}{100} \qquad \therefore X = 0.450 \text{ g.}$$

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