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THESIS

# SYNTHESIS OF BIODIESEL CATALYZED BY RARE EARTH SOLID CATALYST

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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Rare earths obtained from decomposition of monazite ore by alkali process were used to synthesize the solid catalyst for a biodiesel production. In this work, the pure rare earth oxide catalysts such as $La_2O_3$, $CeO_2$ and $Nd_2O_3$ were prepared by a precipitation method. They were used to catalyze the transesterification of palm oil with methanol. The catalysts were characterized by X-ray powder diffraction (XRD), Nitrogen adsorption isotherm (BET) and Scanning electron microscope (SEM). The $La_2O_3$ was found to be the best catalyst with highest FAME content of 90.25%.

The optimization of reaction parameters was carried out with this active catalyst temperature (120-200℃), catalyst loading (4-10 %wt) and molar ratio of oil to methanol (1:10-1:30). Under the condition namely catalyst loading 10 %wt, molar ratio of oil to methanol of 1:30, reaction temperature of 200℃, reaction pressure of 39 bar and stirring rate at 600 rpm, the highest rate of reaction was achieved. The FAME content of 94.85 % was obtained at 45 min. Besides, the prepared $La_2O_3$ catalyst showed high reaction rate over that of commercial catalyst. The higher crystalline size of prepared $La_2O_3$ catalyst causes the fast rate reaction.

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Student's signature Thesis Advisor's signature

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Phansiri Soodjit

March 2014

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# LIST OF ABBREVIATIONS AND SYMBOL

| | | |
|---|---|---|
| $cm^3$ | = | cubic centimeter |
| °C | = | degree Celsius |
| CTC | = | commercial transesterification catalyzed reaction |
| FAME | = | fatty acid methyl ester |
| FFA | = | free fatty acid |
| g | = | gram |
| GC | = | gas chromatography |
| h | = | hour |
| HREE | = | heavy rare earth element |
| K | = | kelvin |
| kg | = | kilo gram |
| L | = | liter |
| LREE | = | light rare earth element |
| m | = | meter |
| M | = | molarity |
| mg | = | milligram |
| min | = | minute |
| ml | = | milliliter |
| mol | = | mole |
| nm | = | nanometer |
| TC | = | transesterification catalyzed reaction |
| TNC | = | transesterification non-catalyzed reaction |
| rpm | = | rotation per minute |
| sec | = | second |
| %wt | = | Percent weight by weight |
| W | = | Weight |

# SYNTHESIS OF BIODIESEL CATALYZED BY RARE EARTH SOLID CATALYST

## INTRODUCTION

An increasing problem of the petroleum oil price in the world oil market causes by the consuming large amounts of energy of human in the form fuel and natural gases. These energies are finite and can be used within a short period of time (Sun *et al*., 2010). Therefore, research is now being directed towards the use of alternative renewable fuels. In terms of technical and economic potential, the biodiesel is more efficient than any other alternative fuels. Biodiesel has many advantages. It is biodegradable, safer, non-toxic and simple to use.

Biodiesel can be produced from transesterification of vegetable oils and fats with methanol in the presence of a suitable catalyst. The catalyst used to synthesize biodiesel it can be divided into 2 types including homogeneous and heterogeneous catalysts. Even though homogeneous catalyst has benefits in terms of fast reaction rate and high yield and mild operating condition, the drawback of this application is the difficulty of removal of catalyst, and a large amount of wastewater during biodiesel separating and cleaning. Therefore, the use of heterogeneous catalyst can be advantageous since simply catalyst separation, nontoxic, non-corrosive and minimizing of environmental pollution (Kim *et al*., 2004).

Rare earth elements are found in nature minerals such as Monazite ore (REE Handbook, 2013). They are used in a variety of industrials such as ceramic, glass, electronic, nuclear and petroleum. In the petroleum industry, the rare earth was used as catalyst and catalyst support in the distillation of petroleum oil (Gamal, 1996).

In this work, pure rare earth oxides such as $La_2O_3$, $CeO_2$ and $Nd_2O_3$ were prepared by precipitation method. The textural property, crystalline structure and morphology of these catalysts were characterized by different techniques. They were also used to

catalyze the transesterification of palm oil with methanol to produce biodiesel. The effect of the reaction parameters namely reaction temperature, catalyst loading and molar ratio of oil to methanol on the rate of transesterification reaction were investigated. Finally, the comparison of synthesized catalyzed, commercial catalyzed and non-catalyzed reaction was investigated.

# OBJECTIVES

1. To prepare pure rare earth oxides catalysts ($La_2O_3$, $CeO_2$ and $Nd_2O_3$) by precipitation method.

2. To study the textural property, crystalline structure and morphology of these catalysts by different techniques

3. To investigate the transesterification of palm oil with methanol using pure rare earth oxide to produce biodiesel

4. To compare with commercial catalyst.

## Scope of work

1. Rare earth EDTA solutions such as Lanthanum (La), Cerium (Ce) and Neodymium (Nd) from Rare Earth Research and Development Center (Thailand Institute of Nuclear Technology) will be prepared by precipitation method.

2. The purification of rare earth oxide catalysts was analyzed from the energy dispersive X-ray fluorescence (ED-XRF).

3. The rare earth oxide catalysts were characterized by X-ray powder diffraction (XRD), Nitrogen adsorption isotherm (BET) and Scanning electron microscope (SEM).

4. All experimental reactions were carried out in 600 ml of Parr stirred batch reactor (model 4568).

# LITERATURE REVIEW

This chapter is composed of literature survey and related theory from various sources. These literatures are used as the guideline for this work.

## 1. Biodiesel

In 1900 in an exhibition in Paris, the peanut oil or vegetable oil was first used as fuel for a diesel engine invented by Rudolph Diesel. The vegetable oil would be equally important fuel in the period of 1930s and 1940s, particularly during the World War II, the vegetable oils were used in emergency to substitute diesel. In the mid-1970s petroleum fuel crisis, the vegetable oils and their derivatives were revived interest in developing biodiesel as an alternative to petroleum diesel (Pacific Biofuel, 2009). At present, Biodiesel as one promising alternative to fuel for diesel engines has become increasingly important due to the decreasing petroleum resources, increasing in crude oil price and concerns of environmental. Therefore, it seems to be the most feasible solution for this situation

For the environmental concerns, biodiesel has significant influences in reducing engine emissions such as unburned hydrocarbons (68%), particulars (40%), carbon monoxide (44%), sulfur oxide (100%), and polycyclic aromatic hydrocarbons (PAHs) (80–90%)( Leduc *et al*., 2009).

Biodiesel is defined by the American Society for Testing and Materials (ASTM standard) as mono alkyl ester of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oils or animal fats, for use in compression ignition (diesel) engines. “Bio” presents its renewable and biological source in contrast to traditional petroleum-based diesel fuel, “Diesel” refers to its used in diesel engines (Zhang *et al*., 2003).

The technical properties of biodiesel are given in Table 1. Biodiesel is a clear light yellow liquid with a viscosity similar to that of petroleum diesel. Biodiesel is non-flammable and non-explosive, with a flash point of 423 K for biodiesel as compared to 337 K for petroleum diesel. Unlike petroleum diesel, biodiesel is

biodegradable, non-toxic, and it significantly reduces toxic and other emissions when burned as a fuel (Demirbas, 2009).

**Table 1** Technical properties of biodiesel.

| **Common name** | **Biodiesel (bio-diesel)** |
|---|---|
| **Common chemical name** | Fatty acid (m)ethyl ester |
| **Chemical formula range** | $C_{14}$-$C_{24}$ methyl esters or $C_{15\text{-}25}H_{28\text{-}48}O_2$ |
| **Kinematic viscosity range ($mm^2/s$, at 313 K)** | 3.3-5.2 |
| **Density range ($kg/m^3$, at 288 K)** | 860-894 |
| **Boling point range (K)** | >475 |
| **Flash point range (K)** | 420-450 |
| **Distillation range (K)** | 470-600 |
| **Vapor pressure (mmHg, at 295 K)** | <5 |
| **Solubility in water** | Insoluble in water |
| **Physical appearance** | Light to dark yellow, clear liquid |
| **Odor** | Light musty/soapy odor |
| **Biodegradability** | More biodegradable than petroleum diesel |
| **Reactivity** | Stable, but avoid strong oxidizing agents |

**Source:** Demirbas (2009)

## 2. Sources of biodiesel

In general, biodiesel sources can be categorized into three groups such as vegetable oils (edible and non-edible oils), animal fats, and used waste cooking oil. Table 2 shows some sources of biodiesel and their physicochemical properties.

**Table 2** Some source for biodiesel production and their physicochemical properties

| Type of oil | Species | Main chemical composition (fatty acid composition wt.%) | Density ($g/cm^3$) | Flash point (°C) | Kinematic viscosity (cst, at 40 °C) | Acid value (mg KOH/g) | Heating value (MJ/kg) |
|---|---|---|---|---|---|---|---|
| **Vegetable oil** | | | | | | | |
| **Edible oil** | Soybean | C16:0, C18:1-2 | 0.91 | 254 | 32.9 | 0.2 | 39.6 |
| | Rapeseed | C16:0, C18:0-2 | 0.91 | 246 | 35.1 | 2.92 | 39.7 |
| | Sunflower | C16:0, C18:0-2 | 0.92 | 274 | 32.6 | - | 39.6 |
| | Palm | C16:0, C18:0-2 | 0.92 | 267 | 39.6[a] | 0.1 | - |
| | Peanut | C16:0, C18:0-2, C20:0, C22:0 | 0.90 | 271 | 22.72 | 3 | 39.8 |
| | Corn | C16:0, C18:0-3 | 0.91 | 277 | 34.9 | - | 39.5 |
| | Camelina | C16:0, C18:0-2, C20:0-3 | 0.91 | - | - | 0.76 | 42.2 |
| | Canola | C16:0, C18:0-3 | | | 38.2 | 0.4 | |
| | Cotton | C16:0, C18:0-2 | 0.91 | 234 | 18.6 | | 39.5 |
| | Pumpkin | C16:0, C18:0-2 | 0.92 | >230 | 35.6 | 0.55 | 39 |
| **Non-edible oil** | Jatrophacurcas | C16:0-1, C18:0-2 | 0.92 | 255 | 29.4 | 28 | 38.5 |
| | Pongaminap | C16:0, C18:0-2 | 0.91 | 205 | 27.8 | 5.06 | 34 |

**Table 2** (Continued)

| Type of oil | Species | Main chemical composition (fatty acid composition wt.%) | Density ($g/cm^3$) | Flash point (°C) | Kinematic viscosity (cst, at 40 °C) | Acid value (mg KOH/g) | Heating value (MJ/kg) |
|---|---|---|---|---|---|---|---|
| **Vegetable oil** | | | | | | | |
| **Non-edible oil** | Sea mango | C16:0, C18:0-2 | 0.92 | - | 29.6 | 0.24 | 40.86 |
| | Palanga | C16:0, C18:0-2 | 0.90 | 221 | 72.0 | 44 | 39.25 |
| | Tallow | C14:0, C16:0-1, C17:0, C18:0 C18:1-2 | 0.92 | - | - | - | 40.05 |
| | Nile tilapia | C16:0, C18:1, C20:5, C22:6, other acids | 0.91 | - | 32.1[b] | 2.81 | - |
| | Poultry | C16:0, C18:0-2, C20:0, C22:0 C16:0, C18:0-3 | 0.90 | - | - | - | 39.4 |
| **Others** | Used cooking oil | Depends on fresh cooking oil | 0.90 | - | 44.7 | 2.5 | - |

[a] Kinematic viscosity at 38 °C, $mm^3/s$. [b]Kinematic viscosity at 38 °C, $mm^3/s$.

**Source:** Leung *et al*. (2010)

## 2.1 Vegetable oils

Vegetable oils are renewable fuels. They have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. Vegetable oils are a renewable and potentially inexhaustible source of energy, with energy content close to that of diesel fuel. On the other hand, extensive use of vegetable oils may cause other significant problems such as starvation in developing countries. The vegetable oil fuels were not acceptable because they were more expensive than petroleum fuels (Demirbas, 2005).

For vegetable oils can be divided into two types such as edible oils and non-edible oils. More than 95% of biodiesel production raw materials come from edible oils such as soybean, palm, rapeseeds, sunflower etc. Since they are mainly produced in many regions and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute (Gui *et al*., 2008). However, continuous and large-scale production of biodiesel from edible oils has been concern because they compete with food supply in the long term. Therefore, Non-edible oils are alternative interesting for biodiesel production.

The non-edible oils such as *J. curcas, M. indica, Ficus elastica, Azardirachta indica, Calophyllum* inophyllum jatropha, neem, *P. pinnata*, rubber seed, mahua, silk cotton tree, and tall oil microalgae are easily available in developing countries and are very economical comparable to edible oils (Demirbas, 2009). Moreover, it is not effect to food supply.

The main components of vegetable oils are triglycerides. Triglycerides are ester of glycerol with long-chain acids, commonly called fatty acids (Gerpen *et al*., 2004). Vegetable oils consist of 90 to 98% of triglycerides, small amounts of monoglyceride and diglyceride, free fatty acids (generally 1 to 5 %), phospholipids, phosphatides, tocopherols, caratenes, sulphurcomponds and trace of water (Srivastava and Prasad, 2000). The chemical structure of triglyceride, diglyceride and monoglyceride molecule are shown in Figure 1.

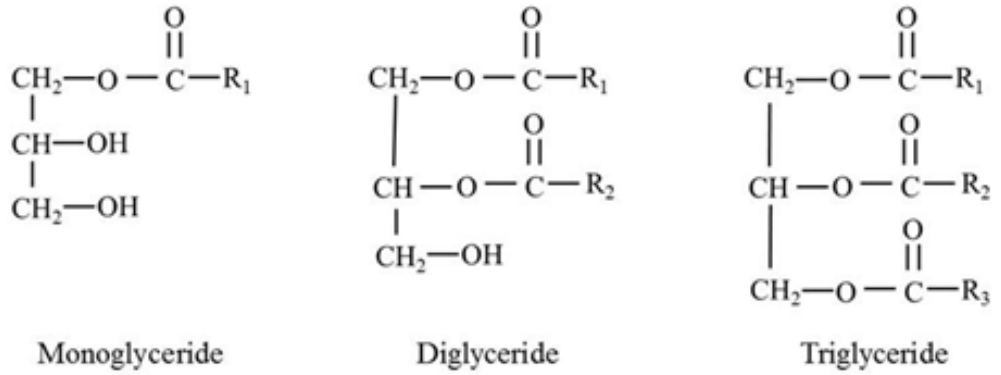


**Figure 1** Chemical structure of monoglyceride, diglyceride and triglyceride molecule; $R^1$, $R^2$ and $R^3$ represent carbon chain of fatty acid.

**Source:** Leung *et al*. (2010)

2.2 Animal fats

Animal fats contain higher saturated fatty acids and normally exist in solid form at room temperature that may cause problems in the production process. Its cost is also higher than vegetable oils (Singh *et al*., 2010).

Another raw material source for biodiesel production is fats derived from animals. Animal fats used to produce biodiesel include tallow, choice white grease or lard, and chicken fat. Compared to vegetable oils, these fats frequently offer an economic advantage because they are often priced favourably for conversion into biodiesel. Animal fat methyl ester has some advantages such as high cetane number, non-corrosive, clean and renewable properties. Animal fats tend to be low in FFAs and water, but there is a limited amount of these oils available, meaning these would never be able to meet the fuel needs of the world (Balat, 2011).

2.3 waste cooking oil

The production of biodiesel from waste cooking oil (WCO) to partially substitute petroleum diesel is one of the measures for solving the double problems of environment pollution and energy shortage. In order to reduce the cost of production, WCO would be a good choice as raw material since it is cheaper than virgin vegetable

oils. Note that the WCO is categorized by its FFA content. For example, if the FFA content of WCO is <15%, then it is called ‘‘yellow grease”; otherwise, it is called ‘‘brown grease”

The amount of WCO generated in each country is huge and varies depending on the use of vegetable oil. Management of WCOs poses a significant challenge because of its disposal problems and possible contamination of the water and land resources. Thus, biodiesel derived from WCO has taken a commercial patent as an alternative fuel to petroleum-based diesel fuel for diesel engines in the markets of Europe and the United States. Every year many millions of tons of WCO are collected and used in a variety of ways throughout the world. This is a virtually inexhaustible source of energy which might also prove an additional line of production for ‘‘green” companies (Balat, 2010).

**3. Advantages of biodiesel**

There are many advantages of using biodiesel rather than petroleum diesel, the main advantages of biodiesel as follows:

3.1Availability and renewability

Biodiesel can be made from domestically produced, renewable fuel for diesel engines derived from natural oils. Thus, biodiesel is aone of alternative fuel in which low-concentration biodiesel–diesel blends run on conventional unmodified engines. It can be stored anywhere that petroleum diesel fuel is stored. Biodiesel is safe to handle and transport because it is as biodegradable as sugar and has a high flash point compared to petroleum diesel fuel. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. The most general blend is a mix of 20% biodiesel with 80% petroleum diesel (B20) (Demirbas, 2007).

3.2 Lower emissions

Biodiesel can reduce global warming and gas emission such as carbon dioxide ($CO_2$). The carbon cycle of biodiesel is dynamic through the photosynthesis

process. Plants absorb $CO_2$, which is more than those discharged by the biodiesel combustion process. Thus, using biodiesel can more effectively reduce the emission of $CO_2$, protect the natural environment and maintain the ecological balance, compared to the use of fossil fuel (Lapuerta *et al.*, 2008).

The emission of $SO_2$ in the combustion process of biodiesel is much lower than normal diesel oil because of the low sulfur content in it. Therefore, the use of biodiesel instead of normal diesel oil will effectively reduce acid rain, which represents a serious threat to the environment and human. Furthermore, particulate matters (PM), hydrocarbon (HC) and carbon monodioxide (CO) will be less discharged, because ester compounds in biodiesel contains oxygen promoting clean burning (Huang *et al*., 2012).

3.3 Biodegradability

Biodiesels have an expanding range of potential applications and they are environmentally friendly. Biodiesel is non-toxic and degrades about four times faster than petroleum diesel. Its oxygen content improves the biodegradation process, leading to an increased level of quick biodegradation (Demirbas, 2009). The biodegradabilites of several biodiesels in the aquatic environment show that all biodiesel fuels are readily biodegradable. After 28 days all biodiesel fuels were 77%–89% biodegraded, while diesel fuel was only 18% biodegraded (Zhang, 1996).

3.4 Higher combustion

Structural oxygen content of a fuel improves combustion efficiency due to the increase of the homogeneity of oxygen with the fuel during combustion. Because of this the combustion efficiency of biodiesel is higher than petroleum diesel. Biodiesel contains 11% oxygen by weight and contains no sulfur. The use of biodiesel can extend the life of diesel engines because it is more lubricating than petroleum diesel fuel (Demirbas, 2007).

3.5 Higher lubricity

Biodiesel has good lubricant properties compared to petroleum diesel oil, in particular very-low-sulfur diesel. This is very important to reduce wear in the engine and the injection system (Carraretto *et al*., 2004). Biodiesel provides significant lubricity improvement over petroleum diesel fuel. Lubricity results of biodiesel and petroleum diesel using industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel. Even biodiesel levels below 1% can provide up to a 30% increase in lubricity (Demirbas, 2009).

Not only do biofuels help protect the planet from global warming by emitting less pollution than fossil fuels, but they also add jobs to the economy and by doing so, help farmers, construction workers and those living in poor rural.

**4. The production of biodiesel**

The production of biodiesel technique can be divided into four techniques such as direct use and blending, micro-emulsification, Thermal cracking/pyrolysis, andtransesterification.

Different techniques of biodiesel production represents in Table 3. Among all these techniques, the transesterification seems to be the best choice due to the physical characteristics of fatty acid esters are very close to those of petroleum diesel fuel and the process is relatively simple (Leung *et al*., 2010).

**Table 3** Different methods of production

| Methods | Definition | Advantage | Disadvantage | Problems of using in engines |
|---|---|---|---|---|
| Direct use and blending | Direct use as diesel fuel or blend with diesel fuel | Liquid nature-portability<br>Heat content (~80% of diesel fuel)<br>Readily available; renewability | Higher viscosity<br>Lower volatility<br>Reactivity of unsaturated hydrocarbon chain | Coking and trumpet formation<br>Carbon deposits<br>Oil ring sticking; thickening and gelling of the lubricating oil |
| Micro-emulsions | A colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two immiscible liquids and one or more ionic or non-ionic amphiphiles | Better spray patterns during combustion<br>Lower fuel viscosities | Lower cetane number<br>Lower energy content | Irregular injection needle sticking; incomplete combustion<br>Heavy carbon deposits; increase lubrication oil viscosity |

**Table 3** (Continued)

| Methods | Definition | Advantage | Disadvantage | Problems of using in engines |
|---|---|---|---|---|
| Thermal cracking (pyrolysis) | The conversion of long-chain and saturated substance (biomass basis) to biodiesel by means of heat | Chemically similar to petroleum-derived gasoline and diesel fuel | Energy intensive and hence higher cost | - |
| Transesterification | The reaction of a fat or oil with an alcohol in the presence of catalyst to from ester and glycerol | Renewability; higher cetane number; lower emission; higher combustion efficiency | Disposal of by-product (glycerol and waste water) | - |

**Source:** Leung *et al*. (2010)

**5. Transesterification**

Transesterification is a chemical reaction in which the triglyceride is converted into diglyceride and diglyceride is converted into monoglyceride and is consequential converted to methyl or ethyl ester or biodiesel. In fact, transesterification is the reaction of vegetable oil, animal fat or waste cooking oils (Triglyceride) with an alcohol (with or without catalyst) to form esters and glycerol. Fig. 2 shows the overall scheme for the transesterification of triglycerides.

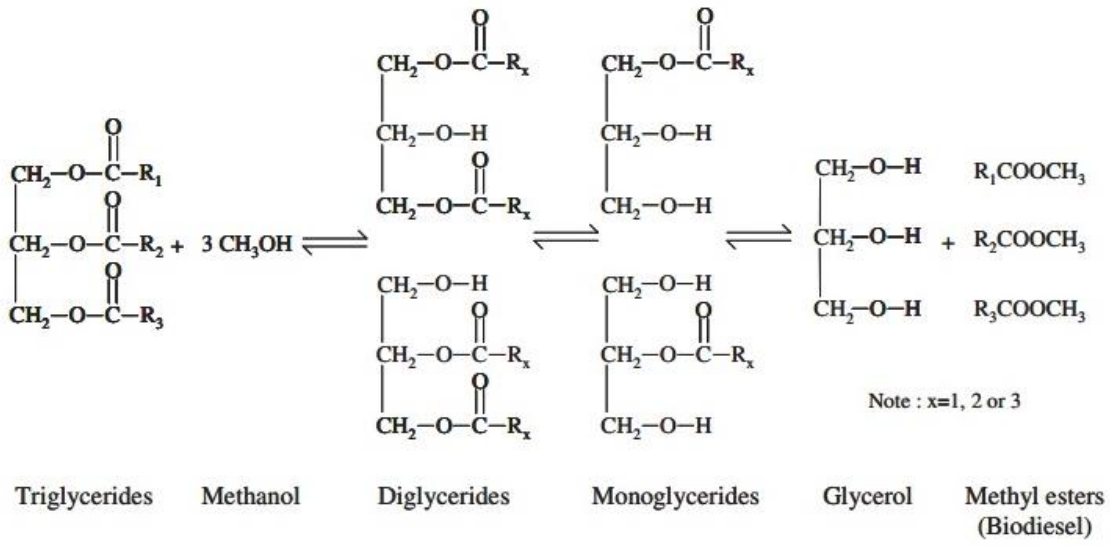


**Figure 2** The overall scheme for the transesterification of triglycerides.

**Source:** Abdullah *et al*. (2007)

Catalyst is used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side (Vyas *et al*., 2010). In general, all the catalysts for the transesterification of vegetable oils can be fitted into three classifications known as homogeneous, enzyme or heterogeneous catalysts. Enzyme can fall into either homogeneous or heterogeneous categories depending on its mobility (Helwani *et al*., 2009). Table 4 represents comparison of factors in relation between homogeneous and heterogeneous catalyzed transesterification.

Alcohols are the primary and secondary monohydric aliphatic compounds having 1–8 carbon atoms. The alcohols employed in the transesterification are generally short chain alcohols such as methanol, ethanol, propanol, and butanol. Methanol and ethanol are used most frequently in the transesterification process. Ethanol is a preferred alcohol in transesterification reaction compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment. However, methanol is preferred because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol) (Balat, 2010).

**Table 4** Comparison of homogeneous and heterogeneous catalyzed transesterification

| **Factors** | **Homogeneously catalysis** | **Heterogeneously catalysis** |
|---|---|---|
| Reaction rate | Fast and high conversion | Moderate conversion |
| After treatment | Catalyst cannot be recovered, must be neutralized leading to waste chemical production | Can be recovered |
| Processing methodology | Limited used of continuous methodology | Continuous fix bed operation possible |
| Presence of water/ free fatty acids | Sensitive | Not sensitive |
| Catalyst reuse | Not possible | Possible |
| Cost | Comparatively costly | Potentially cheaper |

**Source:** Helwani *et al*. (2009)

## 6. Homogeneous catalyzed transesterification

### 6.1 Homogeneous acid-catalyzed transesterification

The acid catalyst used for transesterification of vegetable oil include sulfuric acid ($H_2SO_4$), hydrochloric acid (HCL), boron trifluoride ($BF_3$), phosphoric

acid and organic sulfonic acids. Actually, acid catalysts can simultaneously catalyze both esterification and transesterification reaction. Thus, a great advantage with acid catalyst is that they can directly produce biodiesel from high FFA feedstock, such as waste cooking oil and greases, commonly have FFA level of >6% (Vyas *et al*., 2010). However, acid-catalyzed system is not a popular choice for commercial applications due to slower reaction rate, requirement of high reaction temperature, high molar ratio of alcohol to oil, separation of the catalyst, serious environmental and corrosion related problem (Lam *et al*., 2010).

Figure 3 illustrates the mechanism of homogeneous acid-catalyzed transesterification of triglycerides in three steps. First, protonation of carbonyl group is followed by nucleophilic attack of alcohol that produces tetrahedral intermediate. Finally, the proton migration and the tetrahedral intermediate breakdown will omit glycerol to create a new ester and reforms the catalyst (Lotero *et al*., 2005).

6.2 Homogeneous base-catalyzed transesterification

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. The transesterification can be catalyzed by alkaline metal alkoixides (sodium methoxide, NaOCH3; sodium ethoxide, $NaOCH_2CH_3$) and hydroxides potassium carbonates (Narasimharao *et al*., 2007). These catalysts are commonly used in the industries due to several reasons: (i) able to catalyze reaction at low reaction temperature and atmospheric pressure; (ii) high conversion can be achieved in a minimal time, (iii) widely available and economical (Lotero *et al*., 2005). The alkaline catalysts normally show high performance when vegetable oil with high quality is used. However, when the oils contain significant amounts of free fatty acids, they cannot be converted into biodiesels but into a lot of soap. These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of biodiesel, glycerin and wash water (Helwani *et al*., 2009).

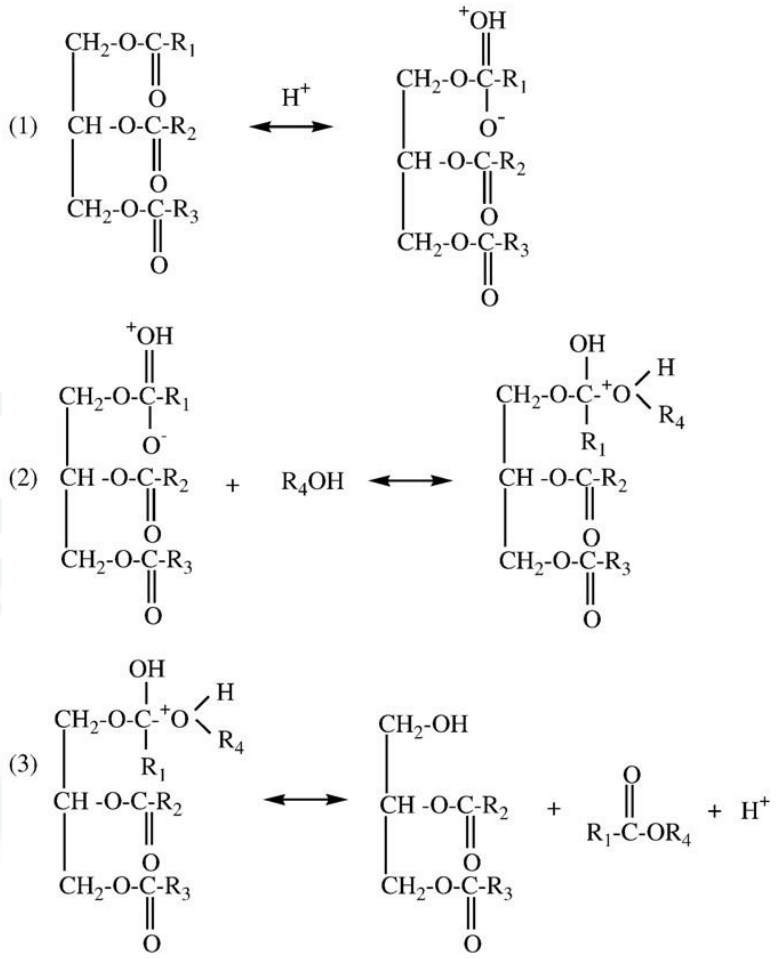

**Figure 3** General mechanism of the acid-catalyzed transesterification, $R_1$, $R_2$ and $R_3$ are carbon chain of fatty acid, and $R_4$ is alkyl group of alcohol.

**Source:** Lotero *et al*. (2005)

The general mechanism of base-catalyzed transesterification is described in Figure 4. The first is the reaction of base with alcohol, producing an alkoxide and protonated catalyst. The nucleophllic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (2), from which the alkly ester and corresponding anion of diglyceride are formed (3). The latter deprotonates the catalyst, thus regenerating the active species (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 (Lotero *et al*., 2005).

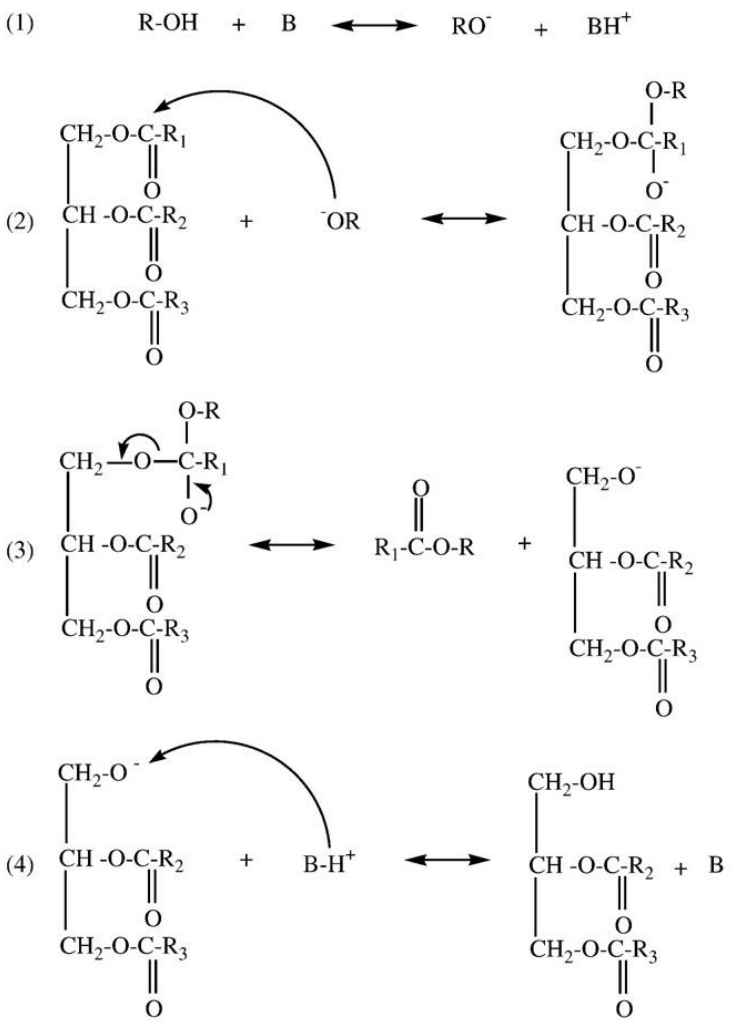

**Figure4** General mechanism of the base-catalyzed transesterification, B is base catalyst, R is alkyl group of alcohol, and $R_1$, $R_2$ and $R_3$ are carbon chain of fatty acid

**Source:** Lotero *et al*. (2005)

### 7. Heterogeneous catalyzed transesterification

The homogeneous reaction has some disadvantages such as low tolerance towards FFA, water contamination in the purification process (Talebian-Kiakalaieh *et al*., 2013). Moreover, the problems associated with the homogeneous catalyst are that they cannot be reused or regenerated, because the catalysts are consumed as raw material in the side-reaction (saponification reaction). Nevertheless, they also

dissolved in the reaction. These lead to serious contamination problems, make essential the implementation of good separation and product purification protocols, resulting in higher production costs (Jothiramalingam and wang, 2009). Besides, the process is not environmentally friendly because a large amount of waste water is produced in the separation step (Zabeti *et al*., 2009).

The heterogeneous (also called ‘‘solid”) catalyst seems to be an appropriate solution to overcome these problems. The use of a heterogeneous catalyst can be retained in the reactor by a simple filtration and avoided saponification (Vyas *et al*., 2010).The catalyst leaves no neutralization salts in the glycerol by-product, as the catalyst is not continuously added and disposed of, the inputs and waste are reduced. Moreover, the reaction step of biodiesel production using heterogeneous catalyst would improve the economics of the process. This would reduce the final product cost and, therefore, market penetration of biodiesel would increase (Guo and Fang, 2011). Various types of heterogeneous base and acid catalysts employed for transesterification reaction are shown in Table 5.

Heterogeneous base catalysts refer mainly to solids with Brønsted basic and Lewis basic activity centers, that can supply electrons (or accept protons) for (or from) reactants. Heterogeneous base catalyzed transesterification for biodiesel synthesis has been studied intensively over the last decade (Guo and Fang, 2011).The catalysts have been quite successful with high conversion and yield of biodiesel obtained. Furthermore, heterogeneous base catalysts include a wide group of compounds in the category of alkaline earth metal hydroxides, hydrotalcites/layered double hydroxides, alumina loaded with various compounds, zeolites, and various other compounds showing high basicity coupled with active basic sites, pore size, and other parameters (Sharma *et al*., 2008).

Although heterogeneous base catalyst have a higher catalytic activity and reaction rates as compared to heterogeneous acid catalyst, but they could help in processing low-cost and low-qualified oil feedstocks with high FFAs. In addition, they can simultaneously carry out transesterification of triglycerides (Serio *et al*., 2008). Now, synthetic solid acids have already amounted to hundreds of species, most

of them can be used in esterification and transesterification reactions. Solid acids keep stable activity in conversion of low-qualified oils or fats to biodiesel. Currently, developed solid acid catalysts are introduced in the following sections namely cation exchange, mineral salts, supported solid acid and heteropoly acid catalysts (Guo and Fang, 2011).

**Table 5** Various types of heterogeneous catalysts employed for transesterification reaction

| **Heterogeneous base catalysts** | **Heterogeneous acid catalysts** |
|---|---|
| Hydrotalcites (Mg-Al) | Sulphonic ion exchanged resin |
| Cs-exchanged sepiolite | Amberlyst-15 |
| Quanidine anchored cellulose/polymer | Nafion |
| Metal salts of amino acids | Unsated zirconia-alumina |
| $CaCo_3$,$Ba(OH)_2$ | Sulphated tin oxide |
| KxX/Al2O3 (X-halideion or other mono/ divalent anion) | MCM family |
| Li-promoted CaO | Zinc acetate on silica |
| Zinc aluminates | Organosulphonic acid on mesoporous silica |
| **Alkaline earth oxide based catalysts:** MgO,CaO,$La_2O_3$, ZnO (The base strength: Mg<Ca<Sr<Ba) | Mesoporous unstated zirconium phosphate |
| **Alkali metal salt loaded on alumina:** $K_2CO_3/Al_2O_3$, KF/ZnO, $KOH/Al_2O_3$, $LiNO_3$, NaOH, $(AL_2O_3)4(SnO)$, $(Al_2O_3)_4ZnO$ | **Heteropoly acids:** $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ |

**Table 5** (Continued)

| Heterogeneous base catalysts | Heterogeneous acid catalysts |
|---|---|
| **Basic zeolites:** N N'N"tricyclohexxyl in Y zeolite Ca-exchanged faujasites | **Sulfated zirconia/alumina:** Tetragonal $ZrO_2$, monoclinic $ZrO_2/WO_3$<br><br>**Zeolites:** (H-Y) H-Beta, H-ZSM-5, ETS-4,10 |

**Source:** Glisic *et al*. (2009)

**8. Parameters variable**

The yield of biodiesel by transesterification depends on many parameters. The most important of which are amount and type of catalyst, amount and type of alcohol (molar ratio oil to alcohol), the reaction temperature, and reaction time.

8.2.1 Catalyst concentration

Generally, catalyst concentration affects the yield of biodiesel production. As the catalyst concentration increases the conversion of triglyceride and the yield of biodiesel increase. An insufficient amount of catalyst results in an incomplete conversion of the triglycerides to the fatty acid ester (Leung *et al*., 2010).

Asria *et al*.(2013) studied palm oil transesterification in sub and supercritical methanol with heterogeneous base catalyst ($CaO/KI/\gamma\text{-}Al_2O_3$). $CaO/KI/\gamma\text{-}Al_2O_3$ catalyst was prepared by precipitation and impregnation methods. The effect of catalyst amount (w/w% of oil) was studied by varying the amount of catalyst from 1 to 4% at a reaction temperature of 290 ºC, molar ratio of oil to methanol 1:24 and reaction time of 30 min. They found that without the use of catalyst, the obtained biodiesel yield was only 22%. In the other hand, the yield of biodiesel increased from 48 to 81% by using 1 and 3% catalyst, respectively. For the use of 3.5 to 4% of catalyst cause decrease in biodiesel yield due to agglomeration occurring on the

catalyst, which caused a decreasein the number of active sites and finally reduced the activity of thecatalyst. Therefore, the best catalyst of this work was 3% of catalyst.

Deshmane and Adewuyi (2013) prepared a calcium methoxide (CaO) base catalyst to catalyze transesterification of soybean oil with methanol. They noted that the increase of catalyst loading from 0.6 to 1%wt showed substantial effect on conversion of triglycerides. However, when the catalyst loading was further increased to 1.4%wt, the initial rate of reaction increased to the same final yield of ester as 1%wt catalyst loading.

8.2.2 Reaction temperature

Temperature obviously affects the yield and reaction of the biodiesel production. A higher reaction temperature can decrease the viscosities of oil, result in the increasing of reaction rate and shortened reaction time. The reaction temperature should be lower than boiling point of alcohol for making sure about leaking out of alcohol through vaporization (Leung *et al*., 2010).

Transesterification of soybean oil with calcium methoxide as base catalyst was studied by Deshmane and Adewuyi (2013). Under the conditions was catalyst concentration at 1% and methanol to oil molar ratio of 12:1. The three different temperatures such as of 55 ºC, 60 ºC and 65 ºC were carried out in the reaction. The maximum conversion was 95% at 65 ºC for 120 min. They found that increasing the temperature has influence on the transesterification reaction.

Yan *et al*. (2009) have been studied simultaneous esterification and transesterification of soybean oil with 5.4%wt of FFA using $Zn_3La_1$ as catalyst at temperature ranging from 180 to 210 ºC. The increase of reaction temperature form 180 to 210 ºC resulted in increasing of fatty acid methyl ester (FAME) yield, however, further increase of reaction temperature to 210 ºC slightly increased the yield of FAME. Asria *et al*. (2013) described that the yield of FAME markedly increased from 64% to 81% with the increase of temperature from 210 to 290 ºC. They found that the optimal reaction temperature was 290 ºC

8.2.3 Molar ratio oil to alcohol

Molar ratio of oil to alcohol is one of the important parameter which has affected to the yield of ester. Theoretically, the ratio for transesterification reaction requires 3 mol of alcohol for 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time (Leung *et al*., 2010).

Deshmane and Adewuyi (2013) Found that the increase of molar ratio of methanol to oil from 6:1 to 9:1 resulted in a significant effect on the ester yield, however further increase of methanol to oil to 12:1 did not show any significant effect on the ester yield for transesterification of soybean oil with methanol using calcium methoxide as a catalyst. Asria *et al*. (2013) reported that an increase of the molar ratio from 1:12 to 1:24, biodiesel yield significantly increased from 51 to 81%, respectively. Thus, the optimum molar ratio of oil to methanol was 1:24, the excess added methanol had no significant effect on biodiesel yield.

Yan *et al*. (2009) revealed that a 1:6 molar ratio of palm oil to methanol gave poor yield of FAME in simultaneous esterification and transesterification of soybean oil with 5.4%wt of FFA using $Zn_3La_1$ as a catalyst, and higher molar ratios of oil to methanol (1:36 to 1:42) led to higher yields than 95% within 1 hour.

8.2.4 Reaction time

Another important parameter which has influence on the yield of ester is reaction time. Leung *et al*. (2010) described that the conversion rate of fatty acid esters increases with reaction time. At the starting point, the reaction is slow because of the mixing and dispersion of alcohol into the oil. Afterwards, the reaction proceeds very fast. Furthermore, abundant reaction time will cause a reduction in the yield of product because of the backward reaction of transesterification.

Asria *et al*. (2013) investigated transesterification of palm oil with methanol using CaO/KI/γ-$Al_2O_3$ solid catalyst. The biodiesel reaction process was conducted under the following conditions: amount of catalyst was 3% wt., the molar ration of methanol to palm oil was 24:1 and reaction temperature was 290 °C. The reaction times have been observed by varying from 30 to 90 min at 10 min intervals. They reported that the yield of biodiesel increased with the increasing reaction time which the highest yield of these conditions was 95% at 60 min of reaction time. Deshmane and Adewuyi (2013) noticed that increasing the temperature has favorable effect on the transesterification reaction or reaction time. At 55 ºC the reaction was noticeably slow and took about 240 min to obtain 95% conversion of oil on the contrary it took 160 and 120 min, for reaction at 60 ºC and 65 ºC, respectively

**9. Rare earth elements**

Contrary to the name, rare earths are not "rare." Rather, they are relatively abundant in the earth's crust. At the same time, however, they are highly scattered and are usually found mixed together in other deposits, which makes it difficult to find rare earths in a concentration high enough to be mined and separated economically. When rare earths are extracted from the mine, the ore containing the rare earths must go through complex separation processes to produce each individual element. It is the separation process that largely drives the cost of rare earth production (Morrison and Tang, 2012).

The International Union of Pure and Applied Chemistry (IUPAC) define rare earth elements (REE) or rare earth metals as a collection of 17 chemical elements in the periodic table, specifically the 15 lanthanides plus scandium and yttrium. Scandium and yttrium are considered rare earth elements since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties (http://www.periodni.com/rare_earth_elements.html).

The lanthanides comprise a group of 15 elements with atomic numbers 57 to 71 that include the following in order of atomic number (atomic symbol): lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm),

samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

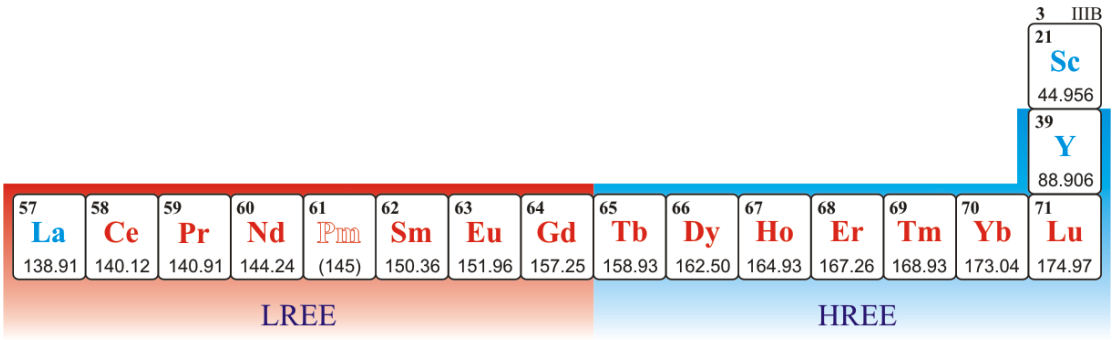


**Figure 5** The Rare earth elements (metals) are often subdivided into light rare earth elements (LREE) and heavy rare earth elements (HREE)

**Source:** Generalic (2013)

The rare earth elements are often described as being a 'light-group rare earth element' (LREE) or 'heavy-group rare earth element' (HREE). The definition of a LREE and HREE is based on the electron configuration of each rare-earth element. The LREE are defined as lanthanum, atomic number 57 through gadolinium, atomic number 64. The LREE have in common increasing unpaired electrons, from 0 to 7. The HREE are defined as terbium, atomic number 65 through lutetium, atomic number 71, and also yttrium, atomic number 39. All of the HREE are differ from the first eight lanthanides in that they have 'paired' electrons (a clockwise and counter-clockwise spinning election). The LREE have no paired electrons. Yttrium is included in the HREE group based on its similar ionic radius and similar chemical properties. Scandium is also trivalent; however, its other properties are not similar enough to classify it as either a LREE or HREE (REE Handbook, 2013).

The rare earths are a moderately abundant group. The elements range in crustal abundance from cerium, which is more abundant than copper, at 60 parts per million (ppm), to thulium and lutetium, the least abundant rare earth elements at about 0.5 ppm. Since they have similar chemical and physical characteristics, the lanthanide elements and yttrium often occur together in nature and can be mined only together as

co-products. Therefore, the recoverable amount of individual rare earth oxides depends on the deposit composition. Generally, the light REE are more common and more easily extracted. In most rare earths deposits, the light rare earth elements, La, Ce, Pr, and Nd, constitute 80 to 99% of the total. Therefore, deposits containing relatively high grades of the scarcer and more valuable heavy rare earths (Gd to Lu, Y) and Eu are particularly desirable (Polinares Consortium, 2012).

**9. Applications of rare earths**

The list of rare earth applications is extensive and these applications can be found in many industries. Rare earths are used in petroleum refining and as diesel additives in the oil industry; they are important to the automotive industry because of their wide application in catalytic converters, hybrid vehicle batteries, motors and generators; they are used by the electronics industry to make hard disk drives and cell phones; and they are used in powerful magnets in wind turbines (Morrison and Tang, 2012). The application by individual rare earths shows in Table 6.

Yan *et al*. (2009) prepared the ZnO-$La_2O_3$ as catalyst for transesterification of unrefined and waste oil. ZnO-La2O3 was prepared by homogeneous co-precipitation method where 2 M $Zn(NO_3)_2$ and 1 M$La(NO_3)$ solutions were prepared in deionized water. These solutions of various Zn–La ratios were mixed with a 2 M urea solution, the resulting mixture calcined at 450°C for 8 h. The catalyst with 3:1 ratio of Zn–La was found to show highest activity in the transesterification of unrefined or waste oil. A strong interaction between Zn and La species was noticed with enhanced catalytic activities. The catalyst can active in both transesterification and esterification reactions, and without hydrolytic activity.

Russbueldt and Hoelderich (2010) studied rare earth oxides ($La_2O_3$) as catalysts for the transesterification of rapeseed oil with methanol at the reaction temperature ranging from 150 to 200 °C and the molar ratio of methanol to oil from 20:1 to 50:1. Under these conditions, the highest fatty acids methyl ester (FAME) yield was 97.1% for the upper limits of 200 °C and 50:1 of molar ratio.

**Table 6** Application by individual rare earths.

| Rare earth elements | Applications |
|---|---|
| Lanthanum | Used to make rechargeable lanthanum nickel metal hydride batteries – the type used in electric and hybrid vehicles, laptop computers, cameras; fibre optics to increase transmission rates, high-end camera lenses, telescopes, binoculars – as lanthanum improves visual clarity; infrared absorbing glass for night vision goggles, used to reduce the level of phosphates in patients with kidney disease. |
| Cerium | Used to polish glass, metal and gemstones, computer chips, transistors and other electronic components; automotive catalytic converters to reduce pollution, added in glass making process to decolorize it, gives compact fluorescent bulbs the green part of the light spectrum. |
| Praseodymium | Used in combination with neodymium, its primary use is to make high power magnets. Used to make welder and glass blower goggles as praseodymium oxide protects against yellow flare and UV light; plastic, vibrant yellow ceramics. |
| Neodymium | An elemental twin of praseodymium, the principal use of Neodymium is in the manufacture of the strongest magnets in the world. These magnets are so strong that one the size of a coin cannot be removed from a refrigerator by hand. Other important applications include laser range finders and guidance systems. |
| Samarium | Primary use is in the production of permanent magnets but also in X-ray lasers, precision guided weapons and white-noise production in stealth technology. |
| Europium | Primarily used in phosphors used in pilot display screens, televisions (reddish-orange), and energy efficient fluorescent lights (reddish-orange and blue). |

**Table 6** (Continued)

| Rare earth elements | Applications |
|---|---|
| Gadolinium | Used to enhance the clarity of MRI scans by injecting Gadolinium contrast agents into the patient. Used in nuclear reactor control rods to control the fission process. |
| Terbium | Primarily used in phosphors, particularly in fluorescent bulbs and tubes (yellow-green), high intensity green emitter used in projection televisions and X-ray intensifying screens (yellow-green, violet, and blue). |
| Dysprosium | Most commonly used in the manufacture of neodymium-iron-boron high strength permanent magnets. Dysprosium-165 is injected into joints to treat rheumatoid arthritis. Dysprosium is used in radiation badges to detect and monitor radiation exposure. |
| Erbium | Used in glass coloring, as an amplifier in fiber optics, and in lasers for medical and dental use. |
| Yttrium | Yttrium phosphors are used in energy efficient fluorescent lamps and bulbs. Yttrium stabilized zirconium oxide is used in high temperature applications, such as thermal barrier coating to protect aerospace high temperature surfaces. Can increase the strength of metallic alloys. |

**Source:** IAMGOLD Coperation (2012)

Sun *et al.* (2010) prepared a Zirconia Oxide ($ZrO_2$) supported on Lanthanum Oxides ($La_2O_3$) catalyst to catalyze transesterification of sunflower oil with methanol. The biodiesel reaction process was conducted under the following conditions: loading amount of $La_2O_3$ was 21% $La_2O_3$/ $ZrO_2$, the molar ration of methanol to oil was 30:1, reaction temperature was 200 °C for 5 h reaction time. Under these conditions, the FAME yield was 84.9% and when was reused after 5 cycle, the FAME yield decreased at 28.8%.

Yu *et al*. (2011) studied transesterification of Pistaciachinensis oil (edible oil) with methanol using $CaO\text{-}CeO_2$ mixed oxides as catalysts. They had studied the optimal transesterification performances as following: the effect of Ce/Ca molar ratio, the calcination temperature of catalyst, the effect of methanol to oil molar ratio, amount of catalyst and reaction time. The best catalyst was C0.15-973 (Ce/Ca molar ratio of 0.15 and calcined at 973 K). For C0.15-973 regenerated after five reuses, the FAME yield was 91%, slightly less than that of the fresh.

**10. Rare earth production process**

The production process of Rare Earth Research and Development Center (Thailand Institute of Nuclear Technology) has been applying rich caustic soda or Sodium hydroxide (NaOH) on transforming of monazite. It can also be called alkali process that composed 3 groups of activities as following; (1) transforming of monazite, (2) Separation of nuclear materials such as Uranium and Thorium, (3) Separation of rare earths. Figure 6 shows the production process of rare earths.

Once, Uranium and Thorium was separated off from rare earths group, the residue which is the radioactive substances that is the by-product from decomposition of Uranium and Thorium. Therefore, before separating next rare earth, radioactive substances have to be separated from that rare earth first. The main element in this group is Radium (Ra). It will be separated off in the form of sulfate sediment (cake) by precipitation with Barium (Ba).

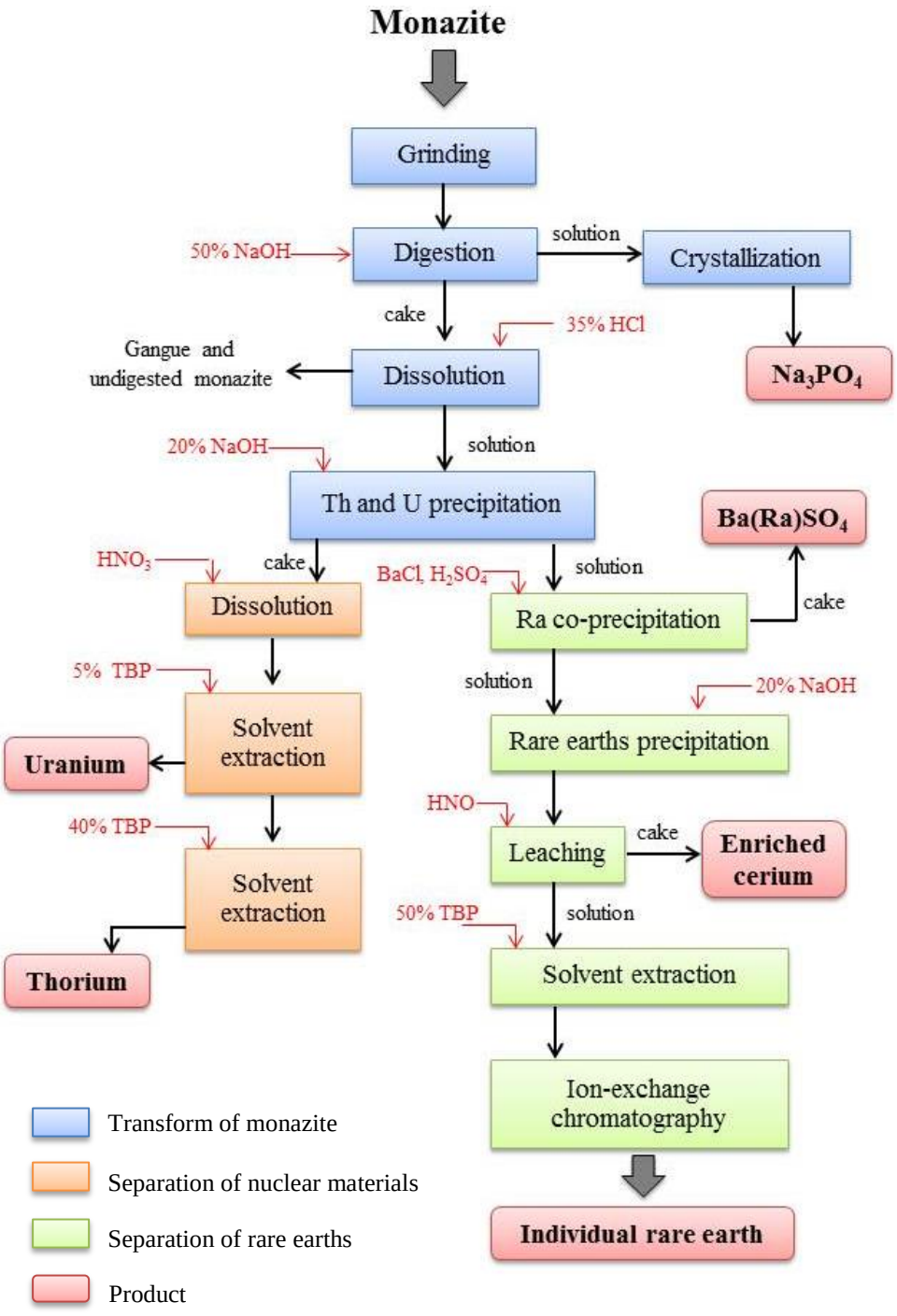


**Figure 6** Production processes of rare earths

**Source:** Thailand Institute of Nuclear Technology (2010)

The separation of rare earths uses liquid extraction method in ratio of TBP to Kerosene: 50 to 50. The extraction can divides into 3 parts.

1. Extraction of Cerium (Ce) by mixer settler.

2. The extraction of residue rare earth has been classified into 2 groups such as Lanthanum (La) interlard with Praseodymium (Pr) group and Neodymium interlarding with other rare earths (mostly is heavy rare earth) group.

3. Neodymium interlards with other rare earths group which was extracted by pulsed perforated-plate column for separation of Neodymium, whereas, other rare earths would be divided into 2 parts. The First part was mixed with $RECl_3$ which came from crystallization. This part can be sold in the market. Other part will be used by applying ion exchange chromatography method for separation of individual rare earth. Although, this method has to be used in a long operating time but it has given high purity of individual rare earth that effects to prices (Thailand Institute of Nuclear Technology, 2010).

# MATERIALS AND METHODS

## Materials

### 1. Chemicals

1.1 Palm olein oil: Morakot Industries PCL, Thailand

1.2 Lanthanum solution: Rare Earth Research and Development Center, TINT

1.3 Cerium solution: Rare Earth Research and Development Center, TINT

1.4 Neodymium solution: Rare Earth Research and Development Center, TINT

1.5 Oxalic acid:

1.6 Methanol 99.9%: HPLC grade, RCI labscan, Thailand

1.7 Lathanum oxide 99.9% : JOHNSON MATTHEY, UK

1.8 Cerium oxide 99.9% : JOHNSON MATTHEY, UK

1.9 Neodymium oxide 99.9% : JOHNSON MATTHEY, UK

### 2. Equipments

2.1 Beaker: 2000ml, 250 ml, 100 ml

2.2 Funnel

2.3 Buchner funnel

2.4 Filter paper: 41, 42

2.5 Burette

2.6 Petri dish

2.7 Crucible with lid

2.8 Agate mortar and pestle

2.9 Analytical balance

2.10 Hot air oven

2.11 Magnetic stirrer hotplate : MSH-20D, WiseStir, UK

2.12 Gas chromatography (GC) : GC-2010, Simadzu, Japan

2.13 X-ray Powder Diffraction (XRD) : D8 Advance, Bruker, France

2.14 X-ray Fluorescence Spectrometry (ED-XRF) : Epsilon 5, PANalytiacl, Almelo, Netherland

2.15 Scanning Electron Microscope (SEM) : HITACHI S3400n, Japan

2.16 Gas Adsorption Analyzer (BET) : Autosorb-1 Quantachrome, USA

## Methods

### 1. Catalyst preparation

A solution of 10 g oxalic acid in 100 ml water was added in 1,400 ml of the rare earth EDTA solution with stirring rate of 400 rpm. The flow rate was maintained at 1 ml/min. The suspension was allowed to stand at room temperature overnight. The precipitate was washed several times with deionized water and then filtered off. The rare earth oxalate was dried at 110 °C for 12 h and calcined at 900 °C for 3 h.

### 2. Determination of catalyst purity

The purification of rare earth oxide catalysts was analyzed from the energy dispersive X-ray fluorescence (ED-XRF) (Epsilon 5, PANalytiacl, Almelo, Netherland). The sample was prepared by combining the rare earth oxides with Boric acid and then was packed in the sample holder. The sample was analyzed.

### 3. Catalyst characterization

3.1 Determination of rare earth oxides crystalline structure and crystalline size using X-ray Powder Diffraction (XRD)

The sample was prepared by packing the rare earth oxides in the sample holder. The sample was recorded on a Bruker D8 Advance powder diffractometer using Cu $K_{\alpha 1}$ radiation at 30 kV and 30 mA, over a $2\theta$ range of 5-90 °C with a resolution of 0.04 at scanning speed of 1°/min. X-ray diffraction pattern of sample was compared with the X-ray diffraction pattern of standard rare earth oxides for structure determination.

3.2 Determination of crystal morphology of rare earth oxides using Scanning Electron Microscope (SEM)

The crystal morphology were determined by scanning electron microscope (HITACHI S3400n). The sample was prepared by thoroughly placing rare earth oxides onto the sample holder. It was then coated with gold thin film by ion sputtering. The sample was placed in the sample chamber of scanning electron microscope. The scanning electron micrographs were taken at the magnification of 3,000.

3.3 Determination of surface area of rare earth oxides using Nitrogen adsorption isotherm (BET)

Surface area of rare earth oxides was determined by Nitrogen adsorption isotherm (Autosorb-1 Quantachrome). The sample was prepared by weighing 1 mg of rare earth oxides sample into a cleaned and dried sample cell. The sample cell was attached to the out gassing station. Heating mantle was installed and the temperature was raised to 300 °C. the sample was out-gassed for 18 hours. The sample cell was then removed from out gassing station after the nitrogen was filled and was attached to the analysis station.

**4. High temperature and pressure batch reactor**

All experimental reactions were carried out in 600 ml of Parr stirred batch reactor (model 4568). The reactor vessel was constructed from stainless steel. The reactor was equipped with a four-blade impeller, thermocouple, sampling tube and pressure sensor. The head assembly of the reactor was equipped with a gas inlet valve for charging nitrogen gas into the reactor and a gas release valve for releasing pressure. A nitrogen gas was provided for the injection of methanol into the reactor vessel. The pressure in the reactor was used to force out the liquid samples through a dip tube. The process conditions including the heating mantle, reaction temperature, pressure, feed rate, and impeller speed were controlled. Schematic diagram of experimental apparatus is presented in Figure 7.

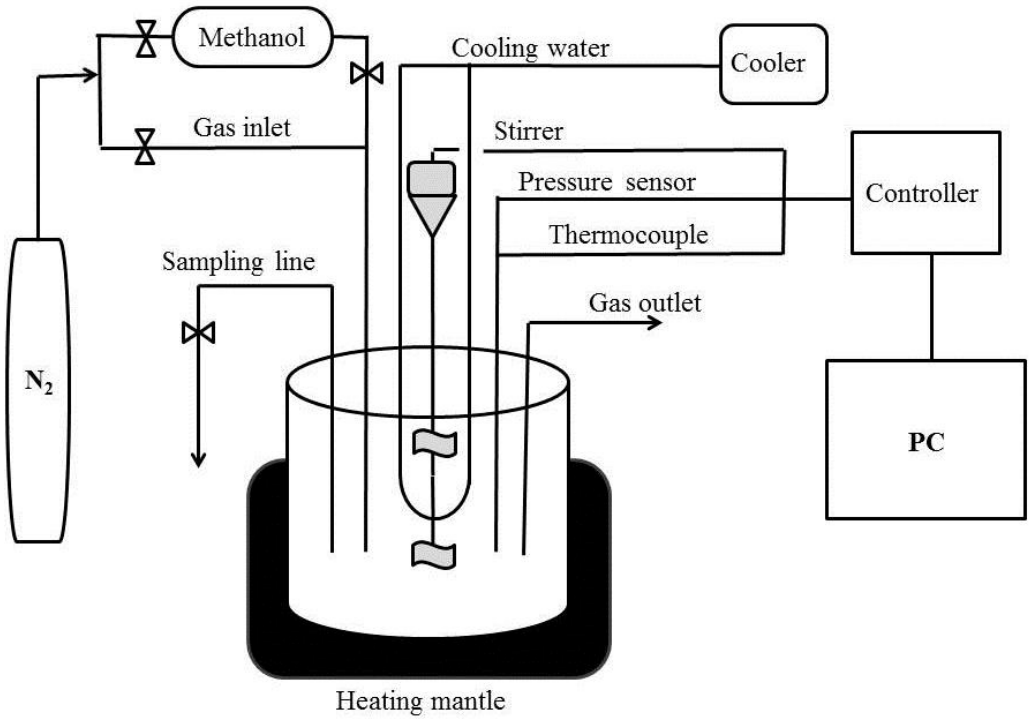


**Figure 7** Schematic diagram of experimental apparatus**.**

**5. Transesterification reaction**

Initially, 100 g of palm oil with 10 %wt of catalyst were charged into reactor. After the reaction was closed, nitrogen was purged to remove the air in the reactor. When the reactant and catalyst were heated to the desired reaction temperature, with constant stirring rate at 600 rpm, nitrogen was introduced to pressurize the system to ensure that the reactants were forced to be liquid. The reaction was start when methanol was added into the reactor by nitrogen gas. Approximately 10 ml of liquid samples was taken from a sampling tube at different periods of time; 15, 25, 30, 45, 60, 120 and 180 minute. All samples were separated by centrifugal. Total fatty acid methyl ester (FAME) was analyzed by a gas chromatography (GC).

**6. Transesterification reaction using pure rare earth oxides as catalyst**

In this section, the pure rare earth oxide catalysts such as $La_2O_3$, $CeO_2$ and $Nd_2O_3$ were used to catalyze the transesterification of palm oil with methanol. Under

the operating conditions: amount of catalyst of 10% wt., the molar ratio of methanol to palm oil of 30:1, stirring speed of 600 rpm, reaction temperature of 200 °C and reaction pressure of 39 bar for 5 h. For finding out of the best catalyst will be chosen from the per cent fatty acid methyl ester. After, the best catalyst was used to catalyze the transesterification to find the optimization of the reaction conditions.

**7. Optimization of the reaction conditions**

7.1 Effect of reaction temperature

For the catalyzed reaction, the effect of reaction temperature was studied at 120 °C, 150 °C, 170 °C and 200 °C. The reaction pressures were adjusted corresponding to reaction temperature as show in Appendix C. The parameters in this experiment were a catalyst loading of 10 %wt, molar ratio of oil to methanol of 1:30 and a stirring rate of 600 rpm was performed. The samples were taken at 15, 25, 30, 45, 60, 120 and 180 min.

7.2 Effect of molar ratio of oil to methanol

The effect of molar ratio of oil to methanol was studied at 1:10, 1:20 and 1:30. The optimal reaction temperature was obtained from the previous experiment. Catalyst loading and a stirring rate were fixed at 10 %wt and 600 rpm. The samples were taken at the same interval time as above.

7.3 Effect of catalyst loading

The effect of catalyst loading was studied using the best rare earth oxides catalysts from section 6. The effect of catalyst loading was investigated at 4 %wt, 7 %wt and 10 %wt. Reaction temperature and molar ratio of oil to methanol were obtained from the previous experiment, were carried out while a stirring rate was fixed at 600 rpm. The samples were taken at the same time interval time as previous experiment.

**8. Comparisons transesterification reaction**

Transesterification commercial catalyzed and the non- catalyzed reaction were studied using only 100 g of the oil. Under the operating conditions: amount of catalyst of 10% wt., the molar ratio of methanol to palm oil of 30:1, stirring speed of 600 rpm, reaction temperature of 200 °C and reaction pressure of 39 bar for 3 h.

# RESULTS AND DISCUSSION

In this study, the experiments were divided into 4 parts. The first part was about the purification and characterization of pure rare earth catalyst ($La_2O_3$, $CeO_2$ and $Nd_2O_3$). The second part involved transesterification catalyzed reaction study. This part was studied about the effect of each pure rare earth oxide catalyst on the rate of total FAME (total fatty acid methyl ester) to choosing one of all catalyst to use in next part. The third part included the study of the effect of reaction temperature, molar ratio of oil to methanol and catalyst loading on the FAME content. The final part, the comparison of synthesized catalyzed, commercial catalyzed and non-catalyzed reaction was investigated.

## Purification and characterization of catalyst

### 1. Catalyst purification

The ED-XRF analysis revealed the presence of several trace elements such as $Na_2O$, $Al_2O_3$, $SiO_2$, CaO, $Fe_2O_3$, $La_2O_3$, $CeO_2$, $Nd_2O_3$, $Pr_2O_3$ and $Sm_2O_3$. Table 7 shows the chemical composition of pure rare earth oxide catalysts. The results show that, the high purity of $La_2O_3$ (95.85 wt.%), $CeO_2$ (97.13 wt.%) and $Nd_2O_3$ (95.59 wt.%) were obtained.

**Table 7** ED-XRF estimation of elemental concentration (%) in pure rare earth oxide catalysts

| **Compounds** | **Purity (wt.%)** | | |
|---|---|---|---|
| | **$La_2O_3$** | **$CeO_2$** | **$Nd_2O_3$** |
| $Na_2O$ | 0.90 | - | - |
| $Al_2O_3$ | 0.80 | 1.51 | - |
| $SiO_2$ | 0.23 | 0.23 | - |
| CaO | 1.58 | 0.21 | 0.19 |
| $Fe_2O_3$ | 0.13 | 0.22 | - |

**Table 7** (Continued)

| Compounds | Purity (wt.%) | | |
|---|---|---|---|
| | **$La_2O_3$** | **$CeO_2$** | **$Nd_2O_3$** |
| $La_2O_3$ | **95.85** | 0.59 | 0.22 |
| $CeO_2$ | 0.51 | **97.13** | 2.03 |
| $Nd_2O_3$ | - | 0.11 | **95.59** |
| $Pr_2O_3$ | - | - | 0.80 |
| $Sm_2O_3$ | - | - | 1.17 |

**2. Catalyst characterization**

2.1 Determination of surface area of rare earth oxides using Nitrogen adsorption isotherm (BET)

The surface area, pore volume and pore size of catalysts are the important factors for the catalysts. All catalysts were analyzed for physical properties which are BET surface area, average pore size and total pore volume by $N_2$ adsorption with high speed gas analyzer (Quantachrome instrument Co Ltd.,). The surface area will be calculated automatically and the results showed in Table 8.

The BET surface, total pore volume and average pore diameter are important characterizations of solid catalyst. Due to, it is closely related to the catalytic activity. Particularly, the reactivity is directly proportional to the external surface area of catalyst (Xuejun *et al*., 2007). From the result, the synthesized $La_2O_3$ and $CeO_2$ catalysts showed a surface area of 5.146 and 5.287 $m^2/g$, respectively that higher than that of commercial catalyst. Moreover, the BET surface area of $Nd_2O_3$ synthesized catalyst was 3.166 $m^2/g$, little smaller than that of commercial catalyst (4.989 $m^2/g$). The average pore size diameters of all samples were under the meso-pore category in the range of 10-50 nm. That is advantageous for the reaction of large reactants such as triglycerides because the internal mass transfer limitation in the transesterification can be reduced using meso-pore catalysts (Dora *et al*., 2005).

**Table 8** BET surface area, total pore volume and average pore diameter of rare earth oxide catalysts

| Catalyst | BET Surface area ($m^2/g$) | Average pore diameter (nm) | Total pore volume ($cm^3/g$) |
|---|---|---|---|
| $La_2O_3$ | 5.146 | 10.97 | 0.014 |
| $La_2O_3$[a] | 3.855 | 15.28 | 0.014 |
| $CeO_2$ | 5.287 | 25.95 | 0.034 |
| $CeO_2$[a] | 0.714 | 29.08 | 0.005 |
| $Nd_2O_3$ | 3.166 | 35.17 | 0.028 |
| $Nd_2O_3$[a] | 4.989 | 10.64 | 0.013 |

[a] Commercial catalyst

2.2 Determination of crystal morphology of rare earth oxides using Scanning Electron Microscope (SEM)

The morphology of the rare earth oxide catalysts was investigated by SEM. Figure 8 shows SEM images of rare earth oxide catalysts(magnification = 3,000x). The commercial catalysts appear uniform shape and size especially $CeO_2$ as shown in Fig. 8(d) that related with surface area, whereas the synthesized catalysts are in the form of irregular-shaped crystalline particles. All prepared rare earth oxide catalysts possessed low specific surface area (<10 $m^2/g$) and low pore volume (0.04–0.01 $cm^3/g$), consistent with the images observed by SEM. However, the sizes of most particles were very fine. It shows the surfaces comprise a large number of conglomerations of catalyst particles. And each particle was mixed in the range of meso to macro particle size. Most of these particles congregate to form agglomerates. Within the particles, fewer meso-pores are observed (10–50 nm) because the catalyst crystals are almost solid with moderate surface areas.

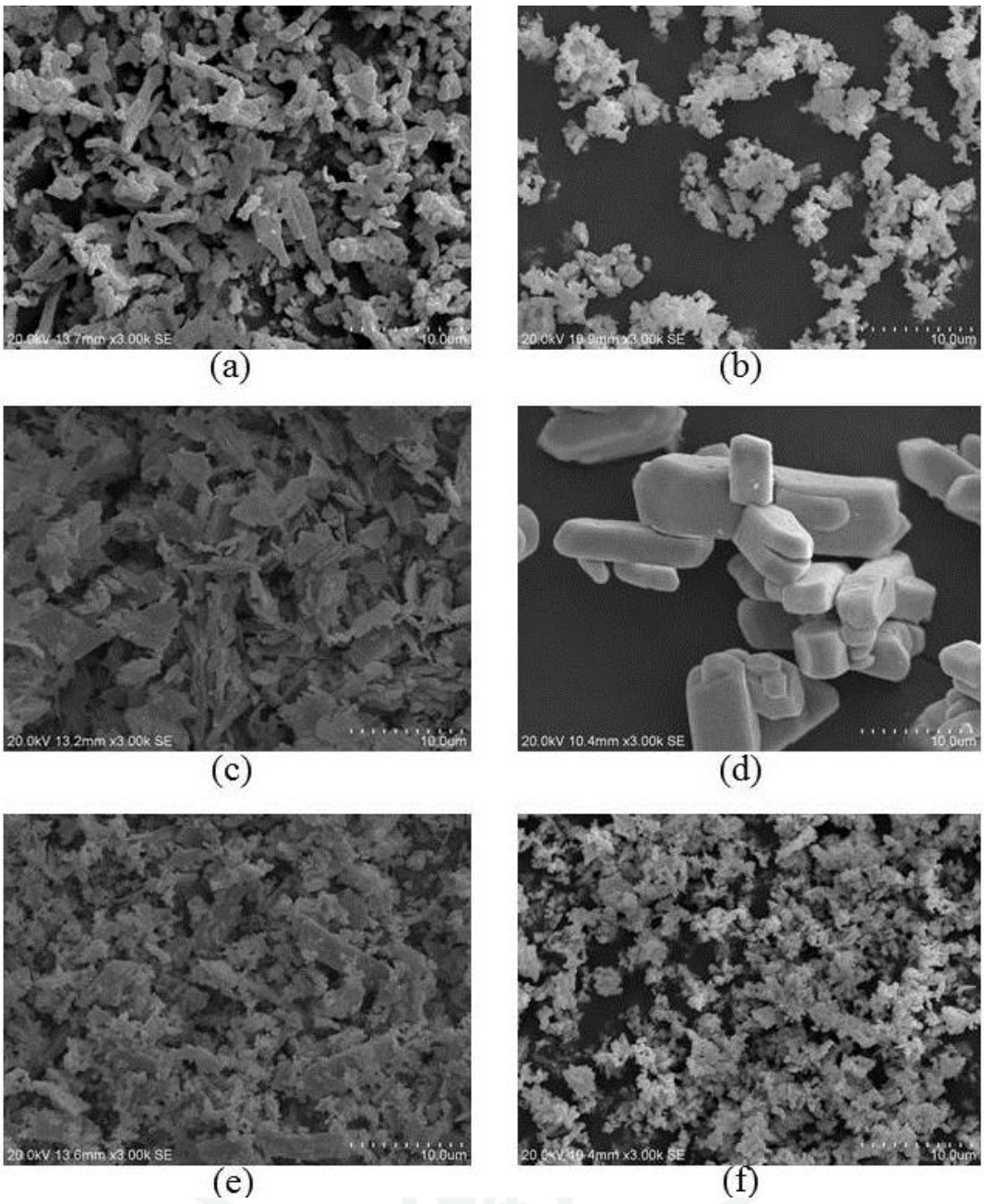


**Figure 8** SEM images of rare earth oxide catalysts. (Synthesized catalysts are (a) $La_2O_3$, (c) $CeO_2$ and (e) $Nd_2O_3$. Commercial catalysts are (b) $La_2O_3$, (d) $CeO_2$ and (f) $Nd_2O_3$.)

2.3 Determination of rare earth oxides crystalline structure using X-ray Powder Diffraction (XRD)

Figure 9, 10 and 11 demonstrates the XRD patterns of commercial and synthesized rare earth oxides catalyst with $2\theta$ from 10 to 90. The X-ray powder diffraction patterns closely matched the well-known rare earth oxide structures (Russbueldt and Hoelderich, 2010). Fig. 9 shows the diffraction peak of $La_2O_3$. The sharp peaks located at 26.11°, 29.96°, 39.48°, 46.09°, 52.16° and 55.46° were observed. The most of $La_2O_3$ commercial and synthesized catalyst patterns matched with JCPDS no.01-074-1144 standard of $La_2O_3$. However, there are some $La(OH)_3$ peaks were observed for commercial catalyst. The ratio of $La(OH)_3$ to $La_2O_3$ for commercial catalyst was 0.75 that indicated surely for $La_2O_3$. The diffraction peak of commercial and synthesized catalyst $CeO_2$ as matched with JCPDS no.00-043-1002 is illustrated in Fig. 10. Both of catalyst shows clearly peaks which no diffraction peak of hydroxide species was detected. Their strong shape peaks appeared at $2\theta$ = 28.48°, 33.03°, 47.45° and 56.28°. The sharp diffraction peaks of $Nd_2O_3$ (JCPDS no.00-041-1089) at $2\theta$ = 26.85°, 29.77°, 40.53°, 47.45°, 53.48° and 57.64° were observed as shown in Fig. 11.

Sesquioxides of trivalent rare earth metals have A-, B-, and C type crystal structures at temperature lower than 2000 °C. The A-, B-, and C-type crystal structures are hexagonal, monoclinic, and cubic, respectively (Sato *et al.*, 2008). The crystal structures of $La_2O_3$ and $Nd_2O_3$ after calcined at 900 °C were A-type hexagonal. A cubic structure of $CeO_2$ was found at the same calcination temperature. It had shown clearly cubic of crystal morphology by SEM in Fig 8.

Table 9 shows the crystalline size of rare earth oxide catalysts. The crystalline size was calculated from Scherrer equation (Appendix A). The crystal size of $CeO_2$ synthesized catalyst is 0.485 nm, which is about the same as commercial $CeO_2$ (0.531 nm). The highest crystalline size for $La_2O_3$ synthesized catalyst was found (6.327 nm) that is higher than the commercial (4.717 nm).

**Table 9** crystallize size of rare earth oxide catalysts

| Catalyst | $2\theta$ | Crystalline size (nm) |
|---|---|---|
| $La_2O_3$ | 29.9581 | 6.327 |
| $La_2O_3$[a] | 29.9970 | 4.717 |
| $CeO_2$ | 56.2769 | 0.485 |
| $CeO_2$[a] | 56.3935 | 0.531 |
| $Nd_2O_3$ | 30.7745 | 0.680 |
| $Nd_2O_3$[a] | 30.8134 | 0.920 |

[a] Commercial catalyst

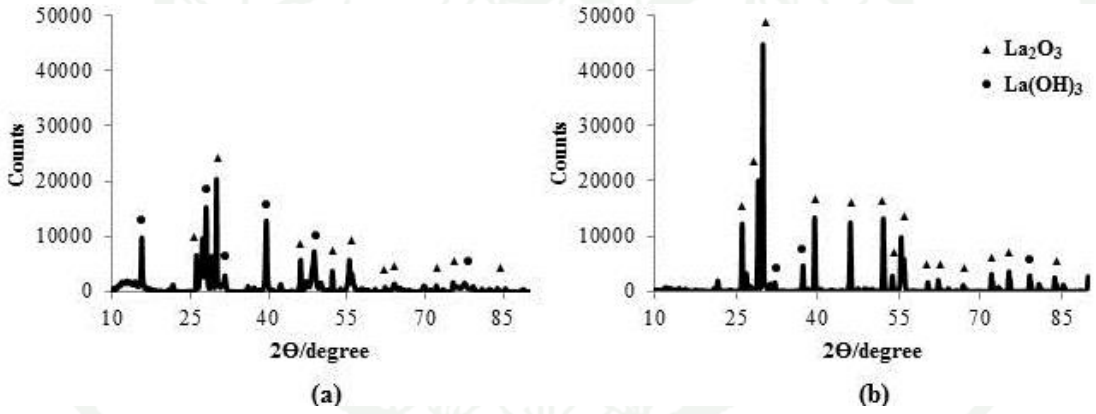


**Figure 9** X-ray powder diffraction patterns of $La_2O_3$. a) Commercial catalyst b) Synthesized catalyst

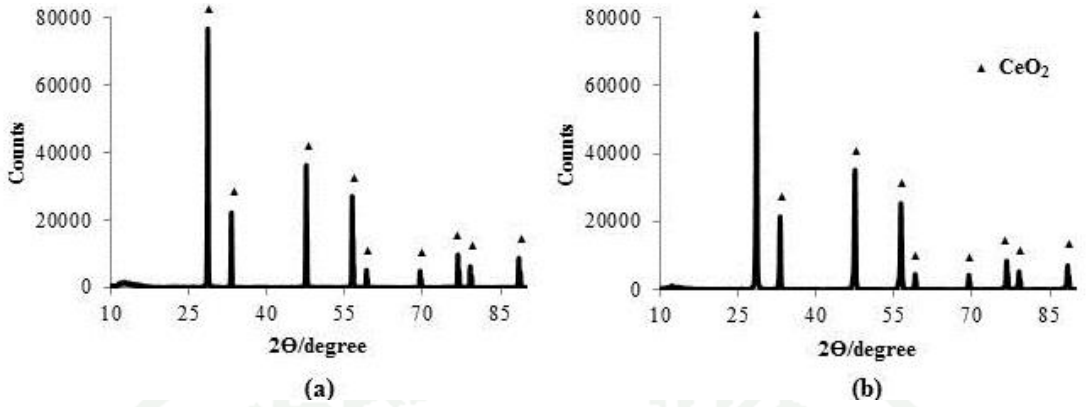


**Figure 10** X-ray powder diffraction patterns of $CeO_2$. a) Commercial catalyst b) Synthesized catalyst

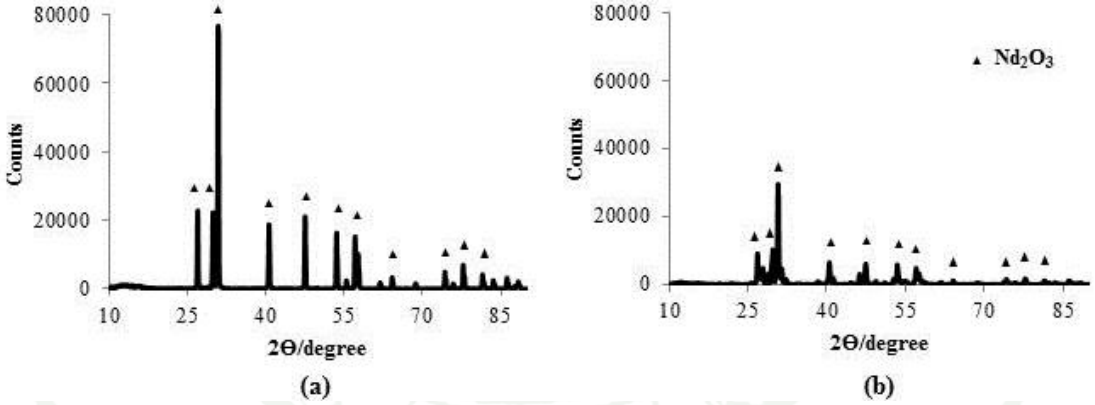


**Figure 11** X-ray powder diffraction patterns of $Nd_2O_3$. a) Commercial catalyst b) Synthesized catalyst

**Transesterification reaction**

Pure rare earth oxide catalysts including $La_2O_3$, $CeO_2$ and $Nd_2O_3$ were prepared. The catalytic activities for transesterification reactions of palm oil with methanol using these catalysts were investigated.

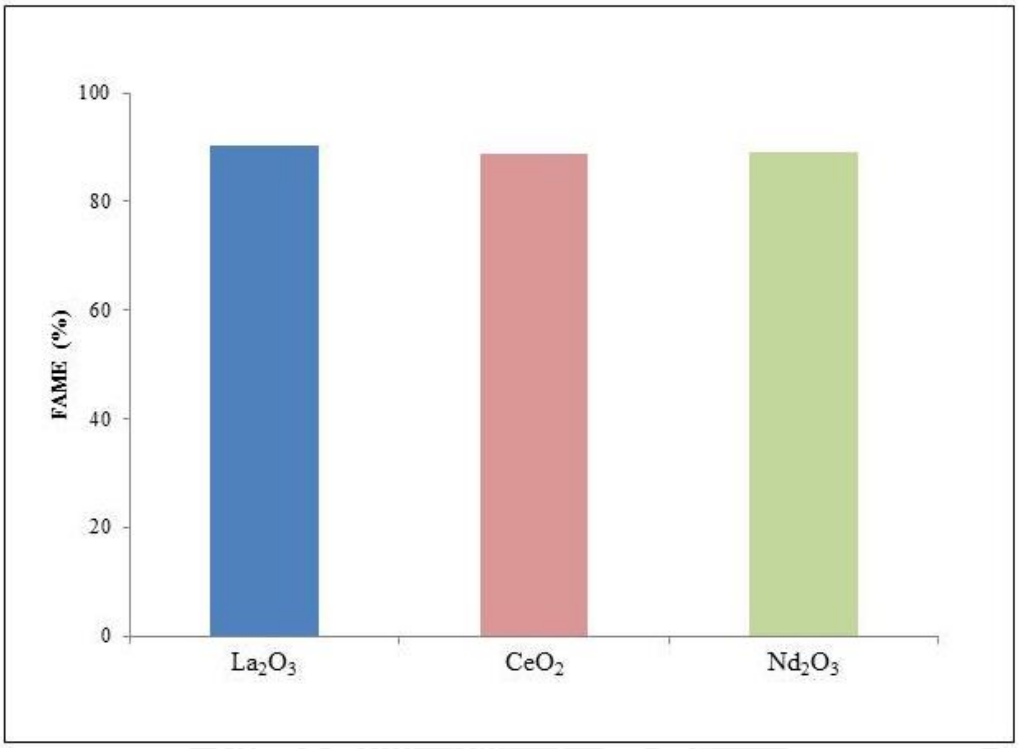


**Figure 12** Fatty acid methyl ester content of pure rare earth oxides

The reactions were carried out at molar ratio of methanol to oil 30:1, catalyst loading 10%wt, reaction temperature 200 °C, reaction temperature 39 bar and stirring rate 600 rpm for 5 h.

Figure 10 shows the fatty acid methyl ester (FAME) contents of pure rare earth oxide catalysts such as $La_2O_3$, $CeO_2$ and $Nd_2O_3$. A little difference between the catalytic activities of their catalysts for transesterification of palm oil with methanol was found. The high FAME contents of $La_2O_3$ (90.25%), $CeO_2$ (88.91%) and $Nd_2O_3$ (89.10%) were obtained.

All rare earth oxide catalysts ($La_2O_3$, $CeO_2$ and $Nd_2O_3$) show high catalytic activity, $La_2O_3$ has attracted a special interest due to its high activity more than other catalysts. Besides, the reviewed literature also reported that $La_2O_3$ has a high catalytic activity and strong base strength ($H\_$) more than other catalysts. These tendencies are in accordance with this work. As shown in Appendix B, the $La_2O_3$ had a strongest base strength in range of 9.8 to 12.2 as compared to that of $CeO_2$ and $Nd_2O_3$. Therefore, The $La_2O_3$ was selected and further studied as a catalyst for transesterification.

**Optimal condition Transesterification ($La_2O_3$ study)**

**1. Effect of reaction temperature**

It is well known that the rate of transesterification reaction is strongly influenced by reaction temperature especially, using the solid catalyst, it needs high temperature to overcome mass transfer problem. Nevertheless, high reaction temperature particularly at higher than 200 °C should be considered due to forming the undesirable components for example polymeric and polar compounds (Mittelbach and Enzelsberger, 1999).

Thus, variation of reaction temperature ranging from 120 to 200 °C was evaluated in this study. Reaction pressure was adjusted corresponding to reaction temperature to ensure that the reactant were in the liquid form. For example at the desired reaction temperature of 200 °C, pressure was controlled at 39 bar (Appendix C). Other reaction parameters were catalyst loading of 10 %wt, molar ratio of oil to methanol of 1:30 and stirring rate of 600 rpm.

**Table 10** Final FAME content for catalyzed reaction at different reaction temperatures (180 minutes)

| Reaction temperature (°C) | Final FAME content (%) |
|---|---|
| 120 | 88.49 |
| 150 | 91.46 |
| 170 | 94.41 |
| 200 | 96.36 |

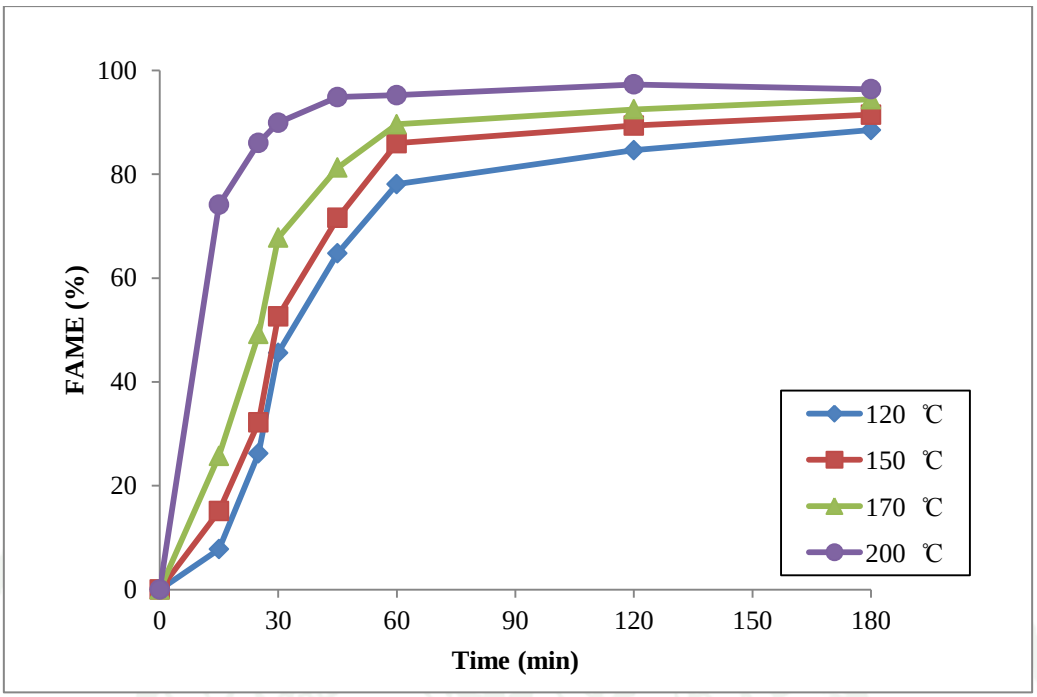


**Figure 13** Effect of temperature on total FAME production for catalyzed reaction; reaction condition: $La_2O_3$ catalyst, catalyst loading of 10 %wt, molar ratio of oil to methanol of 1:30 and stirring rate of 600 rpm

For the catalyzed reaction, the increasing of reaction temperature enhanced markedly the rate of total FAME production as shown in Figure 13. As can be seen in Figure 13, at the reaction temperature of 150℃, the highest total FAME of 91.46% was obtained after 120 min while at the reaction temperature of 170℃ and 200℃ were observed at 60 min and 30 min. A very slow rate was found at the reaction temperature of 120℃.

It can be noted that the increase in reaction temperature from 120 to 170 °C resulted in a significant increase of the final total FAME content as shown in the Table 10. However, when the reaction temperature reached from 170 °C to 200 °C, the final total FAME was insignificantly increased. These results corresponded to shift the balance of reaction to FAME and to overcome mass transfer resistance at high reaction temperature (Gao et al., 2008). For Heterogeneous catalyst system, the mass transfer resistance is not only in the liquid phase between reactants but also in

the liquid-solid phase between reactant and catalyst. In this system, it can be seen that the low initial rate of the reaction at low reaction temperature (120 °C) was obtained. This can be suggested that a large molecule of triglyceride was less soluble in methanol and difficult to chemical reaction on the catalyst. It seems that the mass transfer controlled at the beginning. Hence, the rate of reaction was slow; it led to a hindrance of other molecules to continue the reaction (reaction control). As can be seen at reaction temperature of 120 °C, the total FAME content of 88.49% was obtained at 180 min and then a slight increase of the FAME content was observed

**2. Effect of molar ratio of oil to methanol**

To evaluated the influence of molar ratio of oil to methanol on the rate of reaction and the final FAME content and conversion, the various molar ratios of oil to methanol namely 1:10, 1:20 and 1:30 were carried out. The condition parameters were 200 °C of reaction temperature, reaction pressure 39 bar, catalyst loading 10 %wt and stirring rate 600 rpm.

**Table 11** Final FAME content for catalyzed reaction at different molar ratios of oil to methanol (180 minutes)

| Molar ratio of oil to methanol | Final FAME content (%) |
|---|---|
| 1:10 | 68.42 |
| 1:20 | 87.79 |
| 1:30 | 96.36 |

For catalyzed reaction, the effect of molar ratio of oil to methanol on total FAME production at different molar ratios of oil to methanol is shown in Figure 14. The rate of total FAME production was influenced by the molar ratio of oil to methanol. The increasing of molar ratio of oil to methanol increased the rate of total

FAME production. The final total FAME content for catalyzed reaction at different molar ratios of oil to methanol is summarized in Table 11.

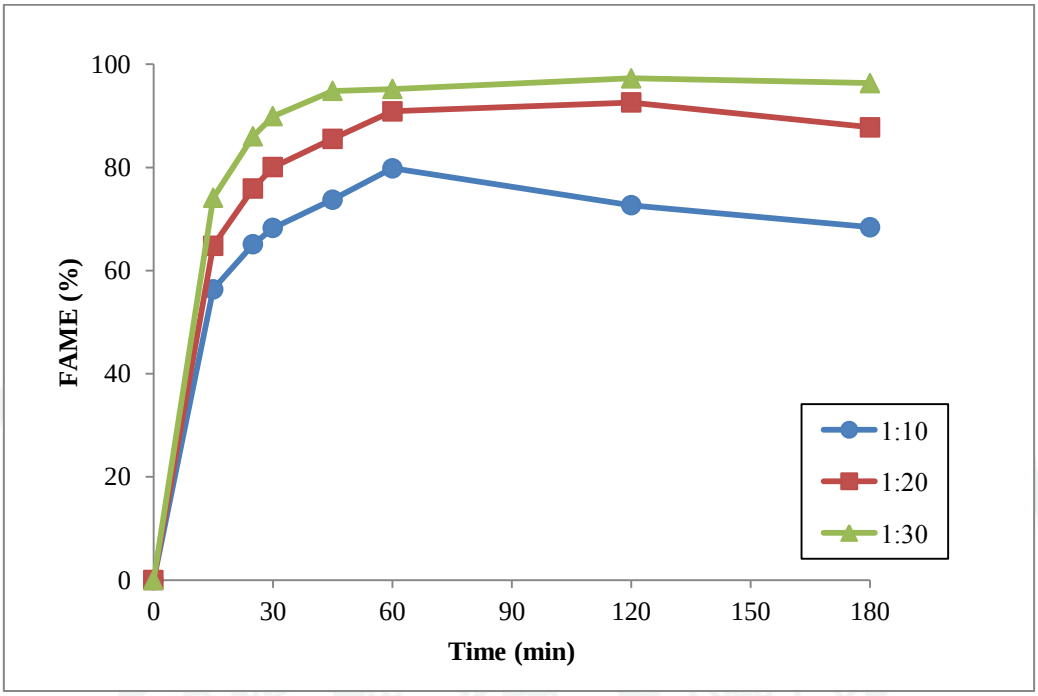


**Figure 14** Effect of molar ratio of oil to methanol on total FAME production for catalyzed reaction; reaction condition: $La_2O_3$ catalyst, catalyst loading of 10 %wt, reaction temperature of 200 °C, reaction pressure of 39 bar and stirring rate of 600 rpm

As a result, the FAME content increased rapidly in the reaction time of 60 min for all reaction tests. The performance of the 10% wt. $La_2O_3$ catalyst strongly depended on the molar ratio of oil to methanol. It can be seen that the ratio of 1:10 which is stoichiometric ratio shows the lowest FAME content throughout the reaction course. The increase in the molar ratios of oil to methanol typically enhanced the ME content, especially at the beginning and final of the reaction course. The greatest yield of biodiesel was obtained at 96.36% for the molar ratio of oil to methanol 1:30 at 180 min. This can be suggested that, the molar ratio of oil to methanol up to 1:30 was necessary to accelerate the rate of reaction and to drive the equilibrium to obtain the high total FAME content. The solid catalyzed transesterification reaction requires the

high molar ratio of oil to methanol not only to shift the forward reaction but also to extract the product either FAME or glycerol from reactant to renew the catalyst surface (Yan et al., 2009). Therefore, high ratio of methanol to oil is beneficial.

### 3. Effect of catalyst loading

There are several factors that can influence the rate of reaction and the final conversion. Catalyst is the dominate factor to accelerate the reaction. In general, the catalyst allows the reaction to proceed by an alternate reaction mechanism with a lower activation energy (compared to non-catalyzed reaction). It is not consumed in the chemical reaction. However, catalyst loading plays an important role in chemical kinetic. To investigate the effect of catalyst loading on the rate of reaction and the final FAME content, the amount of catalyst were varied at 4 %, 7 % and 10 %wt at reaction temperature of 200 °C, reaction pressure of 39 bar, molar ratio of oil to methanol of 1:30 and stirring rate 600 rpm.

**Table 12** Final FAME content at different catalyst loadings (180 minutes)

| Catalyst loading (%wt) | Final FAME content (%) |
|---|---|
| 4 | 93.65 |
| 7 | 96.16 |
| 10 | 96.36 |

Figure 15 shows the changes of total FAME at different catalyst loading. It is visible that the rate of total FAME production increased with increase of catalyst loading. For the reaction of 10%wt catalyst loading, the active site was more readily available to the reaction at initial time (0-30 min) so that the rate of reaction was too fast. After that, in the range of reaction time from 30 min to 120min the active sites of 10 %wt catalyst loading were covered by some of reactants and products that hindered other reactants. It caused in a slow rate reaction. The same phenomenon was

observed at 7 %wt catalyst loading. The rate of reaction at 4 %wt catalyst loading at the initial time was slowest the reaction.

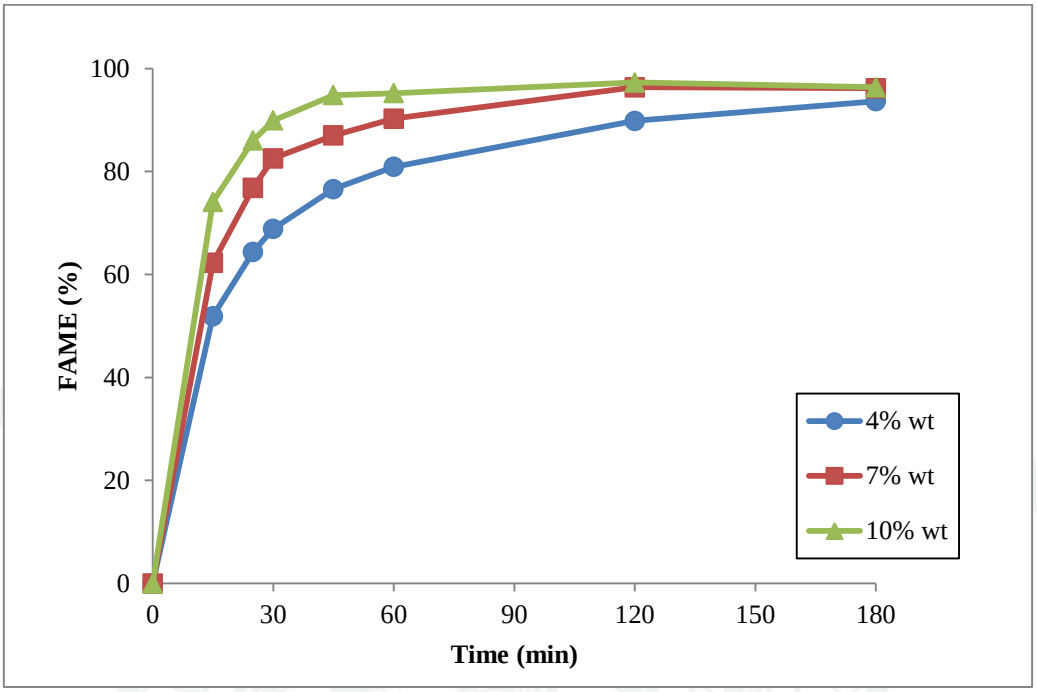


**Figure 15** Effect of catalyst loading on total FAME production for catalyzed reaction; reaction condition: $La_2O_3$ catalyst, molar ratio of oil to methanol of 1:30, reaction temperature of 200 °C, reaction pressure of 39 bar and stirring rate of 600 rpm

Table 12 reveals the final FAME content at different catalyst loading. As can be seen in the Table, increase in catalyst loading did not improve the final total FAME content. This can be explained by the theory that the catalyst only changes the reaction speed and could not shift the balance of equilibrium to obtain the higher conversion.

**Comparison of catalyzed, commercial catalyzed and non-catalyzed reaction**

Comparison of transesterification synthesized catalyzed reaction (TSC), transesterification commercial catalyzed reaction (TCC) and non-catalyzed reaction (TNC) were experimented using $La_2O_3$ catalyst at the operating conditions : catalyst loading of 10 %wt, molar ratio of oil to methanol of 1:30, reaction temperature of 200 °C, reaction pressure of 39 bar and stirring rate of 600 rpm. Moreover, transesterification non-catalyzed reaction (TNC) with the same operating conditions was also examined.

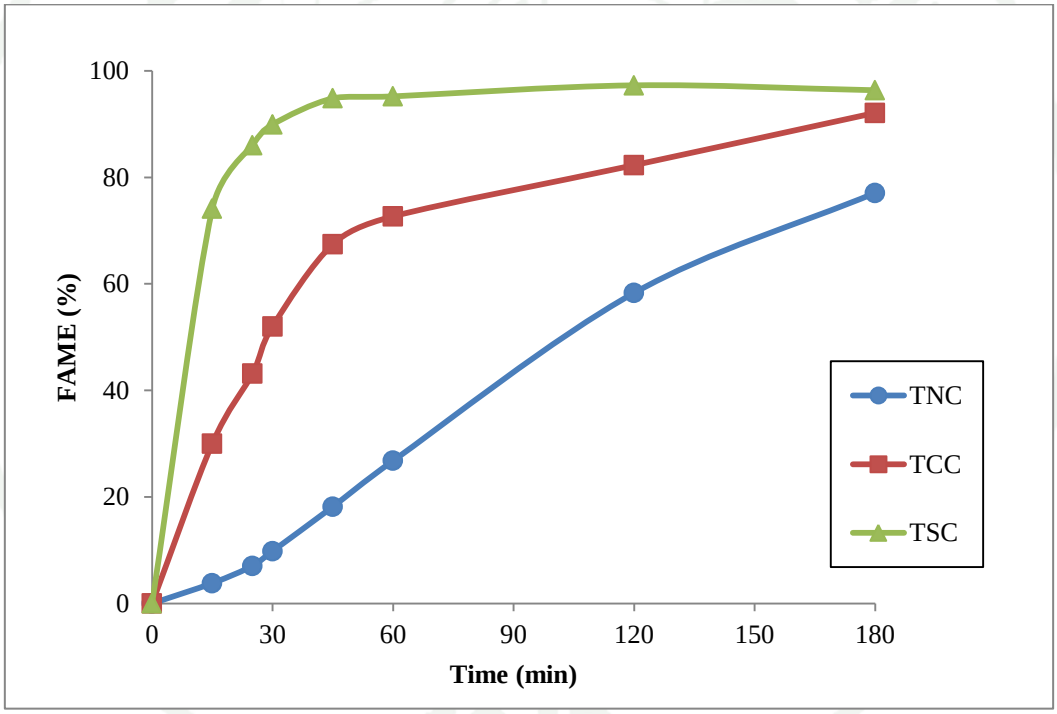


**Figure 16** Comparison of FAME production between TSC, TCC and TNC; reaction condition: catalyst loading of 10%wt, molar ratio of oil to methanol of 1:30, reaction temperature of 200 °C, reaction pressure of 39 bar and stirring rate of 600 rpm.

The profiles of FAME content of TSC, TCC and TNC is shown in Figure 16. It is obvious that the rate of the TSC was higher than that of the TCC. The final FAME content of the TSC and the TCC were 96.36% and 92.11%, respectively. It is

interesting to note that the TSC proceeded very fast with 94.85% of FAME content within 45 min. Because of the TSC showed the crystalline size higher than TCC. The lowest of FAME content was found in TNC. It can be note that $La_2O_3$ catalyst is a promising heterogeneous catalyst for biodiesel synthesis from palm olein. Therefore, TSC shows the highest catalytic activity which obtained the highest yield and methyl ester content.

**Table 13** Final FAME content of TSC, TCC and TNC (180 minutes)

| Reaction | Final FAME content (%) |
|---|---|
| (TSC) Transesterification synthesized catalyzed reaction | 96.36 |
| (TCC) Transesterification commercial catalyzed reaction | 92.11 |
| (TNC) Transesterification non-catalyzed reaction | 77.08 |

# CONCLUSION AND RECOMMENDATIONS

## Conclusion

Rare earth solid based catalysts such as $La_2O_3$, $CeO_2$ and $Nd_2O_3$ were prepared by simple precipitation method. These catalysts showed the high catalytic activity for the transesterification of palm oil with methanol. Because of the large pore volume of their catalysts. The high FAME content of 90.25, 88.92 and 89.1% for $La_2O_3$, $CeO_2$ and $Nd_2O_3$, respectively were obtained under the specific condition as follows: molar ratio of methanol to oil 30:1 catalyst loading 10%wt, reaction temperature 200 °C, reaction pressure 39 bar and stirring rate 600 rpm. for 5 h. The results indicate that rare earth oxide catalysts have great potential for biodiesel production from vegetable oil. Furthermore, the base strength could help to select the suiable catalyst. The $La_2O_3$ had a strongest base strength in range of 9.8 to 12.2 that might effect to FAME content. Therefore, The $La_2O_3$ was selected and further studied as catalyst for transesterification.

$La_2O_3$ catalyst was considered to be an efficient catalyst for transesterification with methanol. The effect of reaction temperature (120-200 °C), catalyst loading (4-10 %wt) and molar ratio of oil to methanol (1:10-1:30) were studied and found to have significant impacts on the final total FAME content. The most suitable conditions for the transesterification of palm olein oil using $La_2O_3$ catalyst were found to be a oil to methanol molar ratio of 1:30, a catalyst loading of 10 %wt, a reaction temperature of 200 °C, a reaction pressure of 39 bar and stirring rate 600 rpm gave the total FAME content of 94.84 % at 45 min. Moreover, the comparison of catalyst performance in transesterification by the proposed and $La_2O_3$ commercial catalyst, it is surprising that our catalyst showed the total FAME higher than the commercial catalysts.

The $La_2O_3$ was shown to be an interesting choice of catalysts due to its reasonably high activity, ease of preparation, simple separation and low cost.

Together, features can make biodiesel production from palm oil become more economically feasible.

## Recommendations

1. Catalyst reusability and catalyst regeneration should be investigated due to this is one of all advantages of heterogeneous catalyst.
2. The proposed side reaction such as leaching of catalyst and water content should be studied.
3. Raw material should be applied to convert inexpensive waste oils to have more benefit and reduce waste.

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# APPENDICES

**Appendix A**

Calculation

**1. Determination of raw materials**

Molecular weight of palm olein oil is 838 g/mol

Molecular weight of methanol ($CH_3OH$) is 32.04 g/mol

Measuring palm olein oil for 100 g

Molar ratio of oil to methanol is 1:30

Calculation of methanol amount

$$\frac{Mole\ oil}{Mole\ methanol} = \frac{1}{30}$$

$$\frac{W_{oil}/Mw_{oil}}{W_{methanol}/Mw_{methanol}} = \frac{1}{30}$$

$$(30)\left(\frac{W_{oil}}{Mw_{oil}}\right) = \frac{W_{methanol}}{Mw_{methanol}}$$

$$W_{methanol} = (30)\left(\frac{100}{838}\right)(32.04)$$

$$W_{methanol} = 114.70\ \text{g}$$

**2. Determination of crystalline size**

Scherrer equation; $$L = \frac{K\lambda}{\beta \cos\theta}$$

Where L = Crystallite size, Å

$K$ = Crystallite-shape factor = 0.9

$\lambda$ = X-ray wavelength, 1.5406 Å of Cu K$\alpha$

$\theta$ = Observed peak angle, degree

$\beta$ = X-ray diffraction broadening, radian

**Appendix B**

Base strength

**1. Determination of base strength**

The base strength of the samples ($H_-$) was determined using Hammett indicators. Approximately 25 mg of the sample was shaken with 1 ml of 0.1%wt ethanol solution of the Hammett indicator. Duration of 2 h was allowed to elapse to achieve equilibrium after which no additional change of color occurred. The basic strength is defined as being stronger than the weakest indicator that exhibits a color change, and weaker than the strongest indicator that produces no color change. Bromthymol blue ($H_-$=7.2), phenolphthalein ($H_-$=9.8), indigo carmine ($H_-$=12.2), 2,4-dinitroaniline ($H_-$=15.0), and 4- nitroaniline ($H_-$=18.4) were used as Hammett indicators.

**Appendix Table B1** Base strength of rare earth oxide catalysts.

| **Synthesized catalyst** | **Base strength ($H_-$)** | **Commercial catalyst** | **Base strength ($H_-$)** |
|---|---|---|---|
| $La_2O_3$ | $9.8<H_-<12.2$ | $La_2O_3$ | $9.8<H_-<12.2$ |
| $CeO_2$ | $H_-<7.2$ | $CeO_2$ | $H_-<7.2$ |
| $Nd_2O_3$ | $H_-<7.2$ | $Nd_2O_3$ | $H_-<7.2$ |

**Appendix C**

Analytical method

**1. Determination of total FAME content by GC**

Total FAME content was determined by GC following EN 14103 standard method. The procedure was carried out as follows:

Preparation of methyl heptadecanoate, 10 mg/ml internal standard solution: accurately weighed approximately 500 mg of methyl heptadecanoate in a 50 ml volumetric flask and made up to mark with heptane.

Preparation of sample: accurately weighed approximately 65 mg of sample in a 10 ml vial, and then added approximately 1.95 ml of methyl heptadecanoate standard solution (10 mg/ml).

GC analysis: the sample was analyzed by using the GC equipped with flame ionization detector (FID) and fused silica capillary column (30 m × 0.32 nm × 0.25 µm). The oven temperature was set up at 210 C, the FID temperature was maintained at 250 C and injector temperature was kept up at 250 C. Helium was used as a carrier gas.

Total FAME content, in percentage by mass, can be calculated using the following formula:

$$\text{Total FAME content} = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\ \%$$

Where

$\sum A$ is the total peak area from the methyl ester in C12 to that in C24:1 defines as 100;

$A_{EI}$ is the peak area corresponding to methyl heptadecanoate;

$C_{EI}$ is the concentration, in mg/ml, of the methyl heptadecanoate solution being used;

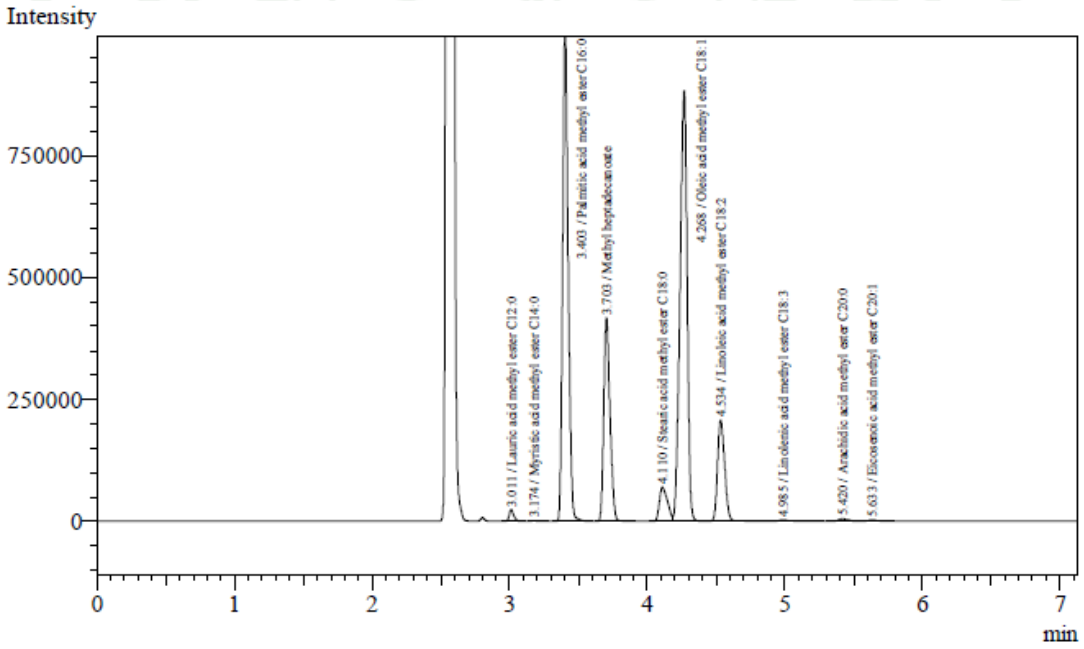
$V_{EI}$ is the volume, in ml, of the methyl heptadecanoate solution being used;

$m$ is the mass, in mg, of the sample.

The peak identification was made by comparing the retention time between of the sample and standard compound.

For example, in the reaction conditions: catalyst loading of 10 %wt, molar ratio of oil to methanol of 1:30, reaction temperature of 200 C, reaction pressure of 39 bar and stirring rate of 600 rpm for 180 min.

- The concentration of standard ($C_{17}$) = 10.078 mg/ml
- The weight of sample = 115.5 mg




| Peak# | Ret.Time | Area | Height | Conc. | Unit | Mark | ID# | Cmpd Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 3.011 | 53804 | 23437 | 0.635 | % | | 3 | Lauric acid methyl e |
| 2 | 3.174 | 2988 | 1127 | 0.035 | % | | 5 | Myristic acid methyl |
| 3 | 3.403 | 2825198 | 996639 | 33.351 | % | | 8 | Palmitic acid methyl |
| 4 | 3.703 | 1316374 | 416797 | 15.540 | % | | 10 | Methyl heptadecano |
| 5 | 4.110 | 284127 | 70034 | 3.354 | % | | 11 | Stearic acid methyl e |
| 6 | 4.268 | 3188618 | 882608 | 37.641 | % | V | 12 | Oleic acid methyl es |
| 7 | 4.534 | 748986 | 207287 | 8.842 | % | V | 13 | Linoleic acid methyl |
| 8 | 4.985 | 16394 | 2585 | 0.194 | % | | 14 | Linolenic acid meth |
| 9 | 5.420 | 23319 | 4794 | 0.275 | % | | 15 | Arachidic acid meth |
| 10 | 5.633 | 11307 | 2217 | 0.133 | % | | 16 | Eicosenoic acid metl |
| **Total** | | 8471115 | 2607525 | | | | | |

**Appendix Figure C1** The graph of gas chromatography

From Figure C1,

The area of standard ($C_{17}$) = 1,316,374

The total area = 8,471,115

$$\%\text{FAME} = \frac{8{,}471{,}115 - 1{,}316{,}374}{1{,}316{,}374} \times \frac{1 \times 10.078}{115.5} \times 100$$

$$= 94.85\ \%$$

**Appendix D**

Reaction pressure

**Appendix Table D1** The relation of reaction pressure and reaction temperature by Antoine equation

| Antoine equation parameter | | | | | Temperature (℃) | Pressure (bar) |
|---|---|---|---|---|---|---|
| **A** | **B** | **C** | **$T_{min}$ (℃)** | **$T_{max}$ (℃)** | | |
| **7.9701** | 1521.23 | 234 | 65 | 214 | 120 | 6.3 (7) |
| | | | | | 150 | 13.6 (14) |
| | | | | | 170 | 21.4 (22) |
| | | | | | 200 | 38.9 (39) |

**Source**: Dortmund Data Bank (2009)

**Appendix E**

Rare earth Catalysts

(a)

(b)

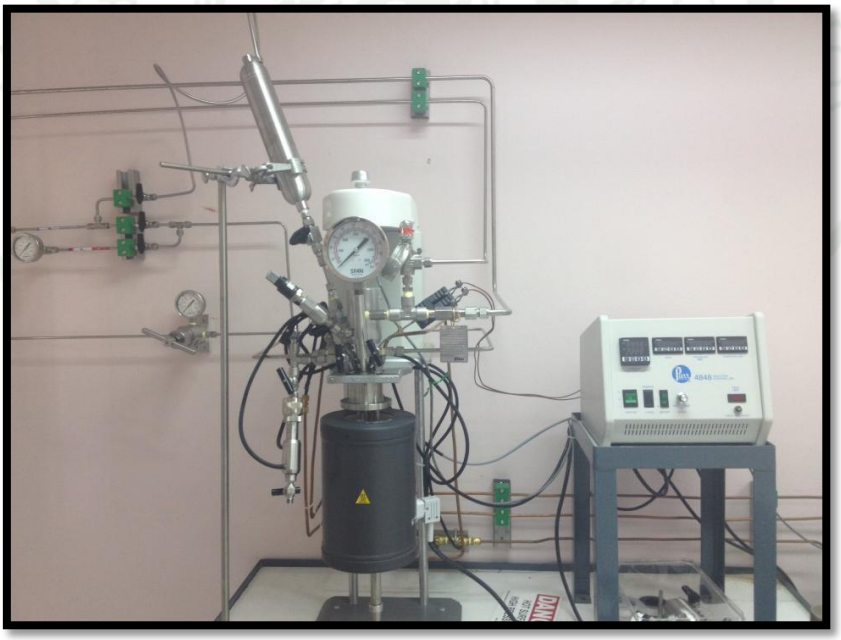
(c)

**Appendix Figure E1** Rare earth catalysts: (a) $Nd_2O_3$, (b) $CeO_2$ and (c) $La_2O_3$

**Appendix F**

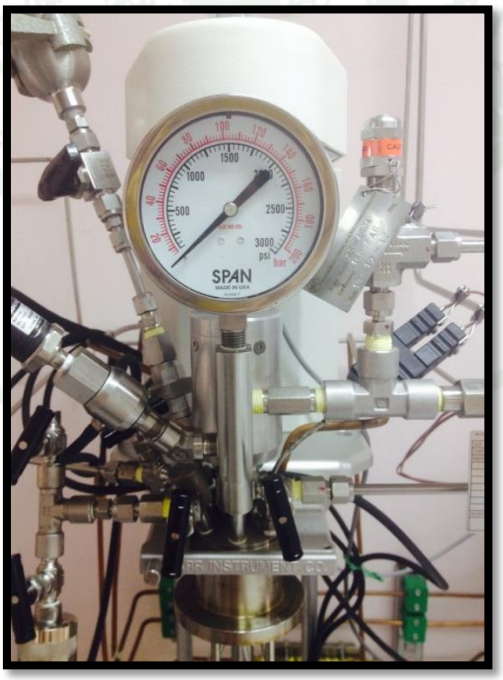
High temperature and pressure batch reactor

**Appendix Figure F1** Overall of high temperature and pressure batch reactor



**Appendix Figure F2** High temperature and pressure batch reactor

**Appendix Figure F3** Four- blade impeller, cooling tube, fine filter thermocouple and pressure sensor




**Appendix Figure F4** Head assembly; gas inlet valve and gas release valve


**Appendix Figure F5** Sampling line

**Appendix Figure F6** Reactor vessel (316 stainless steel)

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