PREPARATION OF BIODIESEL CATALYZED BY ZINC OXIDE NANOPARTICLES

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A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE
OF BACHELOR OF SCIENCE
PROGRAM IN PETROCHEMICAL TECHNOLOGY FACULTY OF SCIENCE
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
2008

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ABSTRACT

In this research, the aim is to study preparation of biodiesel in present of zinc oxide nanoparticles catalyst. Experiments have been performed to determine the optimum condition for preparation of biodiesel catalyzed by zinc oxide nanoparticles. This research has 3 methods of experimental: the reflux method, the microwave method and the hydrothermal method using autoclave. The process variables such as temperature, amount of catalyst and time of reaction, were used for production of methyl ester.

From the experimental results, the percent yield of methyl ester by set reflux method and by microwave oven method were too low and not the suitable condition for production biodiesel from palm oil by transesterification using zinc oxide nanoparticle as a catalyst. However, we have successfully synthesized high percent yield of methyl ester by hydrothermal using autoclave with the optimum condition and the 3 % of nanoparticle zinc oxide (Degussa's brand) was used at temperature 200 degree Celsius and the time of reaction is 8 hour. The percentage of methyl ester is about 99.48%

ACKNOWLEDGEMENT

We would like to express our gratitude to all those who gave us the possibility to complete this special project. We want to thank our adviser Dr. Pesak Rungrojchaipon and Mrs. Sujin Tuntipisitkul whose help, stimulating suggestions and encouragement helped us in all the time of research for and writing of this special project.

We have furthermore to thank the commissions for comment and beneficial suggestions, Assoc.Prof.Dr.Somsak Woramongkolchai and Dr. Samart Kongtaweelert.

We would like to convey our gratitude to Dr. Patchanee Chareanying who identify the samples and guided me in the technique NMR.

We would like to thank the Energy Policy and Planning Office Ministry of Energy for supported us in this special project.

The staff from the Department of Chemistry, KMITL for equipment and helping us to find all item.

We would like to thank the Scientific Instruments Service Centre (SISC) of the Department of Chemistry, KMITL for supported us in my research work. I want to thank them for all their help, facility for laboratory analysis instruments and valuable hints.

Especially, I would like to give my special thanks to my father, mother, family and friends whose love, abet, and support me to complete this work.

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Chapter 1
Introduction

1.1 Background of research

Now a day, crisis about oil in the world is increasing violence, it made a cost of crude oil rising and increasing continuously. Even, amount of reservedly oil is decreasing and effect to economy in domestic and around the world exceedingly. In many times ago, it has many researches to study and develop about a new choice energy which it's significant and kept a close watch on by people around the world. One in all is biodiesel, it is new choice oil and make from transesterification reaction of vegetable oil or animal fats with alcohol.

From the research which popular in many time ago discovered biodiesel has properties about burning not bad from diesel oil petroleum. Biodiesel has many advantages such as high flash point, good lubricant, high cetane number [1], clean burn and little soot because it's lower amount of CO_2,SO_x ,NO_x that release from engine than diesel oil petroleum. So, it's not blocked of exhaust pipe which is a good thing for engine and environment too [2]-[5]. Beside there, it not has sulfur in biodiesel [6], so don't have problem about sulfate. Now, the world's effected to greenhouse effect that make higher temperature and occur natural phenomenon which damage to human and a cost of biodiesel is lower than diesel oil because production process. The composition use vegetable (palm oil) which popular grow in Thailand. Biodiesel production is helping farmer who grow palm tree furthermore, biodiesel can reduce import quantitative from foreign country too. The problem that occur and advantage that got from biodiesel production, it's important to do research in this time.

Since Thailand abounds in agricultural resources, emphasis is placed on producing alternative energy from farm produce available in each locality. In response to His Majesty the King's innovation on alternative energy development, the Ministry of Energy is joining hands with the Ministry of Interior in promoting the efficient use of energy and the production of alternative fuels, such as biodiesel. A target has been set to work out energy plans to cover 80 communities this year in celebration of His Majesty the King's 80th birthday anniversary. The project is expected to save 1,600 million baht a year in domestic energy consumption.

His Majesty the King initiated the production of biodiesel from palm oil in 1985, as a way of applying indigenous means to achieve self-sufficiency in energy. Since then, Thailand has been making progress towards biofuel development, and this initiative has sparked a wave of interest in various sectors of Thai society. His Majesty's innovation on biodiesel from the extraction of palm oil also won the Gold Medal with Mention from Brussels Eureka 2001 in Belgium.

One of the constraints in biodiesel production in Thailand is that palm-planting areas in the country are still limited. So, domestic demand for palm oil is outstripping current production. The Ministry of Energy has decided to adjust its plan to promote biodiesel production on a commercial basis in line with palm production. It earlier planned to produce 8.5 million liters of biodiesel a day by 2012.

At present, Thailand produces 700,000 to 800,000 tonnes of raw palm oil a year. The largest source is in the southern province of Krabi, followed by Surat Thani and Chumphon. Malaysia and Indonesia are now the world's major palm oil producers. Since Thailand has set a policy to promote palm oil as a biofuel source, a target has been set to expand palm plantations to cover 10 million rai, or four million acres, by 2023. Today, palm plantations in Thailand cover only two million rai. It is expected that by the end of 2009, Thailand will be able to produce 1.18 million tonnes of raw palm oil.

A survey conducted by the National Statistical Office shows that the expenditure for energy in each family in Thailand has increased significantly. From 2004 to 2006, energy consumption here rose by 16 percent on average, against 6.9 percent recorded in 2002. As a result, energy expenditure now represents 10 percent of the total costs of each family. So the Ministry of Energy deems it necessary to step up campaigns to promote the efficient use of energy and energy saving. The campaigns must be carried out on a continual basis and in the long run.

In this research, aim is study synthesis biodiesel by use zinc oxide nanoparticle as a base catalyst. From the research at the pass, nanoparticles have special physical and chemical properties such as high surface area that is opportunity to good reaction and transesterification reacton especially [7, 8]. From properties above, we interested in study variable that effect to percent yield of synthesize methyl ester product such as amount of zinc oxide nanoparticles temperature and reaction time to find a suitable state. This research is a based to biodiesel development in indurtry to produce biodiesel compensate petroleum oil fuel efficiently.

1.2 Objective

1. Synthesize biodiesel from palm oil by transesterification process and use nano-zinc oxide as a catalyst.

2. Study variable that effect to amount of methyl ester product which synthesize from transesterification process, such as amount of nano-zinc oxide, temperature and time in the reaction.

1.3 Scope of study

1. Study property of catalyst (nano zinc–oxide) by XRD.

2. Synthesize Biodiesel from palm oil by thansesterification by metal oxide (nano zinc oxide)

3. Obtain the optimum condition of nano zinc oxide using for synthesis of biodiesel.

1.4 Expected result

1. Find the best condition in synthesis of biodiesel from palm oil by transesterification and use nano zinc-oxide as catalyst to produce high efficiency biodiesel.

2. Produce biodiesel from palm oil to increase salaries to farmers.

3. Biodiesel is that it tends to reduce fuel economy. Reduce the capital of Diesel fuel from abroad.

4. Apply the biodiesel production in industry and used in place of petroleum diesel.

5. The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter compared to emissions from diesel fuel.

Chapter 2
Literature review and theory

2.1 Vegetable oil [9]

The most important component for vegetable oil is fatty acid that consists of two groups which are saturated fatty acids and unsaturated fatty acids in difference ratio of two fatty acid groups that make difference properties of vegetable oil.

2.1.1 Fatty acid [10]

In chemistry, especially biochemistry, a fatty acid is a carboxylic acid often with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. Carboxylic acids as short as butyric acid (4 carbon atoms) are considered to be fatty acids, whereas fatty acids derived from natural fats and oils may be assumed to have at least 8 carbon atoms, e.g., caprylic acid (octanoic acid). Most of the natural fatty acids have an even number of carbon atoms, because their biosynthesis involves acetyl-CoA, a coenzyme carrying a two-carbon-atom group Fatty acids are produced by the hydrolysis of the ester linkages in a fat or biological oil (both of which are triglycerides), with the removal of glycerol. Fatty acids are aliphatic monocarboxylic acids, derived from, or contained in esterified form in an animal or vegetable fat, oil or wax. Natural fatty acids commonly have a chain of 4 to 28 carbons (usually unbranched and even numbered), which may be saturated or unsaturated. By extension, the term is sometimes used to embrace all acyclic aliphatic carboxylic acids. This would include acetic acid, which is not usually considered a fatty acid because it is so short that the triglyceride triacetin made from it is substantially miscible with water and is thus not a lipid. Fatty acids can be saturated and unsaturated, depending on double bonds. They differ in length as well.

2.1.1.1 Saturated fatty acids

Saturated fatty acids do not contain any double bonds or other functional groups along the chain. The term "saturated" refers to hydrogen, in that all carbons (apart from the carboxylic acid [-COOH] group) contain as many hydrogens as possible. In other words, the omega (ω) end contains 3 hydrogens (CH_3-), and each carbon within the chain contains 2 hydrogen atoms. Saturated fatty acids form straight chains and, as a result, can be packed together very tightly, allowing living organisms to store chemical energy very densely. The fatty tissues of animals contain large amounts of long-chain saturated fatty acids. In IUPAC nomenclature, fatty acids have an [-*oic* acid] suffix. In common nomenclature, the suffix is usually -*ic*.

The shortest descriptions of fatty acids include only the number of carbon atoms and double bonds in them (e.g., C18:0 or 18:0). C18:0 means that the carbon chain of the fatty acid consists of 18 carbon atoms, and there are no (zero) double bonds in it, whereas C18:1 describes an 18-carbon chain with one double bond in it. Each double bond can be in either a cis- or trans- conformation, and stands in a different position with respect to the ends of the fatty acid; therefore, not all C18:1s (for example) are identical. If there is one or more double bonds in the fatty acid, it is no longer considered saturated, but rather, mono- or polyunsaturated.

2.1.1.2 Unsaturated fatty acids

Unsaturated fatty acids are of similar form, except that one or more alkenyl functional groups exist along the chain, with each alkene substituting a single-bonded " -CH2-CH2-" part of the chain with a double-bonded "-CH=CH-" portion (that is, a carbon double-bonded to another carbon).The two next carbon atoms in the chain that are bound to either side of the double bond can occur in a cis or trans configuration.

A cis configuration means that adjacent hydrogen atoms are on the same side of the double bond. The rigidity of the double bond freezes its conformation and, in the case of the cis isomer, causes the chain to bend and restricts the conformational freedom of the fatty acid. The more double bonds the chain has in the cis configuration, the less flexibility it has. When a chain has many cis bonds, it becomes quite curved in its most accessible conformations. For example, oleic acid, with one double bond, has a "kink" in it, whereas linoleic acid, with two double bonds, has a more pronounced bend. Alpha-linolenic acid, with three double bonds, favors a hooked shape. The effect of this is that, in restricted environments, such as when fatty acids are part of a phospholipid in a lipid bilayer, or triglycerides in lipid droplets, cis bonds limit the ability of fatty acids to be closely packed, and therefore could affect the melting temperature of the membrane or of the fat.

A trans configuration, by contrast, means that the next two hydrogen atoms are bound to opposite sides of the double bond. As a result, they do not cause the chain to bend much, and their shape is similar to straight saturated fatty acids.

In most naturally-occurring unsaturated fatty acids, each double bond has 3n carbon atoms after it, for some n, and all are cis bonds. Most fatty acids in the trans configuration (trans fats) are not found in nature and are the result of human processing (e.g., hydrogenation).

The differences in geometry between the various types of unsaturated fatty acids, as well as between saturated and unsaturated fatty acids, play an important role in biological processes, and in the construction of biological structures.

Table 2.1: Structural Formula, Melting and Boiling Points for Fatty Acids [11]

Fatty Acid	No. of carbons and double bonds	Chemical structure	Melting Point deg C	Boiling Point deg C
Caprylic	C8	CH3(CH2)6COOH	16.5	239
Capric	C10	CH3(CH2)8COOH	31.3	269
Lauric	C12	CH3(CH2)10COOH	43.6	304
Myristic	C14	CH3(CH2)12COOH	58	332
Palmitc	C16:0	CH3(CH2)14COOH	62.9	349
Palmitoleic	C16:1	CH3(CH2)5CH=CH(CH2)7COOH	33	-
Stearic	C18:0	CH3(CH2)16COOH	69.9	371
Oleic	C18:1	CH3(CH2)16COOH	16.3	-
Linoleic	C18:2	CH3(CH2)7CH=CH(CH2)7COOH	-5	-
Linolenic	C18:3	CH3(CH2)2CH=CHCH2CH=CHCH2CH=CH(CH2)7COOH	-11	-
Arachidic	C20:0	CH3(CH2)18COOH 75.2	75.2	-
Eicosenoic	C20:1	CH3(CH2)7CH=CH(CH2)9COOH 23	23	-
Behenic	C22:0	CH3(CH2)20COOH 80	80	-
Eurcic	C22:1	CH3(CH2)7CH=CH(CH2)11COOH	34	-

Table 2.2: Percentage of fatty acid type for different oils [11]

Fatty Acid **Fat or oil**	**C8:0**	**C10:0**	**C12:0**	**C14:0**	**C16:0**	**C16:1**	**C18:0**	**C18:1**	**C18:2**	**C18:3**	**C20:0** **C22:0**	**C20:1** **C22:1**	**Other**
Yellow Grease				1	23	1	10	50	15				
Tallow	-	-	0.2	2-3	25-30	2-3	21-26	31-42	2	-	0.4-1	0.3	0.5
Lard	-	-	-	1	25-30	2-5	12-16	41-51	4-22	-	,	2-3	0.2
Butter	1-2	2-3	4-1	8-13	25-32	2-5	25-32	22-29	3	-	0.4-2	.2-1.5	1-2
Coconut	5-9	4-10	44-51	13-18	7-10	-	1-4	5-8	1-3	-	-	-	-
Palm Kernal	2-4	3-7	45-52	14-19	6-9	0-1	1-3	10-18	1-2	-	1-2	-	-
Palm	-	-	-	1-6	32-47	-	1-6	40-52	2-11	-	-	-	-
Safflower	-	-	-	-	5.2	-	2.2	76.3	16.2	-	-	-	-
Peanut	-	-	-	0.5	6-11	1-2	3-6	39-66	17-38	-	5-10	-	-
Cottonseed	-	-	-	0-3	17-23	-	1-3	23-41	34-55	-	-	2-3	-
Corn	-	-	-	0-2	8-10	1-2	1-4	30-50	34-56	-	-	0-2	-
Sunflower	-	—	-	-	6	-	4.2	18.7	69.3	0.3	1.4	-	-
Soybean	-	-	-	0.3	7-11	0-1	3-6	22-34	50-60	2-10	5-10	-	-
Rapeseed	-	-	-	-	2-5	0.2	1-2	10-15	10-20	5-10	0.9	50-60	-
Linseed	-	-	-	0.2	5-9	-	0-1	9-29	8-29	45-67	-	-	-
Tung	-	-	-	-	-	-	-	4-13	8-15	72-88	-	-	-

2.2 Biodiesel [12]

Biodiesel refers to a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, made by transesterification of vegetable oil or animal fat (tallow), which can be used (alone, or blended with conventional petrodiesel) in unmodified diesel-engine vehicles. Biodiesel is distinguished from the straight vegetable oil (SVO) (sometimes referred to as "waste vegetable oil", "WVO", "used vegetable oil", "UVO", "pure plant oil", "PPO") used (alone, or blended) as fuels in some converted diesel vehicles. "Bio diesel" is standardized as mono-alkyl ester and other kinds of diesel-grade fuels of biological origin are not included.

Biodiesel is a biodegradable and non-toxic alternative fuel produced from new or used vegetable oil that is produced from renewable resources. It can be used in any Diesel engine without modification. Pure biodiesel has the highest BTU content of any alternative fuel. It also has the highest energy balance of any fuel. For every unit of fossil energy needed to produce biodiesel, more than 3 units of energy are gained. As for gasoline and diesel, every one unit put in yields only about one half units. Because biodiesel is made from plant oil or animal fat and not from 40,000,000 year old organic matter, it is renewable. Moreover, the carbon dioxide taken up by plants during photosynthesis helps to mitigate the carbon dioxide emitted from using biodiesel so there is no net carbon introduced to the atmosphere. Compared to diesel fuel, biodiesel emissions are substantially better for the environment and, in turn, better for the health of the environment's inhabitants. Specifically, the emissions of particulate matter, carbon monoxide and total unburned hydrocarbons from biodiesel are each much less than those from petroleum diesel.

2.2.1 Properties

Biodiesel has better lubricating properties than today's lower viscosity diesel fuels. Biodiesel addition reduces engine wear increasing the life of the fuel injection equipment that relies on the fuel for its lubrication, such as high pressure injection pumps, pump injectors (also called unit injectors) and fuel injectors.

The calorific value of biodiesel is about 37.27 MJ/L. This is 9% lower than regular Number 2 petrodiesel. A variation in biodiesel energy density is more dependent on the feedstock used than the production process. Still these variations are less than for petrodiesel. It has been claimed biodiesel gives better lubricity and more complete combustion thus increasing the engine energy output and partially compensating for the higher energy density of petrodiesel.

Biodiesel is a liquid which varies in color - between golden and dark brown - depending on the production feedstock. It is immiscible with water, has a high boiling point and low vapor pressure. *The flash point of biodiesel (>130 °C, >266 °F) is significantly higher than that of petroleum diesel (64 °C, 147 °F) or gasoline (−45 °C, -52 °F). Biodiesel has a density of ~ 0.88 g/cm³, less than that of water.

Biodiesel has a viscosity similar to petrodiesel, the current industry term for diesel produced from petroleum. Biodiesel has high lubricity and virtually no sulfur content, and it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel.

2.3 Process to produced biodiesel [13]

2.3.1 Direct use and blending

The direct use is vegetable oil or animal fats that use as fuel in diesel engine by don't blend with any substance to change the properties. And blending is diesel oil or kerosene that dilute with vegetable oil or animal oil in difference ratio to decrease viscosity. Although this route is economically attractive, it brings serious problems of adjustment as the physical and chemical properties of the vegetable oil, such as high viscosity because presence of free fatty acids and bad cold start properties. The main problems associated to the use of the vegetable oils in natural as combustibles are incomplete combustion, leading to the accumulation of carbon deposits in the motor, and the thickening of the oil as a result of the polymerization of the unsaturated fatty acids.

2.3.2 Microemulsion

Microemulsion is dispersion of fluid particle that suspended in another fluid. It don't dissolve to homogeneous substance and can disperse by decreasing surfactants in type positive and negative charge. The objective of this method is to solve the problem about high viscosity of vegetable oil and animal fats by use solvent such as methanol, ethanol and 1-buthanol in microemulsion. This method can adjust injection to spray vegetable oil or animal fats from injector.

Microemulsions are typically a slightly opaque, opalescent, non-opaque or substantially non-opaque colloidal dispersion that are formed spontaneously or substantially spontaneously when the components are brought into contact with an aqueous medium.

2.3.3 Thermal cracking or pyrolysis

Pyrolysis is a process of thermal cracking, also known as thermal decomposition. This process occurs when organic or carbonaceous material is heated to high temperatures in the absence of air or oxygen. Any Volatile organic Compounds are cracked and subsequently released (vaporized) from the solid state and a carbon char product remains.

2.3.4 Transesterification [14]

Transesterification is reaction of vegetable oils or animal fats with alcohol in the presence of a strong acid or base, producing a mixture of fatty acid alkyl esters and glycerol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed.

2.3.4.1 Transesterification by acid-catalyzed processes [14]

The transesterification process is catalyzed by BrØnsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, tipically, temperatures above 100 °C and more than 3 h to reach complete conversion.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in figure 2.1, 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^+.

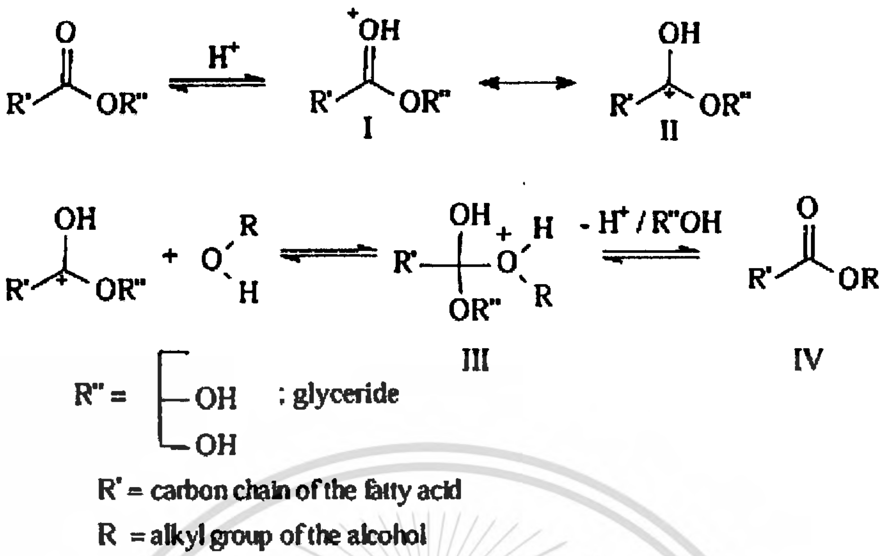


Figure 2.1: Mechanism of the acid-catalyzed transesterification of vegetable oils [14]

2.3.4.2 Transesterification by base-catalyzed processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds but can occur sponification reaction that decrease ester purify. Although transesterification by base-catalyzed process give high percent yield and use short time, but disadvantages are loss energy to occur reaction, hard to recycle glycerol and product will get rid of catalyst.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in figure 2.2. The first step 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. Step two, the alkyl ester and the corresponding anion of the diglyceride are formed. Step 3, the latter deprotonates the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol and converted to a mixture of alkyl esters and glycerol in step 4.

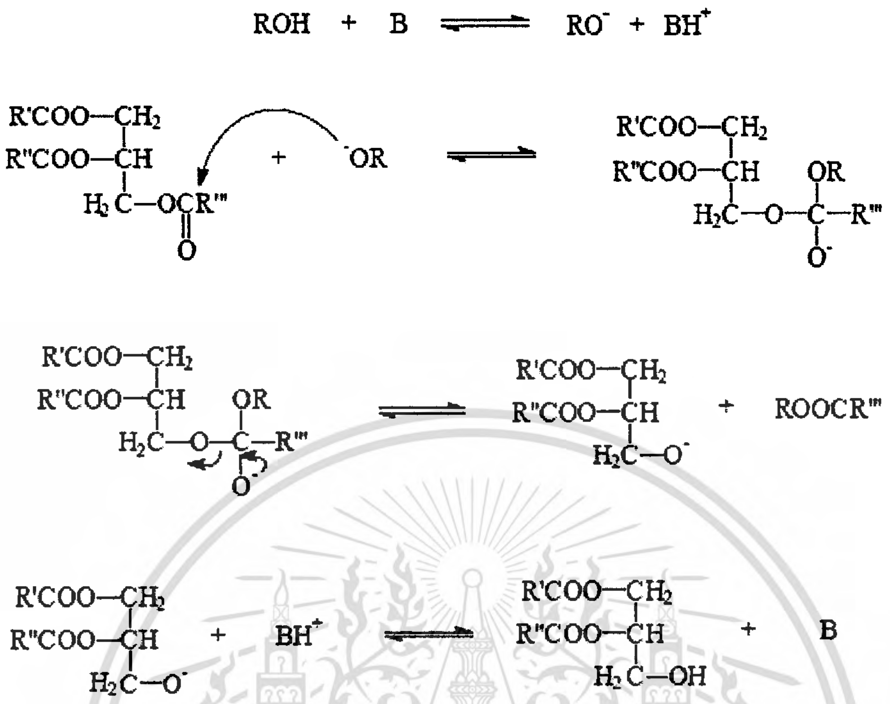


Figure 2.2: Mechanism of the base-catalyzed transesterification of vegetable oils [14]

2.3.4.3 Transesterification by metal oxide catalyst [15]

Metal oxides have been widely used for various applications such as a semiconductor in dye-sensitized solar cell, catalysts, fuel cells, resistors, gas sensors, transparent optical device, optical coating and so on. For a current process of biodiesel production, methanol solution of alkali hydroxide was used as the catalyst. However, it includes some problems like an invites the soap formation and massive wastewater was discharged from the process to wash the dissolved alkali-hydroxide off the produced biodiesel. The acid-catalyzed transesterification is seriously slow as compared to the base-catalyzed one. The transesterification catalyzed by metal oxide is a bright technology for the noble process featuring the fast reaction rate under the mild reacting condition.

Concerning transesterification with methanol using metal oxide catalyst, abstraction of proton from methanol by the basic sites to form methoxide anion is the first step of the reaction. The methoxide anion attacks carbonyl carbon in a molecule of the triglyceride, which leading to formation of the alkoxycarbonyl intermediate. Then, the alkoxycarbonyl intermediate divides into two molecules: FAME and anion of diglyceride in step 2.

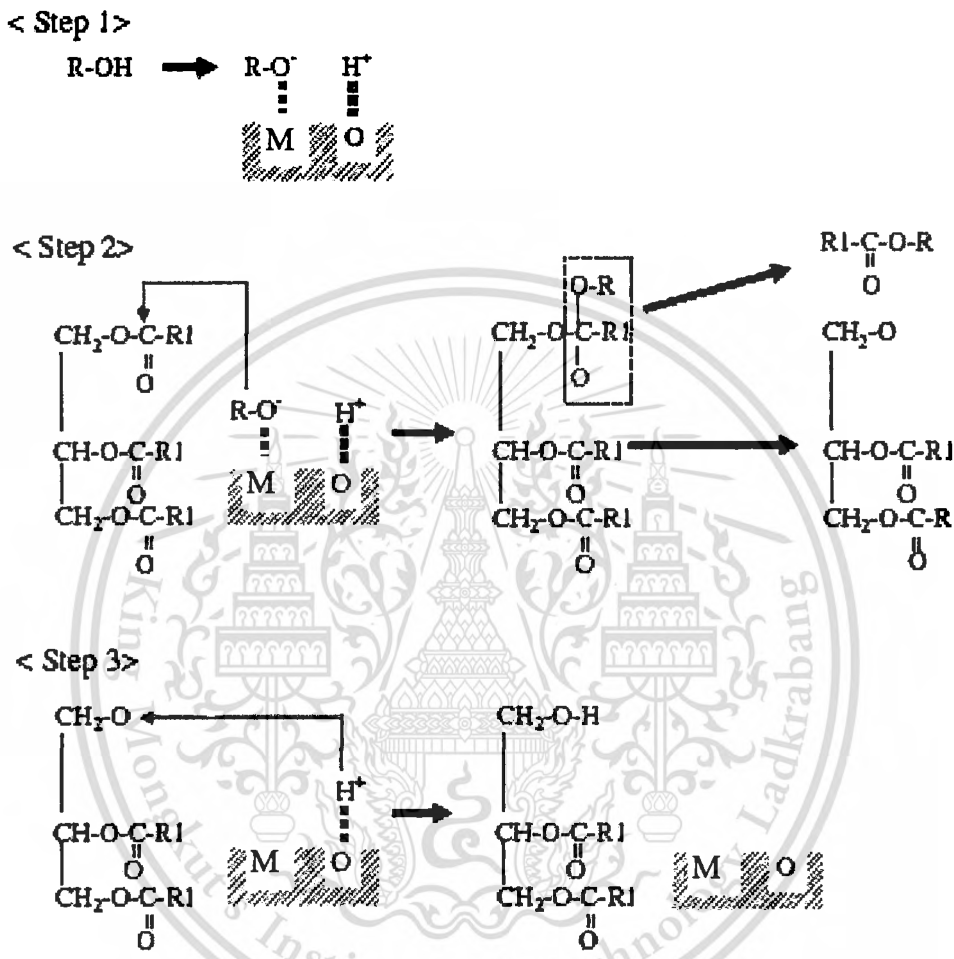
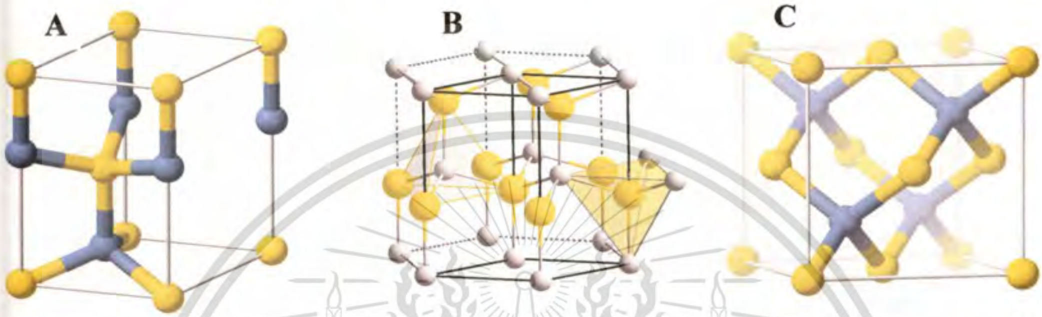


Figure 2.3: Mechanism of the metal oxide catalyst transesterification of vegetable oils [15]

2.3.4.4 Zinc oxide nanoparticle

The outstanding characteristic of nano ZnO lies in nano particle and dual nature both nano material and zinc oxide. Compared with normal zinc oxide, nano zinc oxide has the characteristic of small particle, big surface area and high activity.

Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zincblende, and the rarely observed cubic rocksalt). The wurtzite structure is most stable and thus most common at ambient conditions. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide are tetrahedral. [16]



Unit cell of wurtzite zinc oxide Wurtzite A zincblende unit cell

Figure 2.4: The crystal structure of zinc oxide that A, B and C are unit cell of wurtzite zinc oxide, wurtzite and a zincblende unit cell respectively [16]

The product can be mainly applied as main raw material and auxiliary material in lines of petroleum, chemicals, plastics, shoes, coating, painting, ceramics and pharmaceutical. It can keep the characteristics, enhance resistance to ripping, increasing smoothness, decrease cost and improve the quality of products.

Table 2.3: Advantage and disadvantage of zinc oxide nanoparticle [17, 18]

Advantage	Disadvantage
1. More ecofriendly nature	1. Longer time reaction
2. Easier product separation	2. Lower yield
3. better produce purity since water washes can be eliminated	3. Reactivated catalyst at high temperature (~250°C)
4. Non corrosion	

2.4 Oil that use to produce biodiesel [19]

Generally, biodiesel produce from transesterification reaction of vegetable oil or animal fats with alcohol. The major components of vegetable oils or animal fats are triglycerides which is glyceride in which the glycerol is esterified with three fatty acids. Chain lengths of the fatty acids in naturally occurring triglycerides can be of varying lengths from 10-30 carbon atoms. Chemical and physical properties of each oil are difference following properties of fatty acid composition. Vegetable oil is easy substance to oxidized and occur sticky substance from polymerization reaction at high temperature. It is most common carbon atom composition between 12-18 carbons and different saturated fatty acid. Vegetable oil that has high saturated fatty acid will low iodine value and sticky substance from polymerization reaction in engines. Iodine value derived in 3 groups,

1) Drying oil, iodine value between 160-230 and high polymerization reaction.

2) Semi-drying oil, iodine value between 125-150.

3) Non-drying oil, iodine value lower than 120.

Raw material or feedstocks with potential for biodiesel production in Thailand are following, [20]

1) Palm oil

2) Coconut oil

3) Soy bean oil

4) Ground nut oil

5) Castor oil

6) Sesame oil

7) Sunflower oil

8) Jatropha oil

Table 2.4: Properties and heating value of any vegetable oil [21]

Oil type	Specific gravity (g/mL)	Viscosity (cSt)	Heating value (kJ/kg)
Soy bean oil	0.918	57.2	39,350
Sunflower oil	0.918	60.0	39,490
Coconut oil	0.915	51.9	37,540
Ground nut oil	0.914	67.1	39,470
Palm oil	0.898	88.6	39,550
Palm kernel oil	0.904	66.3	39,720
Jatropha oil	0.915	36.9	39,000
Diesel oil	0.845	3.8	46,800

2.4.1 Palm oil [22]

Palm oil is derived from the flesh of the fruit of the oil palm. It is the second most traded vegetable oil crop in the world, after soy. Palm oil is mostly used to raw material in the manufacture of biodiesel in Thailand because oil palm is a plant with high competitive potential due to its lower costs in production and marketing than other plants. Palm oil is high production capacity more than rape seed that is raw material in Europe 5 times and 10 times for soy bean in America. Due to palm oil is perennial, endure to environment and long harvest to 20 years.

2.4.2 Palm kernel oil [23]

Palm kernel oil is oil which is extracted from the seeds of the oil palm. The fruit which surrounds the seed can also be pressed for oil. Its chemical composition is quite different from that of palm oil, which is obtained from the flesh of the palm fruit. Palm kernel oil is a lauric type, similar to coconut oil. It is extremely high in saturated fats, and low in essential fatty acids.

2.5 Diesel Fuel [24]

Diesel or Diesel fuel in general is any fuel used in diesel engines. The most common is a specific fractional distillate of petroleum fuel oil, but alternatives that are not derived from petroleum, such as biodiesel, biomass to liquid (BTL) or gas to liquid (GTL) diesel, are increasingly being developed and adopted. To distinguish these types, petroleum-derived diesel is increasingly called petrodiesel Ultra-low sulfur diesel (ULSD) is a term used to describe a standard for defining diesel fuel with substantially lowered sulfur contents.

Because of diesel engine have a difference size, so diesel fule must have suitable properties for each diesel engine

2.5.1 Ignition Quality (Cetane Number) [25]

The performance of diesel engines is critically dependent upon the ignition quality of the fuel. The diesel engine relies on the high pressures and temperatures generated during the compression stroke to bring about auto-ignition of the air-fuel mixture. Auto-ignition is defined as the condition when the air-fuel mixture spontaneously ignites without an external source of ignition, such as flame or spark. The tendency of the diesel fuel to ignite under these conditions is known as its ignition quality, which is conveniently expressed in terms of the cetane number. The higher the cetane number, the better the ignition quality. Higher cetane number shortens the ignition delay period, which translates to smoother combustion and thereby optimising the power generated. Cetane number also influences cold start performance, white smoke, engine noise, and emission.

2.5.2 Sulphur Content

Sulphur content of On-Road Diesel Fuel cannot exceed 22 mg/kg after September 1, 2006 and 15 mg/kg after October 15, 2006. These ultra-low sulphur levels are mandated by Federal legislation and required for all 2007 model year vehicles that will be equipped with advanced emission control systems utilizing diesel particulate filters (DPFs) in exhaust systems. High sulphur fuel will be potentially harmful because it will result in premature filter plugging with sulphates.

2.5.3 Lubricity

Lubricity is the ability to reduce friction between two surfaces in relative motion. It is a measure of fuel's effectiveness as a lubricant. Diesel fuel also functions as lubricant in fuel injection equipment such as rotary or distributor- type injection pumps, and injectors. The severe hydro treatment process involved to lower the sulphur content of the diesel fuel to where it is now tends to reduce its natural lubricating properties. Lubricity additives are used to enhance the lubricating property of this severely hydro treated diesel fuel. Industry standards require diesel fuel to provide acceptable performance in accordance with prescribed test methods. Increased wear in the fuel injection system will cause insufficient fuel delivery and will lead to poor engine driveability. In the long term and in extreme cases fuel pumps and injectors will seize and breakdown.

2.5.4 Cloud point

Cloud point is the temperature at which wax crystals begin to form in the fuel. The cloud point temperature of the diesel fuel indicates how well it performs at low temperatures. This property is important because wax crystals can block fuel filters, thus starving the engine of fuel. The industry standard for supplying Diesel Fuel is to ensure the cloud point does not exceed a prescribed temperature for a given half-month period.

2.5.5 Flash point

Flash point is the lowest temperature at which the diesel fuel will start to emit vapour that can be ignited by an external source. Flash point has no direct influence on engine performance, but it is important for safe storage, handling, and transport of diesel fuel. A low flash point fuel can be a fire hazard. In addition, low flash point may provide an indication of contamination with more volatile fuels- such as gasoline.

2.5.6 Viscosity

Viscosity is a measure of a liquid's resistance to flow under pressure and is dependent upon temperature. At higher temperature, the viscosity of the fuel decreases and at lower temperature its viscosity increases. Viscosity of diesel fuel influences engine performance in two ways: injection pump and injector performance, and injected fuel spray pattern and atomization. A very low viscosity fuel can cause internal leakages in the injection pump causing low pressure build up resulting to fuel starvation in the combustion chamber of the engine. This could also lead to undesirable spray pattern that promotes incomplete combustion. Fuel starvation and incomplete combustion will both contribute to reduced power and excessive emission. A very low viscosity fuel also causes excessive wear in the injection system and poor hot re-start.

On the other hand, a very high viscosity fuel will cause poor atomization during injection. As a result, the fuel is not evenly distributed in the combustion chamber to mix well with the air - a requisite for good combustion.

2.5.7 Volatility (Distillation)

The distillation characteristics of a diesel fuel impart an important influence on diesel engine performance. Volatility of the diesel fuel tends to affect power output and fuel economy. A less volatile fuel tends to reduce power output and fuel economy due to poor atomization. A diesel fuel with too high volatility tends to promote vapour lock in the fuel system and unfavourable spray penetration from the injector thereby reducing power output and fuel economy. Distillation characteristics of diesel fuel also influence cold start exhaust smoke and odour.

2.6 Use of Biodiesel [26]

Biodiesel is a clean burning alternative fuel, produced from domestically grown, renewable resources. Biodiesel contains no petroleum products, but can be blended at any concentration with diesel from fossil sources to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modification. Biodiesel is simple to use, biodegradable, non-toxic, and basically free of sulphur compounds and aromatics.

2.7 Advantages of Biodiesel [27]

1. Biodiesel fuel is a renewable energy source that can be made from soy beans grown for fuel, or from cooking oils recycled from restaurants. This means it is a renewable resource unlike petroleum-based diesel.

2. There is an excess production of soybeans in the United States, therefore biodiesel is an economic way to utilize this surplus.

3. Biodiesel is less polluting than petroleum diesel. Compared to petroleum diesel, biodiesel produces less soot (particulate matter), carbon monoxide, unburned hydrocarbons, and sulfur dioxide.

4. The absence of sulfur in 100% biodiesel should extend the life of catalytic converters.

5. Biodiesel fuel can also be used in combination with heating oil to heat residential and industrial buildings. This can reduce dependence on non-renewable and increasingly expensive heating oil.

6. Biodiesel fuel can generally be used in existing oil heating systems and diesel engines without modification, and it can be distributed through existing diesel fuel pumps. This is an advantage over other alternative fuels, which can be expensive to use initially due to high cost of equipment modifications or new purchases. Biodiesel provides almost the same energy per gallon as petroleum diesel.

7. The lubricating effects of the biodiesel may extend the lifetime of engines.

2.8 Disadvantages of Biodiesel [27]

1. Biodiesel is currently about one and a half times more expensive than petroleum diesel fuel. Part of this cost is because the most common source of oil is the soybean, which only is only 20% oil. However, the costs of biodiesel can be reduced by making biodiesel from recycled cooking oils rather than from new soy beans, or by making it from plant matter with higher oil content.

2. Takes energy to produce biodiesel fuel from soy crops, including the energy of sowing, fertilizing and harvesting.

3. Biodiesel fuel can damage rubber hoses in some engines, particularly in cars built before 1994. You should check with the manufacturer before using biodiesel to see if you need to replace any hoses or rubber seals.

4. Biodiesel cleans the dirt from the engine. This dirt then collects in the fuel filter, which can clog it. Clogging occurs most often when biodiesel is first used after a period of operation with petroleum diesel, so filters should be changed after the first several hours of biodiesel use.

5. Biodiesel is not distributed as widely as traditional, petroleum diesel, but distribution infrastructure is improving.

2.9 Instruments

2.9.1 Rotary evaporator [28]

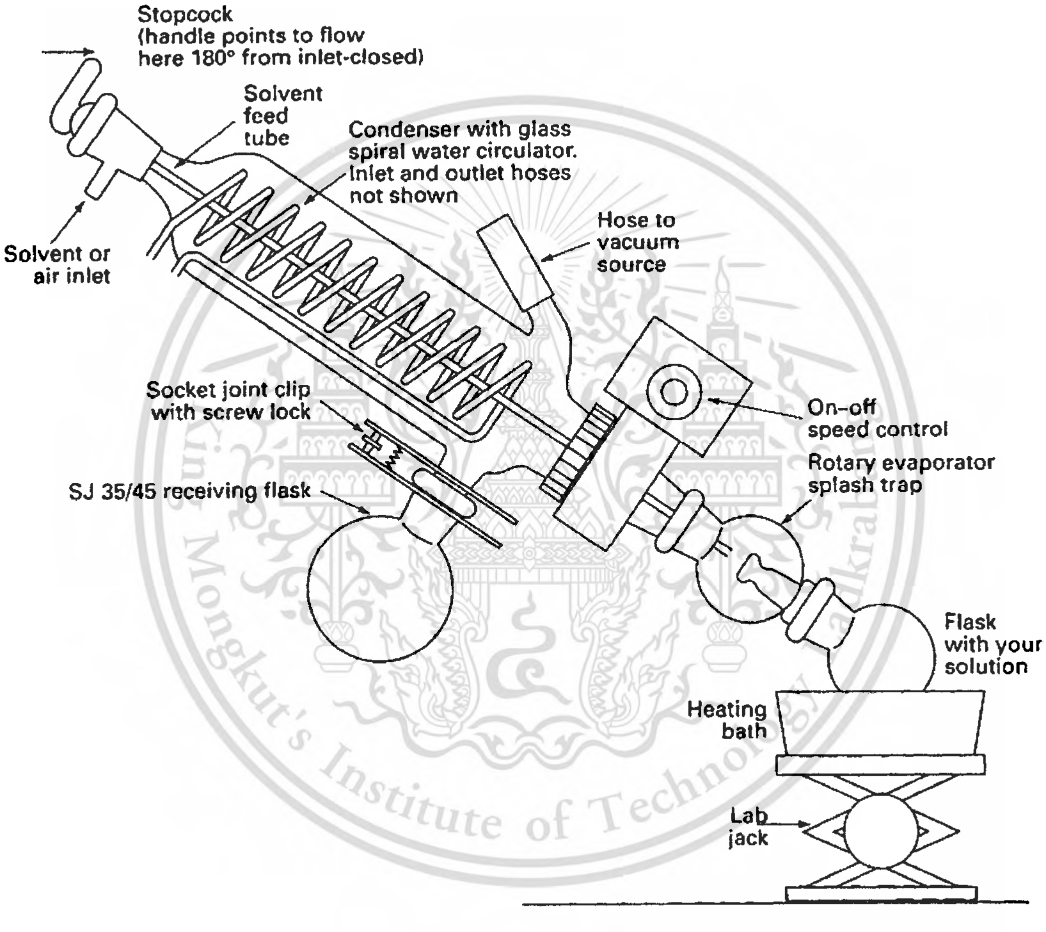


Figure 2.5: Rotary Evaporator [29]

Rotary Evaporator The rotary evaporator is a device for gently and efficiently evaporating solvents from a mixture. It consists of a heated rotating vessel (usually a large flask) which is maintained under a vacuum though a tube connecting it to a condenser. The rotating flask is heated by partial emersion in a hot water bath. The flask's rotation provides improved heat transfer to the contained liquid; the rotation also strongly reduces the occupancy of 'bumps' caused by superheating of the liquid. The solvent vapors leave the flask by the connecting tube and are condensed in the condenser section. The condenser section is arranged so that the condensed vapors drain into another flask where they are collected.

2.9.2 Centrifuge [30]

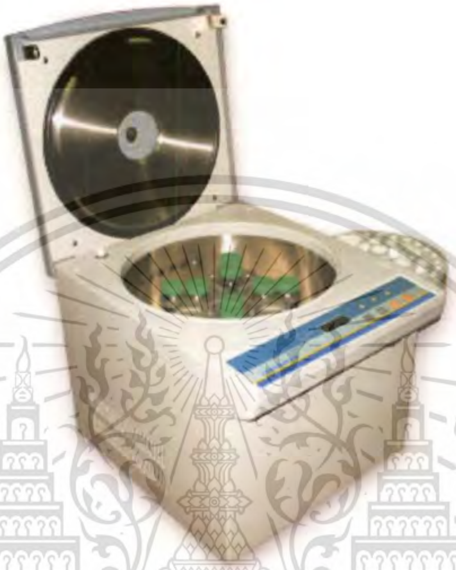


Figure 2.6: Centrifuge [31]

Centrifuge is a piece of laboratory equipment, driven by a motor, which spins liquid samples at high speed. There are two main sizes for laboratory centrifuges. The larger ones are known simply as centrifuges; samples are contained in centrifuge tubes or centrifuge tips. The smaller centrifuges are known as microcentrifuges or microfuges, and microcentrifuge tubes or microfuge tubes are used with them. Like all other centrifuges, laboratory centrifuges work by the sedimentation principle, where the centripetal acceleration is used to separate substances of greater and lesser density.

2.9.3 NMR (Nuclear magnetic resonance spectroscopy) [32]

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is the name given to a technique which exploits the magnetic properties of certain nuclei. This phenomenon and its origins are detailed in a separate section on nuclear magnetic resonance. The most important applications for the organic chemist are proton NMR and carbon-13 NMR spectroscopy.

In principle, NMR is applicable to any nucleus possessing spin. Many types of information can be obtained from an NMR spectrum. Much like using infrared spectroscopy to identify functional groups, analysis of a 1D NMR spectrum provides information on the number and type of chemical entities in a molecule. The impact of NMR spectroscopy on the natural sciences has been substantial. It can, among other things, be used to study mixtures of analysts, to understand dynamic effects such as change in temperature and reaction mechanisms, and is an invaluable tool in understanding protein and nucleic acid structure and function. It can be applied to a wide variety of samples, both in the solution and the solid state.

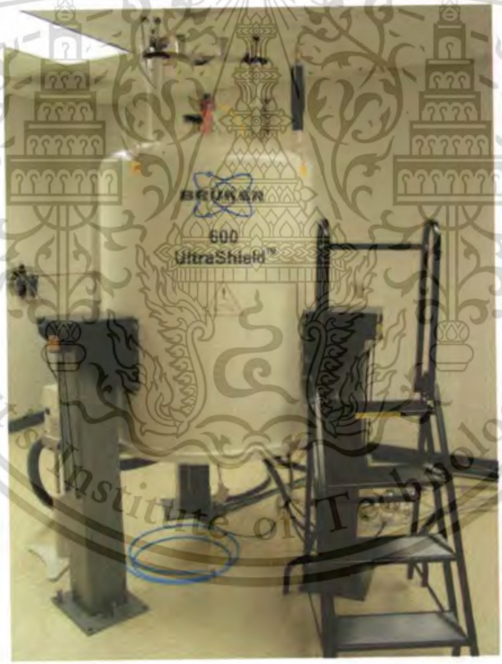


Figure 2.7: Nuclear magnetic resonance spectroscopy [33]

Basic NMR techniques

When placed in a magnetic field, NMR active nuclei (such as 1H or 13C) absorb at a frequency characteristic of the isotope. The resonant frequency, energy of the absorption and the intensity of the signal are proportional to the strength of the magnetic field. For example, in a 21 tesla magnetic field, protons resonate at

900 MHz. It is common to refer to a 21 T magnet as a 900 MHz magnet, although different nuclei resonate at a different frequency at this field strength.

2.9.4 Fourier Transform Infrared Spectroscopy (FT-IR) [34]

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

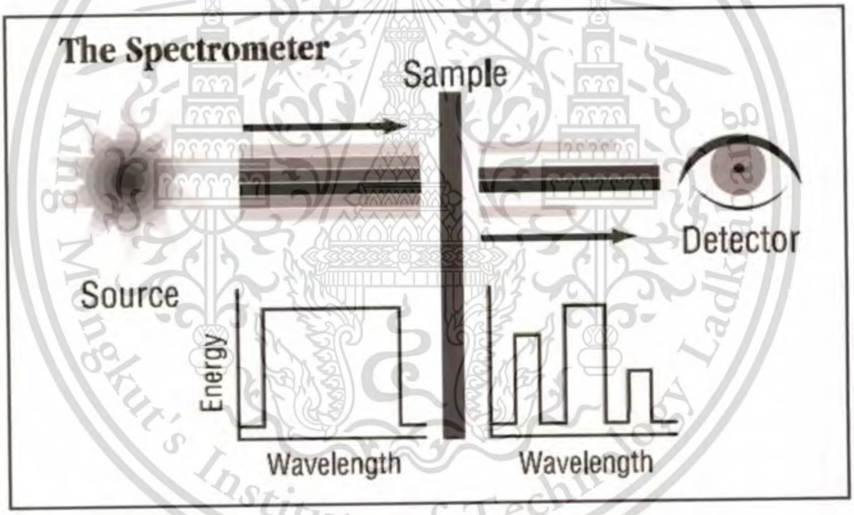


Figure 2.8: Fourier Transform Infrared Spectroscopy [34]

2.10 Literature Review

Ngamcharussrivichai, C. et.al. [35] reported transesterification of palm kernel oil with methanol over mixed oxides of Ca and Zn has beeninvestigated batchwise at 60 °C and 1 atm. CaO-ZnO catalysts were prepared via a conventional co-precipitation of the corresponding mixed metal nitrate solution in the presence of a soluble carbonate saltat near neutral conditions. The catalysts were characterized by using techniques of X-ray diffraction (XRD), scanning electron microscope (SEM), and thermogravimetric analysis (TGA). The results indicatedthat the mixed oxides possess relatively small particle sizes and high surface areas, compared to pure CaOand ZnO. Moreover, the combination of Ca and Zn reduced the calcination temperature required for decomposition of metal carbonate precipitates to active oxides. Influences of Ca/Zn atomic ratio in the mixed oxide catalyst, catalyst amount, methanol/oil molar ratio, reaction time, and water amount on the methyl ester (ME) content were studied. Under the suitable transesterification conditions at 60 °C (catalyst amount = 10 wt. %, methanol/oil molar ratio = 30, reaction time = 1 h), the ME content of >94%can be achieved over CaO-ZnO catalyst with the Ca/Zn ratio of 0.25. The mixed oxide can be also applied to transesterification of palm olein, soybean, and sunflower oils. Furthermore, the effects of different regeneration methods on the reusability of CaO-ZnO catalyst were investigated

Wang, Y. et.al. reported the transesterification of soybean oil to biodiesel using CaO as a solid base catalyst [36] and transesterification of soybean oil to biodiesel using SrO as a solid base catalyst [37]. In the first study they used CaO as a solid base catalyst for the transesterification of soybean oil to biodiesel. The reaction mechanism was proposed and the separate effects of the molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and water content were investigated. The experimental results showed that a 12:1 molar ratio of methanol to oil, addition of 8% CaO catalyst, 65 ºC reaction temperature and 2.03% water content in methanol gave the best results, and the biodiesel yield exceeded 95% at 3 h. The catalyst lifetime was longer than that of calcined $K_2CO_3/\gamma\text{-}Al_2O_3$ and $KF/\gamma\text{-}Al_2O_3$ catalysts. CaO maintained sustained activity even after being repeatedly used for 20 cycles and the biodiesel yield at 1.5 h was not affected much in the repeated experiments. In the second study they used SrO as a solid base catalyst for transesterification of soybean to biodiesel. The reaction mechanism was proposed and the separate effects of reaction temperature, molar ratio of methanol to oil, mass ratio of catalyst to oil and repeated experiments were investigated. The results showed that the yield of biodiesel produced with SrO as a catalyst was in excess of 95% at temperatures below 70°C within 30 min. SrO had a long catalyst lifetime and could maintain sustained activity even after being repeatedly used for 10 cycles. The results proved that transesterification of soybean oil to biodiesel using SrO as a catalyst is a commercially viable way to decrease the costs of biodiesel production.

Dossin, T. et.al. [38] reported Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. A heterogeneous magnesium oxide catalyst is a good alternative for homogeneous catalysts for the transesterification of alkyl esters for the production of fine-chemicals as well as for the production of biodiesel. The transesterification of ethyl acetate with methanol was used as a model reaction to simulate fine-chemical production in a batch slurry reactor at industrial conditions. The transesterification of triolein with methanol to methyl oleate was chosen to simulate continuous production of biodiesel from rapeseed oil. A kinetic model based on a three-step 'Eley–Rideal' type of mechanism in the liquid phase was used in both process simulations. The transesterification reaction occurs between methanol adsorbed on a magnesium oxide free basic site and ethyl acetate or the glyceride from the liquid phase. Methanol adsorption is assumed to be rate-determining in both processes. Activity coefficients were required to account for the significant non-ideality of the reaction mixture in the simulations of both processes. The simulations indicate that a production of 500 tones methyl acetate per year can be reached at ambient temperature in a batch reactor of 10 m^3 containing 5 kg of MgO catalyst, and that a continuous production of 100,000 tones of biodiesel per year can be achieved at 323 K in a continuous stirred reactor of 25 m^3 containing 5700 kg of MgO catalyst. Although various assumptions and simplifications were made in these explorative simulations the assumptions concerning the reaction kinetics used, the results indicate that for both processes a heterogeneous magnesium oxide catalyst shows promising potential as a viable industrial scale alternative.

Verkade, J. et.al. [39] reported room – temperature conversion of soybean oil and poultry fat to Biodiesel catalyzed by nanocrystalline calcium oxides. A promising route for the production of biodiesel (fatty acid methyl ester, FAMES) via transesterification of soybean oil (SBO) and poultry fat with methanol in quantitative conversion at room temperature has been developed using nanocrystalline calcium oxide as catalyst. Under the same conditions, laboratory–grade CaO gave only 2% conversion in the case of SBO, and there was no observable reaction with poultry fat. The soybean oil/methanol ratio in their protocol is 1:27. With their most active catalyst, deactivation was observed after eight cycles with SBO and after three cycles with poultry fat. Deactivation may be associated with one or more of following factors: the presence of organic impurities or adventitious moisture and enolate formation by the deprotonation of the carbon alpha to the carboxy group in the triglyceride or FAMES. The biodiesel from their protocol meets the ASTM D-874 standard for sulfated ash for both substrates.

Songpol Prommoon. et.al. [40] This project is studying of optimization of biodiesel production by transesterification process using microwave irradiation with bath experiment and continues experiment. The essential part of the process is the transesterification of the used refined palm oil with methanol, in the presence of sodium hydroxide catalyst. Experiment vary 3 variable are (1) 0.3% ,0.4% ,0.5% concentration of sodium hydroxide catalyst (2) 100% 200% ,300% excess anhydrous alcohol (3) Low (20%), Medium-Low (30%),medium(50),Medium-High(70%),High(100%) of exist power.

Yield of biodiesel at Low (20%), High (100%) of exist power are not good condition on account of low temperature and high temperature. The optimum of batch system is: 0.4% NaOH catalyst (dissolve in methanol) base of the stoichiometric amount of required methanol and microwave irradiation at Medium-Low (30%) of exit power 800 watt. The optimum of continuous system is : 0.5% NaOH catalyst and 200% excess of the stoichiometric amount of required methanol and microwave irradiation at Medium-High(70%) of exist power of 800 watt.

Shuli Yan, et.al. [41] reported a single-step method was developed for biodiesel production from unrefined or waste oils using a series of heterogeneous zinc and lanthanum mixed oxides. Effects of metal oxide molar ratio, free fatty acids (FFA) and water content in feedstock, molar ratio of methanol and oil, and reaction temperature on the yield of biodiesel were investigated. A strong interaction between Zn and La species was observed with enhanced catalyst activities. Lanthanum promoted zinc oxide distribution, and increased the surface acid and base sites. The catalyst with 3:1 ratio of zinc to lanthanum was found to simultaneously catalyze the oil transesterification and fatty acid esterification reactions, while minimizing oil and biodiesel hydrolysis. A reaction temperature window of 170–220 8C was found for the biodiesel formation. A high yield (96%) of fatty acid methyl esters (FAME) was obtained within 3 h even using unrefined or waste oils.

Chapter 3
Experimental details

3.1 Apparatus

1) Transform Nuclear Magnetic Resonance (NMR), BRUKER Advance DPX 300 frequency 300Hz
2) Fourier Transform Infrared, Perkin Elmer, Pyris 1TGA
3) Hot plate and stirrer, IKA C-MAG HS 7
4) Teflon-line autoclave
5) Variable speed centrifuge, Centurion scientific LTD. 1000 series
6) High Temperature oven,
7) Microwave oven, Samsung MW83Z_Y 850 watt
8) 3- neck Round bottom flask
9) Condenser
10) Cylinder
11) Volumetric flask
12) Stirring rod
13) Magnetic stirrer
14) Thermometer
15) Beaker
16) Separator funnel
17) Pipet
18) Buret
19) Spoon
20) Vial

3.2 Chemical

1) Zinc oxide nanoparticle (Zonop's brand: Type A, and Degussa's brand: Type B)
2) Palm oil (Morrakot's brand)
3) Methanol 99.99 % (CH_3OH) Analytical reagent grade, Fisher scientific
4) Ethanol 99.8 % (C_2H_5OH) Analytical reagent grade, Fisher scientific
5) Sodium hydroxide (NaOH) Analytical reagent grade, Rankem
6) Potassium hydroxide (KOH)
7) Phenolphthalein
8) Potassium hydrogen phthalate (KHP)

3.3 Experimental

3.3.1 Preparation nano zinc oxide catalyst

Before the nano zinc oxide was used as a catalyst, it was pretreated by calcinations in furnace at 600°C for 4 hours to eliminated impurity and moisture (Figure 3.1). Then, it was kept at isotemp vacuum oven (Figure 3.2). The ZnO particle was analyzed by XRD, SEM and FT-IR.

Figure 3.1: Calcinations nano zinc oxide in furnace at 600°C

Figure 3.2: Isotemp vacuum oven

3.3.2 Analysis free fatty acid by AOCS Ca 5a-40 method

Table 3.1: Volume of free fatty acid, methanol and concentration of sodium hydroxide in used

Free fatty acid (%)	Oil (g)	Methanol(ml)	NaOH (N)
0.00-0.2	56.4 ± 0.2	50	0.1
0.2-1.0	28.2 ± 0.2	50	0.1
1.0-30.0	7.05 ± 0.05	75	0.25
30.0-50.0	7.05 ± 0.05	100	0.25 or 1.0
50.0-100	3.525 ± 0.001	100	1.0

According to literature review, the palm oil must have free fatty acid less than 2.5% [42], thus we will used free fatty acid at the period 1.0-30% for preparation of 0.25 N. sodium hydroxide.

First, 0.25 N. sodium hydroxide solution was prepared and determined the exact concentration. Then, it was titrated with standard 0.25 N. solutions of Potassium hydrogen phthalate which phenolphthalein was used as indicator. Next, 7.05 g palm oil was weighed and poured into 250 ml volumetric flask. Then, 75 ml methanol and 2 ml phenolphthalein was added. Finally, the mixture was titrated with sodium hydroxide that determines exact concentration and the volume of sodium hydroxide that use to titrate was recorded for calculate free fatty acid.

3.3.3 Synthesis biodiesel (methyl ester) by reflux method [35, 36]

First step, palm oil was weighed 50 g and poured into 3- neck round bottom flask, the reflux equipment was set (connect condenser, 3- neck round bottom flask and thermometer) (Figure 3.3) and heat until 60°C. Next, 1.5 g zinc oxide nanoparticle was mixed with 21 g methanol, then poured into 3-neck round bottom flask and heat until 1 hour. When the reaction finished, the mixture was heated to evaporate methanol. Then, the catalyst was separated by centrifuge (Figure 3.4) from the mixture and separated in two layers. Finally, the upper layer (triglyceride) was analyzed by ^{1}H-NMR. The experiment was repeated by using each parameter from the Table 3.2.

Figure 3.3: Set of reflux equipment

Figure 3.4: Separate catalyst by centrifuge

Table 3.2: Experimental parameter by reflux method

Catalyst	**Molar ratio of oil to methanol**	**%catalyst (%wt oil)**	**Reaction time (hr.)**	**Temperature (°C)**
ZnO (Type A)	1:12	3%	1	60
	1:12	6%	3	60
	1:12	9%	6	60
	1:12	3%	1	60
	1:12	6%	3	60
	1:12	9%	6	60
ZnO (Type B)	1:12	3%	1	60
	1:12	6%	3	60
	1:12	9%	6	60
	1:12	3%	1	60
	1:12	6%	3	60
	1:12	9%	6	60

3.3.4 Synthesis biodiesel (methyl ester) by microwave Oven [40]

First step, 0.15 g ZnO nanoparticle (3% weight oil), 2.1 g methanol and 5 g palm oil was weighed, and mixed well in glass vial. Then, the mixture was heated in microwave oven (850 watt) until 8 minutes (temperature about 200°C). When the process was finished, the mixture was separated catalyst by centrifuge and the methyl ester layer (upper layer) was analyzed by ^{1}H-NMR. The experiment was repeated by using each parameter from the Table 3.3.

Table 3.3: Experimental parameter by microwave oven

Catalyst	**Molar ratio of oil to methanol**	**%catalyst (%wt oil)**	**Reaction time (min.)**	**Temperature (°C)**
ZnO (Type A)	1:12	3%	8	200
	1:12	6%	8	200
	1:12	9%	8	200
ZnO (Type B)	1:12	3%	8	200
	1:12	6%	8	200
	1:12	9%	8	200

3.3.5 Synthesis biodiesel (methyl ester) by hydrothermal using autoclave [41]

First step, 0.15 g ZnO nanoparticle (3% weight oil), 2.1g methanol and 5 g palm oil was weighed, and mixed well in Teflon-line. Then, Teflon-line autoclave equipment was set (Figure 3.5) and heated in the oven (Figure 3.6) at 200°C until 2 hours. When the process was finished, the mixture was separated catalyst by centrifuge. Finally, the methyl ester layer (upper layer) was analyzed by ^{1}H-NMR. The experiment was repeated by use each parameter from the Table 3.4.

Figure 3.5: Teflon-line auto clave

Figure 3.6: Heat Teflon-line autoclave in high temperature oven

Table 3.4: Experimental parameter by hydrothermal using autoclave

Catalyst	Molar ratio of oil to methanol	%catalyst (%wt oil)	Reaction time (hr.)	Temperature (°C)
ZnO (Type A)	1:12	3	2	200
	1:12	3	4	200
	1:12	3	8	200
	1:12	3	24	200
	1:12	6	2	200
	1:12	6	4	200
	1:12	6	8	200
	1:12	6	24	200
	1:12	9	2	200
	1:12	9	4	200
	1:12	9	8	200
	1:12	9	24	200
ZnO (Type B)	1:12	3	2	200
	1:12	3	4	200
	1:12	3	8	200
	1:12	3	24	200
	1:12	6	2	200
	1:12	6	4	200

Table 3.4: Experimental parameter by hydrothermal using autoclave (continue)

Catalyst	Molar ratio of oil to methanol	%catalyst (%wt oil)	Reaction time (hr.)	Temperature (°C)
ZnO (Type B)	1:12	6	8	200
	1:12	6	24	200
	1:12	9	2	200
	1:12	9	4	200
	1:12	9	8	200
	1:12	9	24	200

Chapter 4
Results and Discussion

In this research, we study about the synthesis of biodiesel (methyl ester) from palm oil with methanol by using zinc oxide nanoparticles as a solid-catalyst which divided into 5 parts. First, the free fatty acid of palm oil was analyzed by AOCS Ca 5a-40 standard method. Then, zinc oxide nanoparticle that used for catalyst in this experiment was characterized by XRD, SEM, and FTIR. Next, methyl ester from palm oil was synthesized by reflux method and the parameter such as catalyst types, the amount of catalyst and reaction time was investigated. The same parameter for preparation of methyl ester synthesized by the reflux method was also used by microwave oven, and by hydrothermal using autoclave.

4.1 Analysis free fatty acid of palm oil before synthesize biodiesel

The amount of free fatty acid in oil is an important factor that affects the percent yield of biodiesel. If amount of free fatty acid of oil was used to synthesis biodiesel is more than 2.5%, the yields are decreasing. Mostly products are soap and water due to sponification reaction follows the equation [42]

The amount of free fatty acid was shown in lauric acid due to most vegetable oils consist of free fatty acid in lauric acid form and shown in palmatic acid due to use palm oil in this experiment.

In this experiment, free fatty acids of palm oil were analyzed by AOCS Ca 5a-40 standard method which determined the exact concentration of sodium hydroxide and titrate with oil. The results were shown in Table 4.1.

Table 4.1: The amount of free fatty acid in lauric and plamitic acids

Weight of oil (g)	**NaOH (ml)**	**Free fatty acid (%)**	
		Lauric acid	**Plamatic acid**
7.04	0.5	0.36	0.46
7.07	0.6	0.43	0.55
7.06	0.6	0.43	0.55
Average		0.40	0.52

The amount of free fatty acid of palm oil was used in this experiment to produce biodiesel is lower than 2.5%.

4.2 Analysis zinc oxide nanoparticle (Type A and Type B)

There are two brands of zinc oxide nanoparticle which were analyzed by x-ray diffraction (XRD) and scanning electron microscope (SEM) following to the Figure 4.1 and 4.2, respectively.

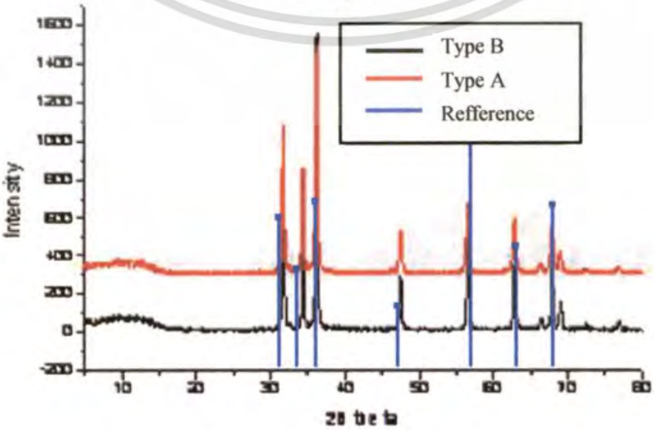


Figure 4.1: Comparison XRD results of ZnO Type A and Type B

The XRD results were shown in Figure 4.1, a peak of ZnO Type B is in black, ZnO Type A is in red and the ZnO reference is in blue. The XRD results of both ZnO are well agreement with ZnO reference peaks.

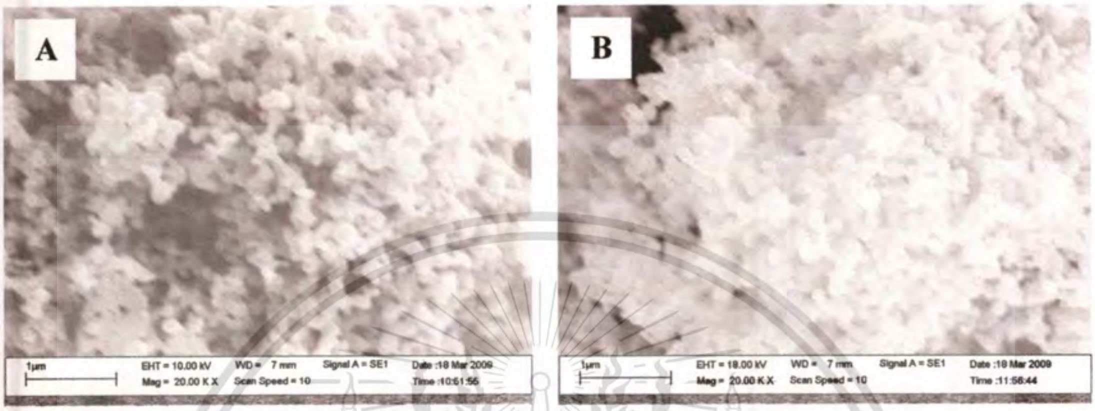


Figure 4.2: SEM of ZnO Type A (A) and Type B (B) with particle size ~200 ± 0.019 nm and ~150 ± 0.018 nm respectively

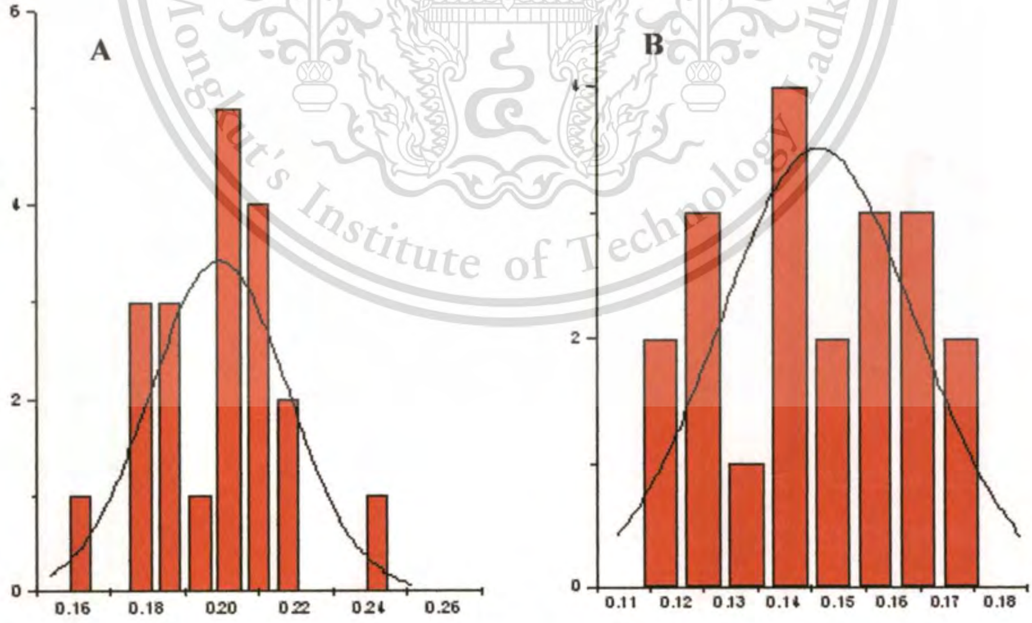


Figure 4.3: Histogram of particle size of ZnO Type A (A) plot of the distribution diameter of growth ZnO nanoparticle with the average diameter about 200 ± 0.019 nm whereas ZnO Type B (B) plot of the distribution diameter of growth ZnO nanoparticle with the average diameter about 150 ± 0.018 nm.

The morphology of ZnO Type A and Type B obtained from SEM which shown in Figure 4.2, both of ZnO Type A and ZnO Type B are globular in shape which particle sizes reported by program ImageJ at approximately 200±0.019 nm and 150±14.098 nm, respectively. Regarding to Figure 4.3, the results presented average diameters of ZnO Type A and Type B.

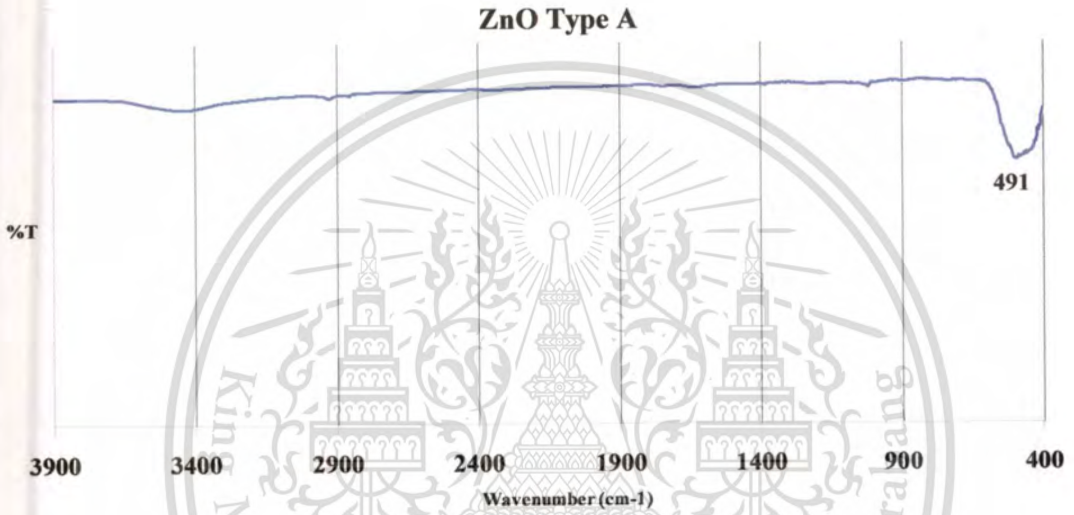


Figure 4.4: FT-IR spectrum of ZnO Type A

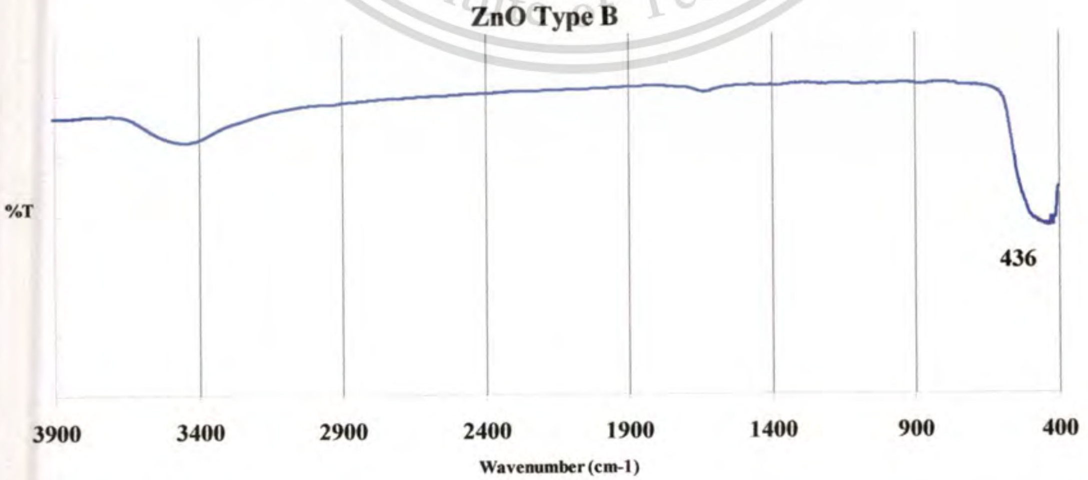


Figure 4.5: FR-IR spectrum of ZnO Type B

According to Figure 4.4 and 4.5, the FT-IR spectra of ZnO Type A and Type B after calcinations in furnace at 600ºC for 4 hours was eliminated impurity and moisture. Absorption bands near 3400 cm^{-1} represent O-H stretching mode and between 400-500 cm^{-1} represent Zn-O.

4.3 The result of yield of methyl ester by reflux method

Methyl ester was synthesized by mixed 50 g palm oil with 21 g methanol (12:1 methanol to oil) on ZnO catalyst which varies parameter following to the Table 4.2. [35,36]

Table 4.2: Parameter of catalyst types, amount of catalyst and reaction time that affect to percent yield of methyl ester for reflux method.

Catalyst	Molar ratio of oil to methanol	%catalyst (%wt oil)	Reaction time (hr.)	Temperature (°C)	% yield methyl ester
ZnO (Type A)	1:12	3%	1	60	N/A
	1:12	6%	3	60	N/A
	1:12	9%	6	60	N/A
	1:12	3%	1	60	N/A
	1:12	6%	3	60	N/A
	1:12	9%	6	60	N/A
ZnO (Type B)	1:12	3%	1	60	N/A
	1:12	6%	3	60	N/A
	1:12	9%	6	60	N/A
	1:12	3%	1	60	N/A
	1:12	6%	3	60	N/A
	1:12	9%	6	60	N/A

From Table 4.2, the percent yields of methyl ester were not available. Due to zinc oxide is not activated, low temperature and reaction time were poor condition for transesterification reaction of palm oil with zinc oxide at a solid-catalyst. Even though we increased the temperature and reaction time, the percent yields of methyl ester still can not be detect by NMR.

4.4 The result of yield of methyl ester by microwave oven

Methyl ester was synthesized by mixed 5 g palm oil with 2.1 g methanol (12:1 methanol to oil) on ZnO catalyst which varies parameter follow the Table 4.3, [40]

Table 4.3: Parameter of types and amount of catalyst that affect to percent yield of methyl ester for microwave oven

Catalyst	**Molar ratio of oil to methanol**	**%catalyst (%wt oil)**	**Reaction time (min.)**	**Temperature (°C)**	**% yield of methyl ester**
ZnO (Type A)	1:12	3%	8	200	0.00
	1:12	6%	8	200	1.15
	1:12	9%	8	200	0.77
ZnO (Type B)	1:12	3%	8	200	0.00
	1:12	6%	8	200	0.23
	1:12	9%	8	200	0.05

From Table 4.3, plot graph between amounts of catalyst versus percent yield of methyl ester in each catalyst types follow the Figure 4.6,

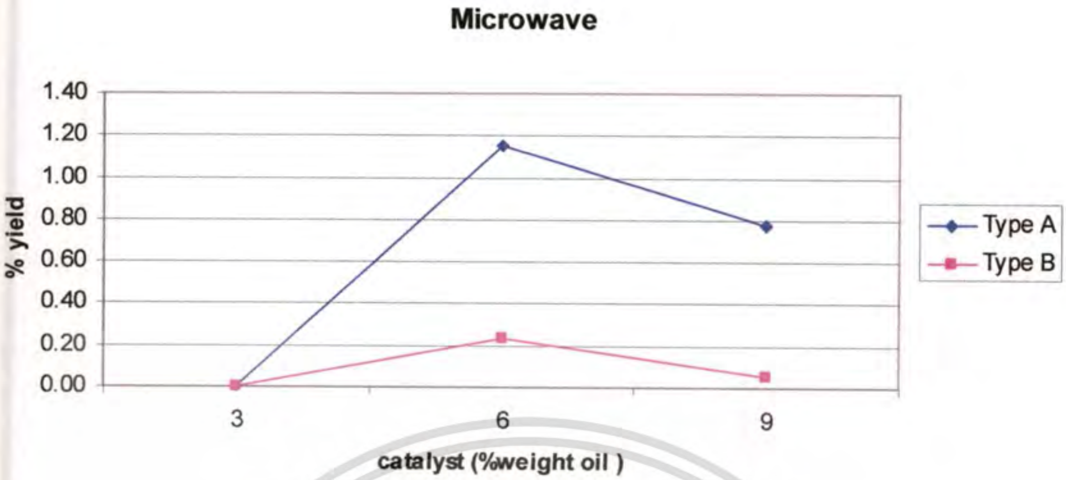


Figure 4.6: Relation between amounts of catalyst versus percent yield of methyl ester

According to Figure 4.6, the relation between amount of catalyst versus percent yield of methyl ester of ZnO Type A and Type B. The results of percent yield of methyl ester are 0.00, 1.15 and 0.77 at Type A catalyst 3%, 6% and 9% respectively whereas percent yield of methyl ester of Type B catalyst at 3%, 6% and 9% are 0.00, 0.23 and 0.05. When we increased the amount of catalyst, normally percent yield of methyl ester will be increased, however, at the parameter of 9% weights oil for both Type A and Type B catalyst the percent yield of methyl ester were decrease. In this method the sample was heated for 8 minutes (~200°C) using commercial microwave with energy 800 watt, and the sample reacted at high temperature with low reaction time. However, the microwave oven can not control the temperature constant. In this project, the reaction was performed more than 8 minutes. Therefore, the bottle may have a chance to burst because they did not design for high temperature and the amount of methanol may evaporate during this process. In the result, the percent yields of methyl ester were so small and we decided that this method would not suitable for us.

4.5 The result of yield of methyl ester by hydrothermal method using autoclave

Methyl ester was synthesized by mixed 5 g palm oil with 2.1 g methanol (12:1 methanol to oil) on ZnO catalyst which varies parameter follow the Table 4.4, [41]

Table 4.4: Parameter of types, amount of catalyst and reaction time that affect to percent yield of methyl ester for hydrothermal method using autoclave

Catalyst	Molar ratio of oil to methanol	%catalyst (%wt oil)	Reaction time (hr.)	Temperature (°C)	% yield methyl ester
ZnO (Type A)	1:12	3	2	200	7.41
	1:12	3	4	200	51.00
	1:12	3	8	200	94.82
	1:12	3	24	200	88.35
	1:12	6	2	200	6.63
	1:12	6	4	200	76.52
	1:12	6	8	200	92.10
	1:12	6	24	200	97.44
	1:12	9	2	200	14.76
	1:12	9	4	200	75.29
	1:12	9	8	200	97.63
	1:12	9	24	200	96.98
ZnO (Type B)	1:12	3	2	200	8.15
	1:12	3	4	200	4.84
	1:12	3	8	200	99.48
	1:12	3	24	200	88.66
	1:12	6	2	200	7.81
	1:12	6	4	200	68.45
	1:12	6	8	200	96.83
	1:12	6	24	200	98.46
	1:12	9	2	200	11.56
	1:12	9	4	200	74.14
	1:12	9	8	200	85.98
	1:12	9	24	200	93.37

From Table 4.4, plot graph between reaction times versus percent yield methyl ester in each amount of catalyst follows the Figure 4.7,

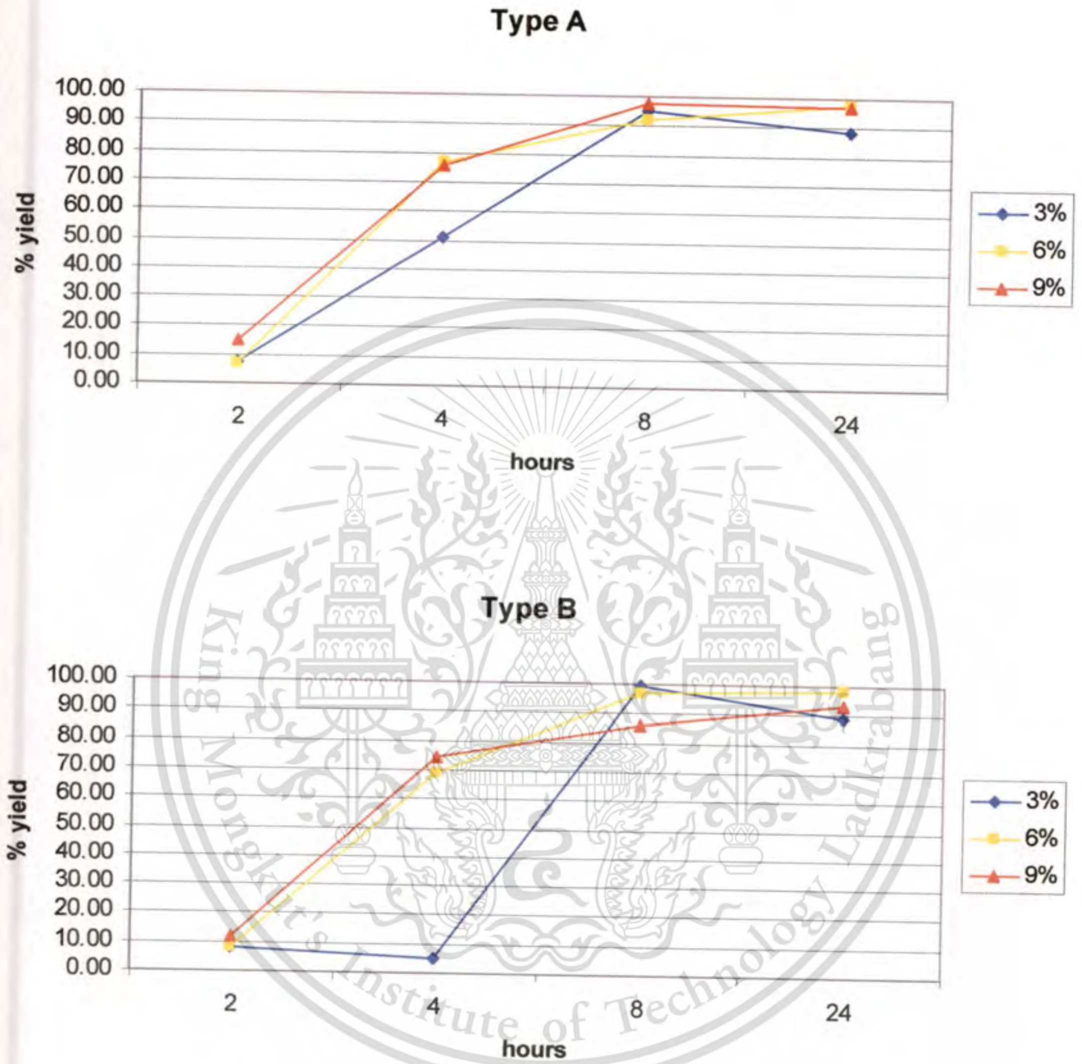


Figure 4.7: Relation between reaction times versus percent yield methyl ester of ZnO Type A and Type B catalyst at 3%, 6% and 9% weight percent oil

From Figure 4.7, the relation between reaction time versus percent yield methyl ester of ZnO Type A and Type B catalysts was 3%, 6% and 9% weight oil, respectively. When the reaction time of ZnO Type A and Type B increased, the percent yield methyl ester increased, However, ZnO quite deactivate at low temperature, and it will activate at high temperature. The increasing in the excess amount of catalyst, the percent yield of methyl-ester were still the same because the amount of catalyst that we used, it were too high comparing to the research of S. Yan et. al. [41]

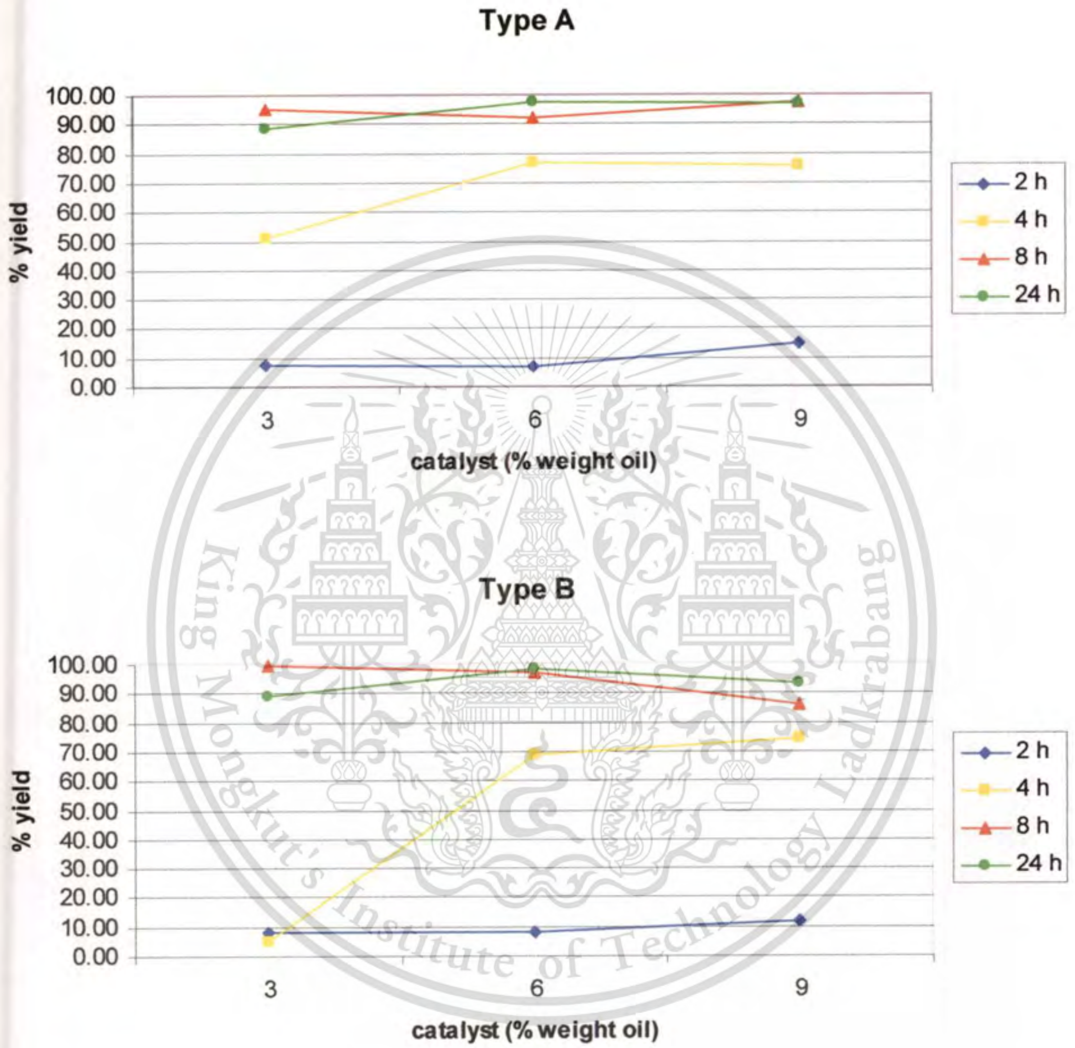


Figure 4.8: Relation between amount of catalyst versus percent yield of methyl ester of ZnO Type A and Type B catalyst at reaction times 2, 4, 8 and 24 hours

Figure 4.8 shows the relation between amount of catalyst for both ZnO Type A and Type B versus percent yield methyl ester at reaction time of 2, 4, 8 and 24 hours. From the above graphs, it is noticed that when the reaction time increased, the percent yield of methyl ester also increased because at reaction time of 2 and 4 the reaction is not complete as a result of methanol react with ZnO to form small amount of methoxide anion in the reaction as shown in Figure 2.4 but at 8 hour the methanol has more time to reacts with ZnO to form more methoxide anion in reaction compare with 2 and 4 hour, however, at 24 hour the reaction was too long and some of the methanol may be loosed form an autoclave. At mention earlier for this project, the increasing the amount of catalyst does not significantly affect the percent yield of methyl ester as shown in Figure 4.8.

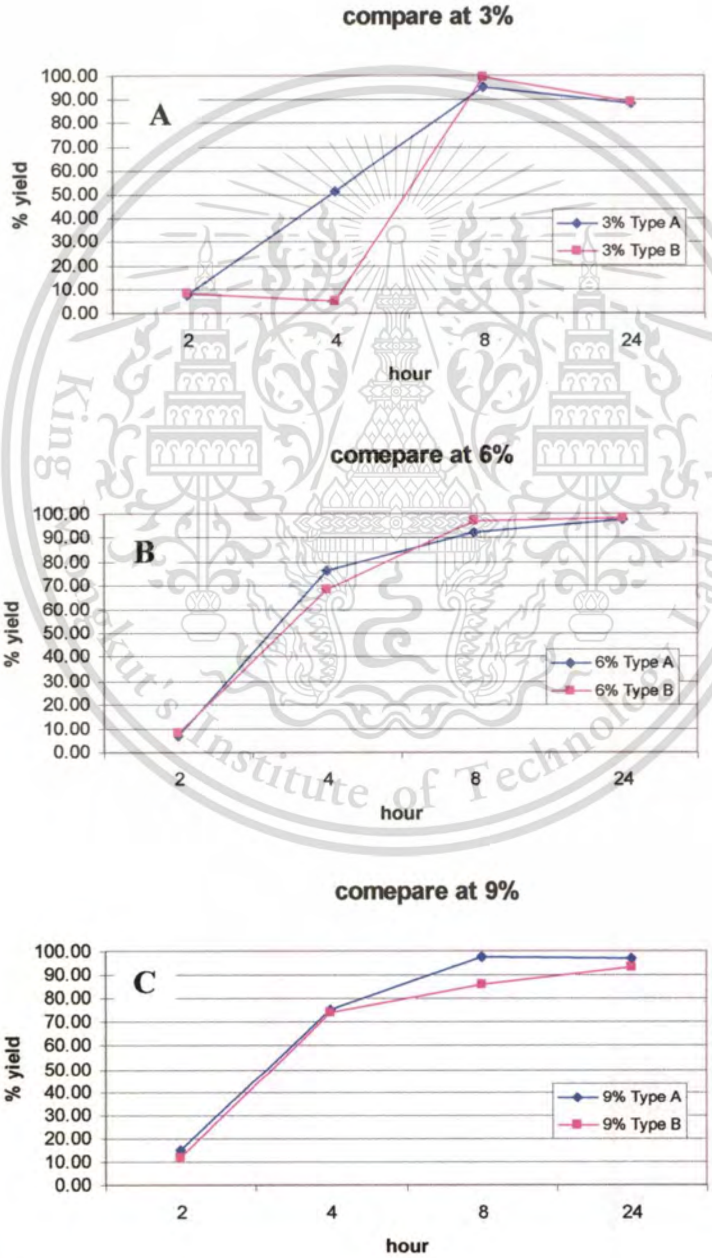


Figure 4.9: Comparison between reaction times versus percent yield of methyl ester of ZnO Type A and Type B catalyst at 3% (A), 6% (B) and 9% (C) weight oil

From figure 4.9, the comparison between reaction times versus percent yield of methyl ester for both ZnO Type A and Type B catalyst at 3% (A), 6% (B) and 9% (C) weight oil. From A, B and C graphs as shown in Figure 4.3, the percent yield of methyl ester of ZnO Type A and Type B were all the same. This is because the particle size of ZnO Type A and Type B were almost the same.

4.6 Analysis functional groups of methyl ester (biodiesel)

Methyl ester (biodiesel) from transesterification reaction was analyzed functional groups by Fourier Transform Infrared spectroscopy (FT-IR) and ^{1}H-Nuclear Magnetic Resonance (^{1}H -NMR). The spectrum of methyl ester which synthesize in 3 methods were similar. Thus, the figures show the example of FT-IR and ^{1}H-NMR spectrum of palm oil and methyl ester.

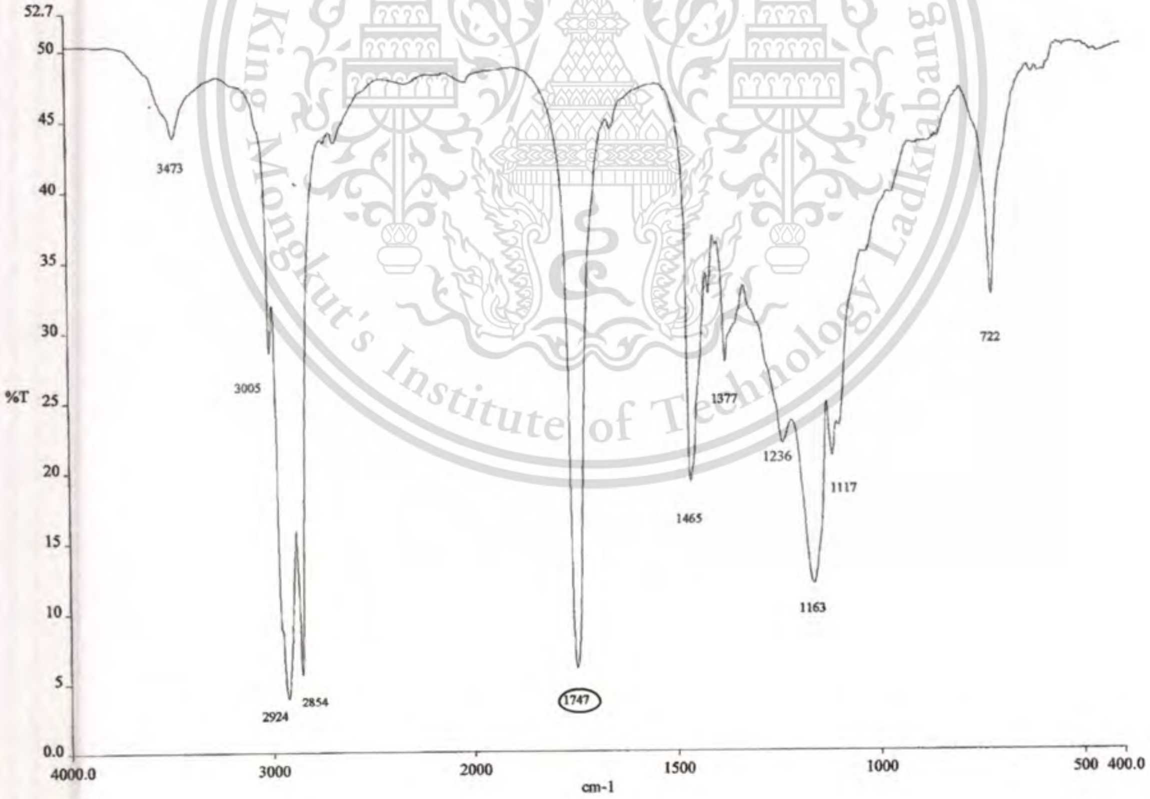


Figure 4.10: FT-IR spectrum of palm oil

The FT-IR spectrum of palm oil before transesterification reaction from figure 4.10 shows wavenumber 2924 cm^{-1} and 2854 cm^{-1} are functional group of C-H. At 1747 cm^{-1} was the functional group of C=O, 1236 cm^{-1} was the functional group of C(=O)-O and at 1163 cm-1 assigned to –C-O stretching.

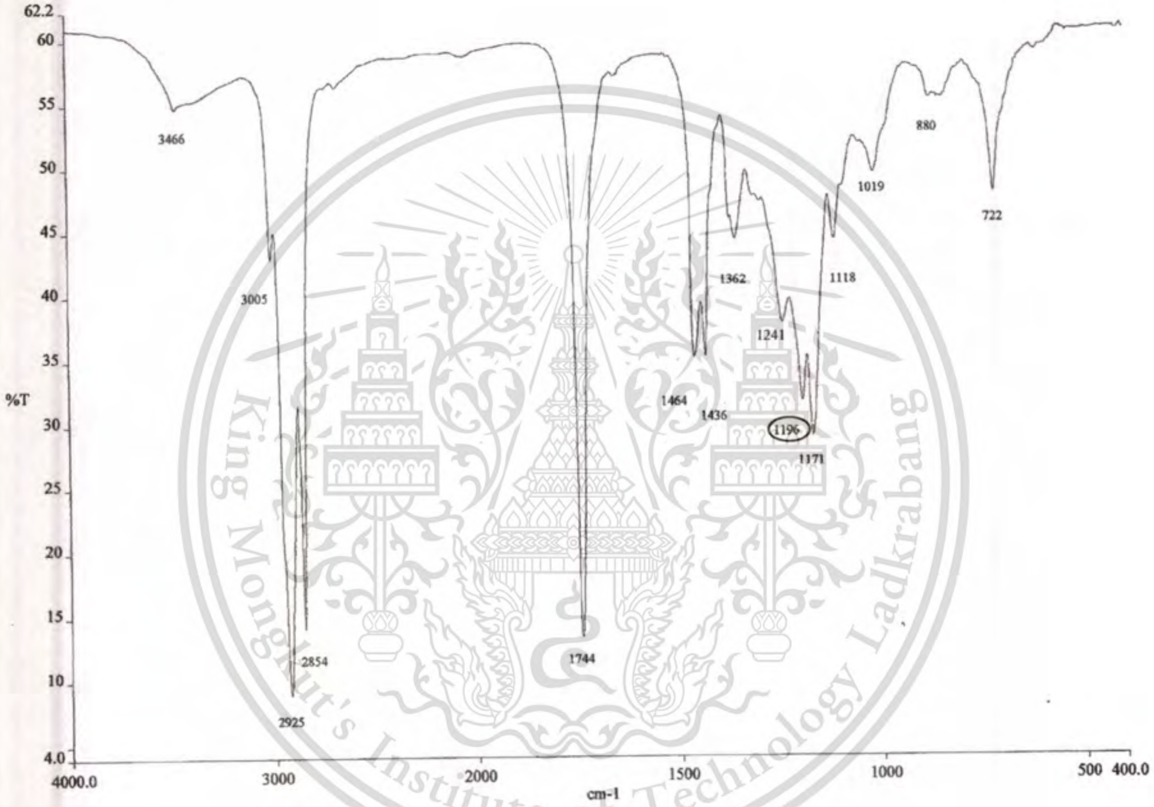


Figure 4.11: FT-IR spectrum of Methyl ester

In figure 4.11, the FT-IR spectrum of methyl ester. The IR absorbance spectra peak at 2925 cm^{-1} and 2854 cm^{-1} are C-H group. At wavenumber 1362 cm^{-1} and 1171 cm^{-1} are functional group of CH_3 and C-H, respectively. At 1196 cm^{-1} which is functional group of CH_3-O that especially show in spectrum of methyl ester.

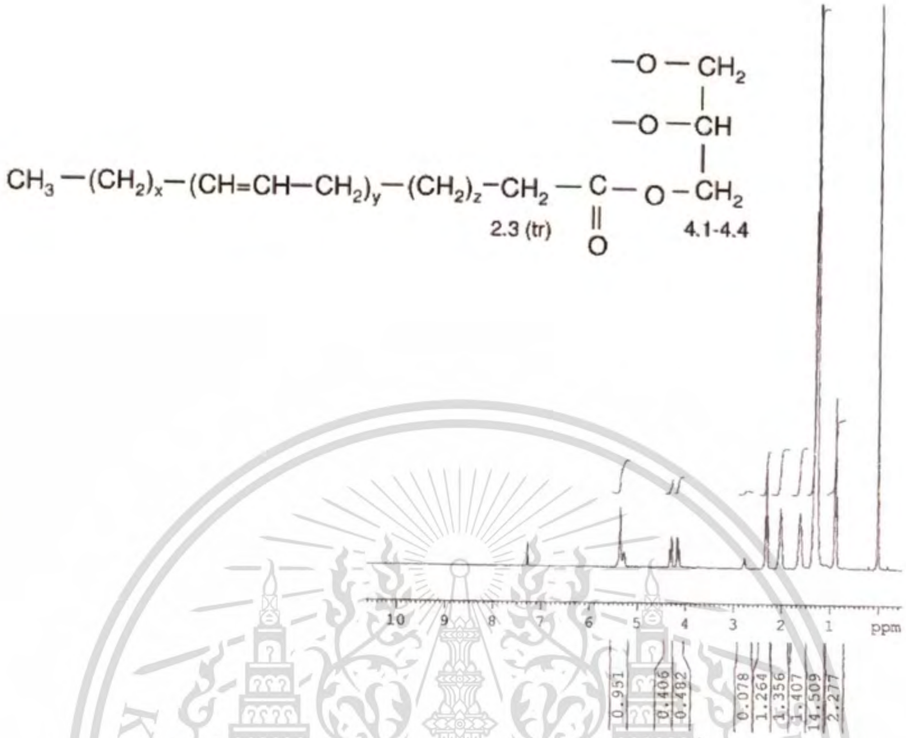


Figure 4.12: ^{1}H-NMR spectrum of palm oil

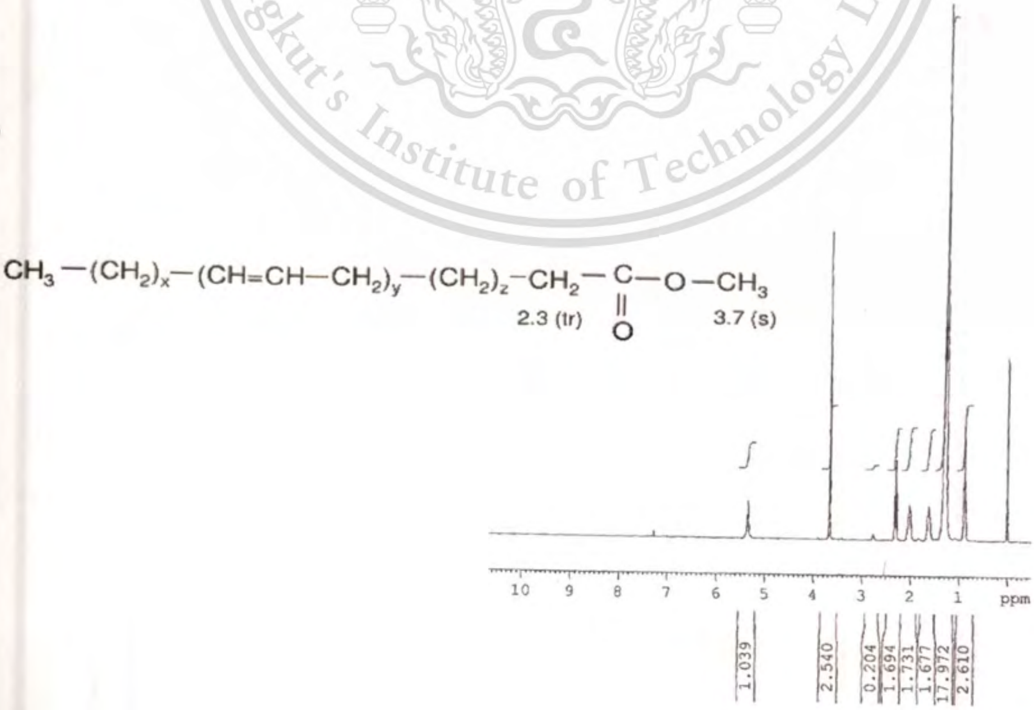


Figure 4.13: ^{1}H-NMR spectrum of methyl ester

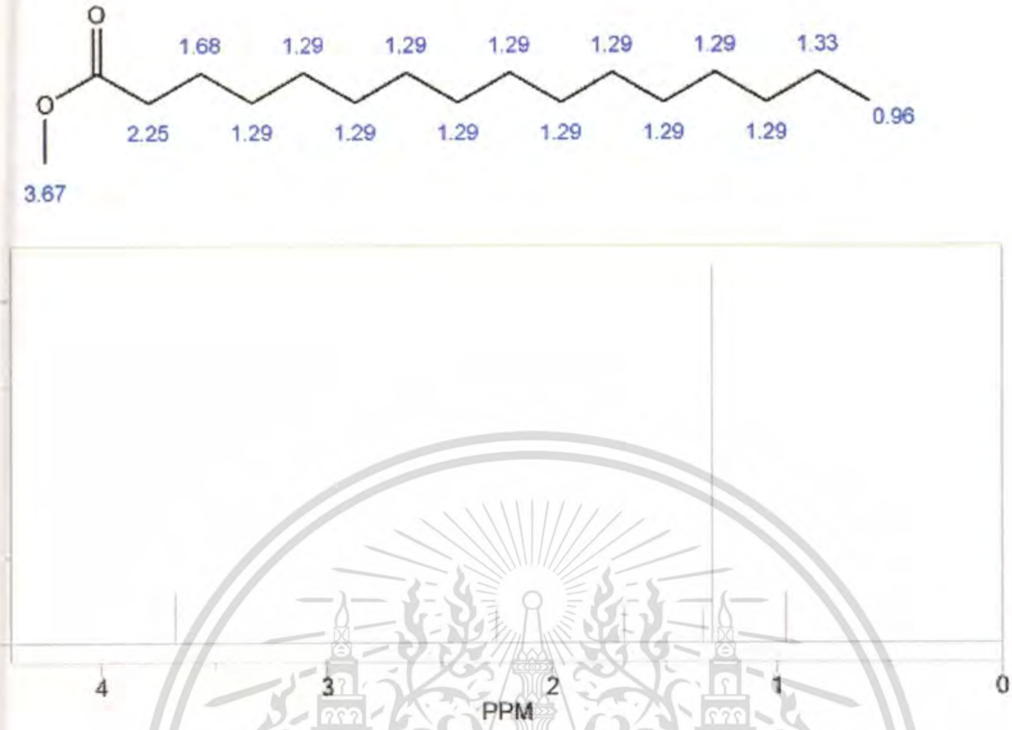


Figure 4.14: The simulated structure and 1H-NMR spectra of methyl-palmitae from CHEM DRAW

We use transform Nuclear Magnetic Resonance (^{1}H-NMR) technique use to calculate percent yield of methyl eater that occur in transesterification reaction of vegetable oil or oil from animal fat (pork fat) that contain triglyceride. From Figure 4.12 and 4.13, the spectra of palm oil and methyl ester were analyzed by ^{1}H-NMR. At the chemical shift of 2.3 ppm, it is the proton signal of R-CH_2-C(=O)-O-. At the chemical shift of 3.7 ppm, it is the proton signal of CH_3-O-C(=O) which the only signal that we can only observed especially in the methyl ester spectrum and at the chemical shift between 4.1-4.4 ppm is the proton signal of CH_2-O-C(=O) which is evanesce when change from oil to methyl ester. The comparison between spectra of palm oil by ^{1}H-NMR (Figure 4.13) was affirmed by the simulated structure and spectra of methyl-palmitate from CHEM DRAW (Figure 4.14).

Chapter 5
Conclusions and Recommendation

5.1 Conclusions

This project is successfully synthesized biodiesel from palm oil by transesterification process and uses nano-zinc oxide as a catalyst. We study the variable which affects the amount of methyl ester product. Firstly, we determine the amount of free fatty acid of palm oil before synthesis. Then, we synthesized biodiesel and determine the suitable variable for produce biodiesel from palm oil by reflux method, microwave oven and hydrothermal using autoclave.

5.1.1 The palm oil with free fatty acid less than 2.5% can be use directly for synthesized biodiesel.

5.1.2 From the result of methyl ester yield by reflux method, we can not find the appropriate condition for produced biodiesel from palm oil by transesterification process and uses nano-zinc oxide as a catalyst.

5.1.3 From the result of methyl ester yield by microwave oven, we can not find the appropriate condition for produce biodiesel from palm oil by transesterification process and uses nano-zinc oxide as a catalyst

5.1.4 From the result of methyl ester yield by hydrothermal using autoclave, the appropriate condition to produce biodiesel from palm oil by transesterification process and using nano-zinc oxide as a catalyst are the reaction of 5 g palm oil with 2.1g methanol (methanol:oil molar ratio is 12:1) and using 0.15 g of zinc oxide nanoparticle, The degussa's brand (catalyst amount is 3%wt oil) and the reaction time is 8 hr at 200°C.

5.1.5 The functional group of biodiesel are analyzed by spectroscopy technique from both Proton Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FT-IR) and the ester structure of biodiesel can be identified.

5.2 Recommendations

5.2.1 Since, the methanol is very important for transesterification reaction and percent yield of methyl ester. Therefore, the methyl esters that we synthesized by the reflux method and by microwave oven method were not successful, and we can not find the suitable condition for produce biodiesel this resulting in too low percent yield of methyl ester. But from the result of methyl ester yield by hydrothermal using autoclave, we got high percent yield of methyl ester because this method most of the methanol still in an autoclave.

5.2.2 Hopefully, we could apply this experiment to produce more efficiency of biodiesel.

5.2.3 The zinc oxide nanoparticle catalyst can be reused and more ecofriendly, which resulting in reduce the cost for biodiesel production.

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Appendix A
Calculation

A-1 Determination the exact concentration of sodium hydroxide solution

Prepare 0.25 N of NaOH by dissolve 10 g NaOH in 1000 ml of water then titrate with 20 ml of KHP.

KHP (g)	KHP (normal)	NaOH (ml)	NaOH (normal)
1.0200	0.2497	20.60	0.2424
1.0301	0.2522	20.70	0.2437
1.0200	0.2497	20.60	0.2424
	Average		0.2429

Calculation

- **Concentration of KHP**

$$\frac{g}{Mw} = \frac{NV}{1000}$$

$$\frac{1.0200}{204.22} = \frac{N(20)}{1000}$$

$$N = 0.2429 \text{ normal}$$

- **Concentration of NaOH**

$$\text{mol NaOH} = \text{mol KHP}$$

$$N_1V_1 = N_2V_2$$

$$\text{N1 } (20.60) = (0.2429)\,(20)$$

$$N_1 = 0.2424 \text{ normal}$$

$$\text{Concentration of NaOH} = (0.2424 + 0.2437 + 0.2424)$$

$$= 0.2429 \text{ normal}$$

A-2 Determination the volume of free fatty acid

Oil (g)	NaOH (ml)	Free Fatty Acid (%)	
		Lauric	Palmitic
7.04	0.5	0.36	0.46
7.07	0.6	0.43	0.55
7.06	0.6	0.43	0.55
Average		0.40	0.52

Calculation

- Free fatty acid in form of lauric (%)

$$= \frac{volume \quad of \quad NaOH \times N \times 20.00}{volume \quad of \quad oil}$$

$$= \frac{(0.5 \times 0.254 \times 20.00)}{7.04}$$

$$= 0.36\ \%$$

$$\text{Average} = \frac{(0.36 + 0.43 + 0.43)}{3}$$

$$= 0.40\ \%$$

- Free fatty acid in form of plamatic (%)

$$= \frac{volume \quad of \quad NaOH \times N \times 25.60}{volume \quad of \quad oil}$$

$$= \frac{(0.5 \times 0.245 \times 25.5)}{7.04}$$

$$= 0.46\ \%$$

$$\text{Average} = \frac{(0.46 + 0.55 + 0.55)}{3}$$

$$= 0.52\ \%$$

A-3 Calculation percent yield of methyl ester by ^{1}H-NMR

Transform Nuclear Magnetic Resonance (^{1}H-NMR) technique use to calculate percent yield of methyl eater that occur in transesterification reaction of vegetable oil or oil from animal fat (pork fat) that contain triglyceride.

Calculation

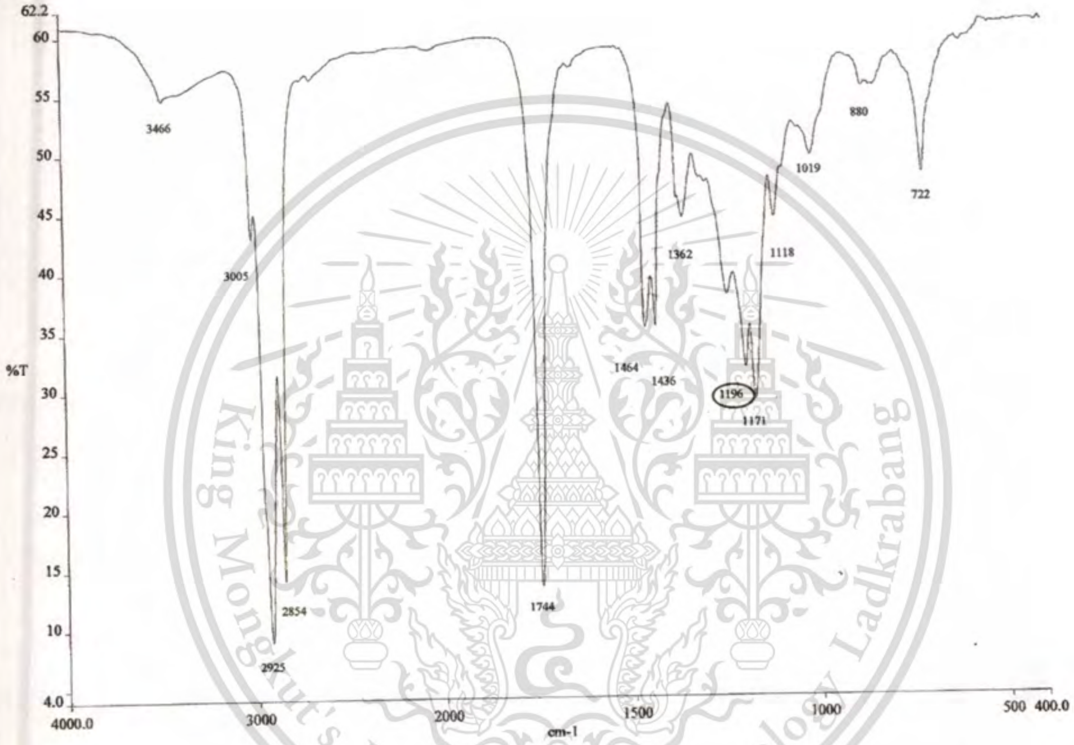
$$\%\ \text{of methyl ester} = 100\times\frac{2\times area\ \ under\ \ peak\ \ of\ \ -OCH_3}{3\times area\ \ under\ \ peak\ \ of\ \ \alpha-CH_2}$$

$$= 100\times\frac{2\times 2.540}{3\times 1.694}$$

$$= 99.96\ \%$$

A-4 Analysis functional groups of methyl ester by FT-IR

Fourier transform infrared (FT-IR) spectroscopy is a measurement technique for collecting infrared spectra. We use FT-IR to analyze the functional group of methyl ester (biodiesel).



From figure above, at wavelength 1196 cm-1 is the functional group of CH_3-O that show in biodiesel product (methyl ester) when use transesterification reaction with nanoparticles zinc oxide as catalyst.

Appendix B
Apparatus

B-1 Introduction of Fourier Transform Infrared Spectroscopy (FT – IR)

1. Turn on UPS and computer

2. Select Spectrum mode

3. Click 'OK'

4. Energy check

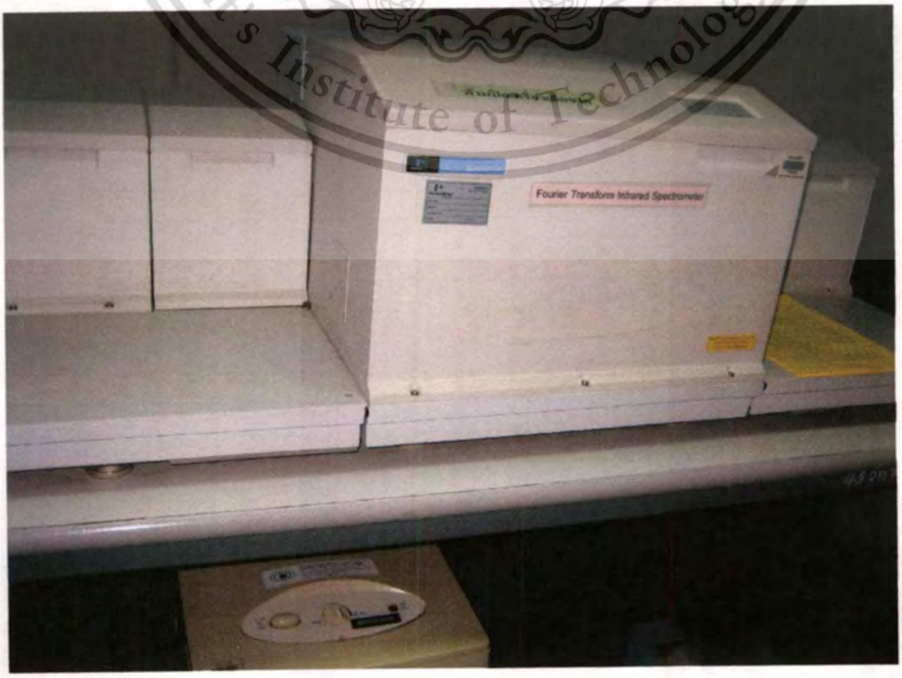
5. Make sure that they is no sample on cell

6. Run standard polystylene (rang start 900.0 end 20) before run the sample

7. Run the sample

8. After scan, you'll get spectrum then click on peaks they'll show wavelength of each peak

9. When you finished, take the sample off of the cell and turn off the computer



B-2 Introduction of Nuclear magnetic resonance (NMR)

1. Calibrate NMR with TMS solution

2. Drop sample on ø 5 mm NMR tube

3. Use $CDCL_3$ as a solvent

4. Put the sample in NMR, the spectrum will record by NMR at 300 megahertz. The sample dissolves in $CDCL_3$ that has TMS as a standard.

B-3 Introduction of Teflon-line auto clave

1. Weight 0.15 g (3%) of ZnO nano particles, 2.10 g of methanol and 5 g of palm oil into Teflon-line and mixed well.

2. Set the Teflon-line autoclave together (figure 32)

3. Heat the Teflon-line autoclave at 200 °C in oven.