CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Bio-fuels

2.1.1 Definition and Classification

Bio-fuels are fuels derived from biomass. There are several types of bio-fuels; the most well-known include:

Bio-ethanol: produced from the fermentation process of biomass that has a high concentration of sugar as the raw material. Today, bio-ethanol has become an important alternative to gasoline. Many countries are producing more bio-fuel to reduce the gasoline consumption. Among them, Brazil is the world's largest bio-fuel producer; their products mostly consist of ethanol fuel from sugar cane, which provides 30% of the country's automotive fuel.

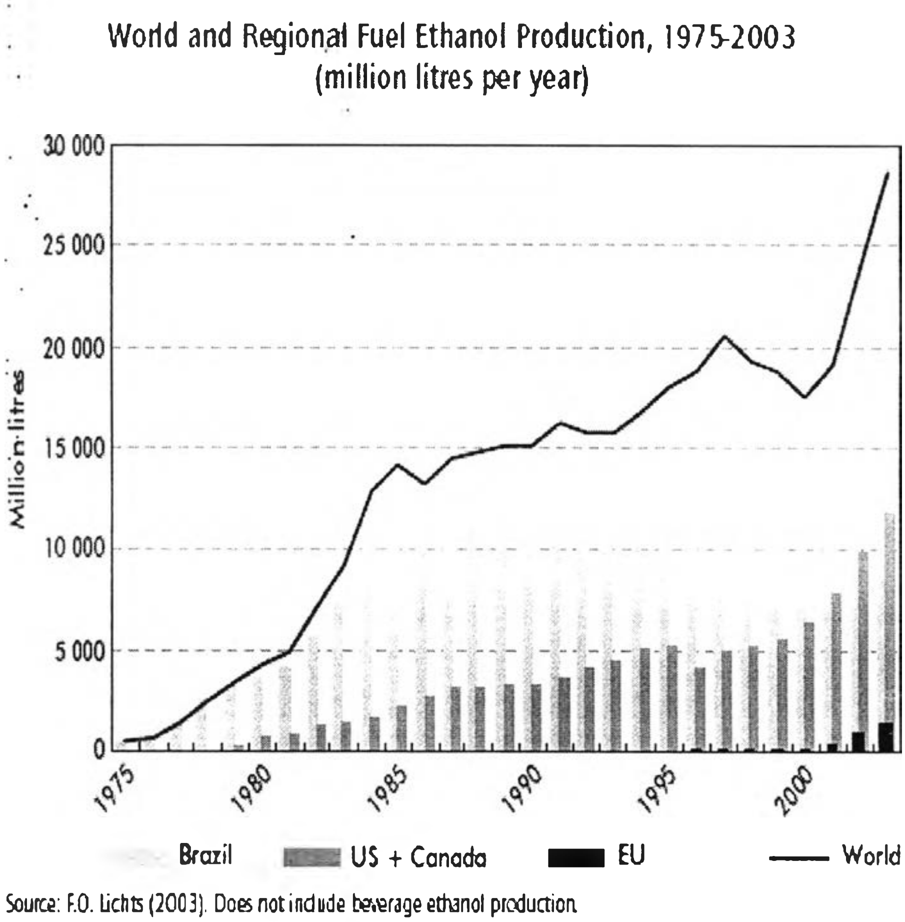
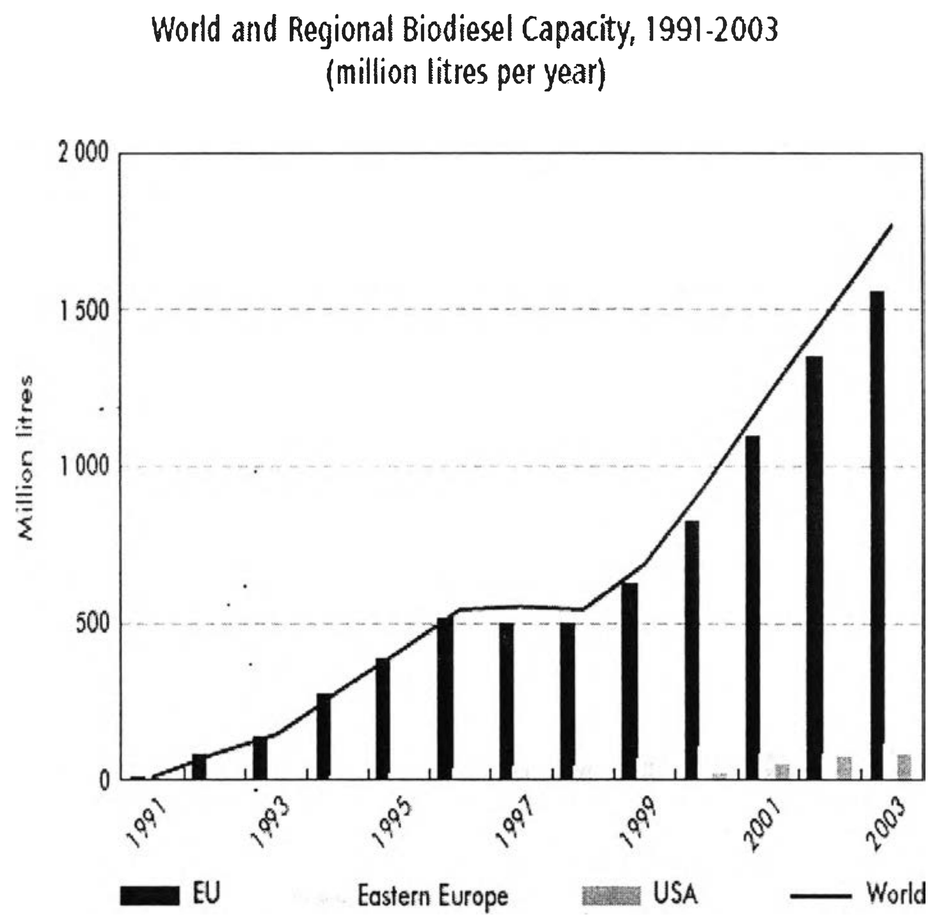


Figure 2.1 World and Regional fuel Ethanol Production, 1975-2003.

Biodiesel: produced from the transesterification process with vegetable oil or animal fats as the raw material. The world consumption of biodiesel has been increasing rapidly as shown below:



Note: EU biodiesel production was about two-thirds of capacity in 2003. Source: F.O. Lichts (2003).

Figure 2.2 World and Regional Biodiesel Capacity, 1991-2003.

2.2 History and Development

In the 1880s, some countries in Europe had already started to research and apply biomass in industry. The first demonstration of bio-fuel, which was a form of a peanut-like fuel, for a diesel engine was seen at the Exhibition of Paris in 1898. Rudolf Diesel, the inventor, said that: "The diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries which use it". He later said, "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of present time."

Due to the petroleum crises of 1973 and 1978, the power policies of the 1980's helped the search of alternative fuels to reduce the dependency on fossil fuels, especially in the US.

Recently, developed countries such as America, Europe, and Japan have sped up research and applications to deal with the energy crises and the skyrocketing of fossil fuel demand.

2.3 Advantages of Bio-fuels

Compared to fossil fuels, bio-fuels have some advantages, as follows:

i. They can reduce the greenhouse gas emissions for both developed and developing countries on the world; carbon dioxide produced by the combustion of bio-fuels can be recycled by photosynthesis, thereby minimizing the impact of bio-fuel combustion on the greenhouse effect. As is known, the CO_2 components produced from bio-fuels and conventional fuels are exactly the same, but the mass of CO_2 resulting from bio-fuels can be converted to biomass by combining with tree leaf photosynthesis. The biomass harvested from this process is the material to re-produce bio-fuels. It is easily realized that this is a closed cycle, and hence we can balance the presence of CO_2 in the air; whereas the CO_2 produced from fossil fuel can only be converted to biomass by plants and we cannot get balance if the biomass is not used as a fuel. As a result, the concentration of CO_2 will keep increasing and fossil oil reserves will continue to deplete.

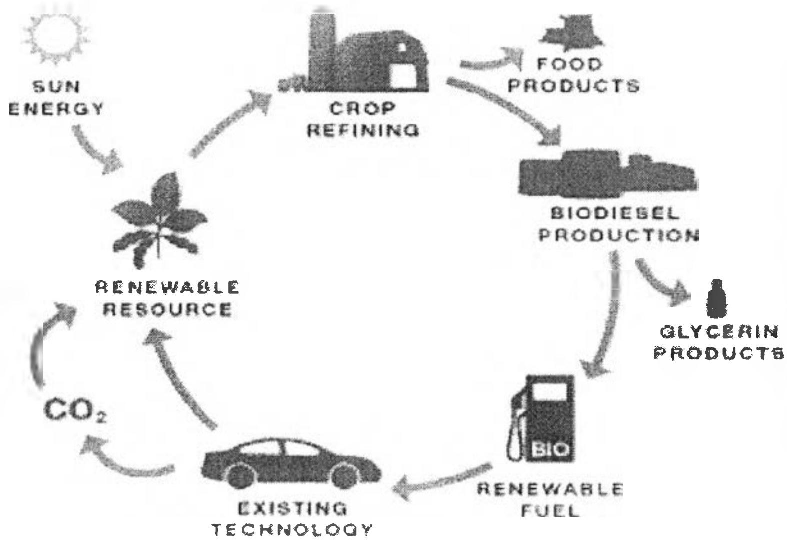


Figure 2.3 Biodiesel life cycle (Source: Wikipidia).

ii. They can reduce air pollutants: Biodiesel has a more favorable combustion emission profile, such as low emissions of carbon monoxide, volatile organic components, polycyclic aromatic hydrocarbon, heavy metals, particulate matter, and unburned hydrocarbons. Especially, bio-fuels have a very low sulfur content, which helps to reduce acid rain.

iii. Bio-fuels are easier to biodegrade than fossil fuels.

iv. In the energy crisis scenario, bio-fuels could help to reduce the risk of sole reliance on petroleum fuel supply.

v. In the socioeconomic scenario, if bio-fuels are widely used, it could help to green cover desert areas, produce more jobs, and increase income for farmers.

2.4 The Current Status of Biodiesel Used, Focus on the Thailand Market

Two kinds of biodiesels available in the Thai market are: B5 biodiesel (the most popular product), which is comprised of a "blend" of 5% biodiesel (B100) and

95% conventional petroleum diesel; and, B10 biodiesel, which is composed of a "blend" of 10% biodiesel and 90% petroleum diesel.

At the end of 2005, Thailand had specifications for B100, but B5 and B10 still used the same quality standard as diesel oil and met the specifications required by the Commerce Ministry for high speed diesel oil (Table 2.1).

Table 2.1 Specifications for Biodiesel applied in Thailand
Source: Ministry of Energy

Item	Property	Limit		Test method
1	Methyl Ester, %wt	Min	96.5	EN 14103
2	Density at 15°C, kg/m^3	Min to	860	ASTM D 1298
		Max	900	
3	Viscosity at 40°C, cSt	Min to	3.5	ASTM D 445
		Max	5.0	
4	Flash Point,°C	Min	120	ASTM D 93
5	Sulphur, %wt	Max	0.0010	ASTM D 2622
6	Carbon Residue, on 10%	Max	0.30	ASTM D 4530
	Distillation residue, %wt			
7	Cetane Number	Min	51	ASTM D 613
8	Sulfated Ash, %wt	Max	0.02	ASTM D 874
9	Water, %wt	Max	0.050	ASTM D 2709
10	Total Contaminate, %wt	Max	0.0024	ASTM D 5452
11	Coppor Strip Corrosion	Max	1 (table)	ASTM D 130
12	Oxidation Stability at 110°C,hours	Min	6	EN 14112
13	Acid Value, mg KOH/g	Max	0.50	ASTM D 864
14	Iodine Value, g Iodine/100 g	Max	120	EN 14111
15	Linolenic Acid Methyl Ester, %wt	Max	12.0	EN 14103
16	Methanol, %wt	Max	0.20	EN 14110
17	Monoglyceride, %wt	Max	0.80	EN 14105
18	Diglyceride, %wt	Max	0.20	EN 14105
19	Triglyceride, %wt	Max	0.20	EN 14105

20	Free glyceride, %wt	Max	0.02	EN 14105
21	Total glyceride, %wt	Max	0.25	EN 14105
22	Group I metals (Na+K), mg/kg	Max	5.0	EN 14108 and EN 14109
	Group II metals (Ca+Mg), mg/kg	Max	5.0	EN 14538
23	Phosphorous, %wt	Max	0.0010	ASTM D 4951

Biodiesel produced from the current process has a lot of advantages in terms of the environment and the economy. Compared to petroleum-based diesel, biodiesel has a more favorable combustion emission profile, such as low emissions of carbon monoxide, particulate matter, and unburned hydrocarbons. Carbon dioxide produced by the combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect. Biodiesel has a relatively high flash point (150°C), so it is less volatile and safer to transport or store than conventional diesel. It has lubricating properties that can reduce engine wear and extend engine life. The volumetric heating values are a little lower, but the cetane index and flash points are higher than conventional diesel. Therefore, biodiesel is the best selection as an alternative to conventional diesel nowadays, especially in environmentally sensitive areas.

2.4.1 Thailand's Market Characteristics

2.4.1.1 Strategy

The biodiesel program in Thailand indicates that from 2005-2008, biodiesel has been produced for community usage (B5 in Bangkok and some southern provinces). From 2009-2011, B5 will be produced nationwide, and from 2012 onwards, B10 will become widely used in Thailand.

2.4.1.2 Prospect

In 2007, the diesel demand in Thailand was 391.75 thousand barrels per day. If all of the diesel on the market is B5, the amount of B100 biodiesel needed would be 19.6 thousand barrels per day (3.11 million liters of B100 biodiesel per day), and in 2012, after B10 is used widely, the amount of B100 biodiesel needed would be around 7 million liters per day. However, up until 2007, there were only five biodiesel producers qualified by the (DEDE) Notification. They include Pathum Vegetable Oil, SookSomBoon Energy, and Bio-Energy Plus, which have a total production capacity of 14,000 l/day (approximately 0.45% of demand in 2007) and two new producers (at a stage of negotiation with PTT-Bangchak) with a total production capacity of 700,000 liters/day (approximately 22.6% of total demand in 2007). The company collaborating with us on this present study is Veerasuwan Company (Thailand) ran start-up in April, 2007 with an estimated capacity of 200,000 liters per day.

2.4.1.3 The Challenges

Economic challenge: At present, the high cost of biodiesel is the major challenge to its commercialization. The price of B100 biodiesel produced in Thailad is 24.54 baht per liter, which is set by the Energy Policy Administration Committee (EPAC); conventional diesel costs 22.95 baht and B5 costs 22.44 baht. This means that the Thai government had to support B5. instead of bio-diesel due to its lower cost (in January 2007). It is reported that the high cost of biodiesel is mainly due to the cost of virgin vegetable oil.

In a different market, the situation may be very different. For example, in January 2007 the average world price of biodiesel produced from rape seed in the German market was 34.43 baht/l, the price of biodiesel produced from fatty acid in the German market was 33.85 baht/l, the price of biodiesel produced from palm oil in the German market = 28.62 baht/l, and the price of conventional diesel oil in the German market was 48.68 baht/l. Therefore, biodiesel is one kind of fuel that is very promising and competitive.

Some conclusions about biodiesel production in Thailand:

- Palm oil is one of the best materials to produce biodiesel.
- The price of biodiesel produced from palm oil in Thailand is much lower than in other countries (cheaper by around 20%, compared to Germany). This is a big advantage for Thailand.

- By 2012, Thailand should rise to the world's third-highest biodiesel producer (after Malaysia and Indonesia). This is an important goal for the Thai government.

2.4.2 Technological Challenges

The storage time permitted for biodiesel will be shorter than for diesel because it can be oxidated at the unsaturated bonds of fatty acids, hydrolysis, so it can increase the acid index of products. The storage time should, therefore, be less than four months.

One of the raw materials used in the production of biodiesel, methanol, is a very toxic substance, so storage and usage must be strictly monitored.

2.4.3 Other Challenges

1. Materials resources are currently not large and stable enough. So the first thing needed is to build material regions. The distribution of current material regions are shown below.

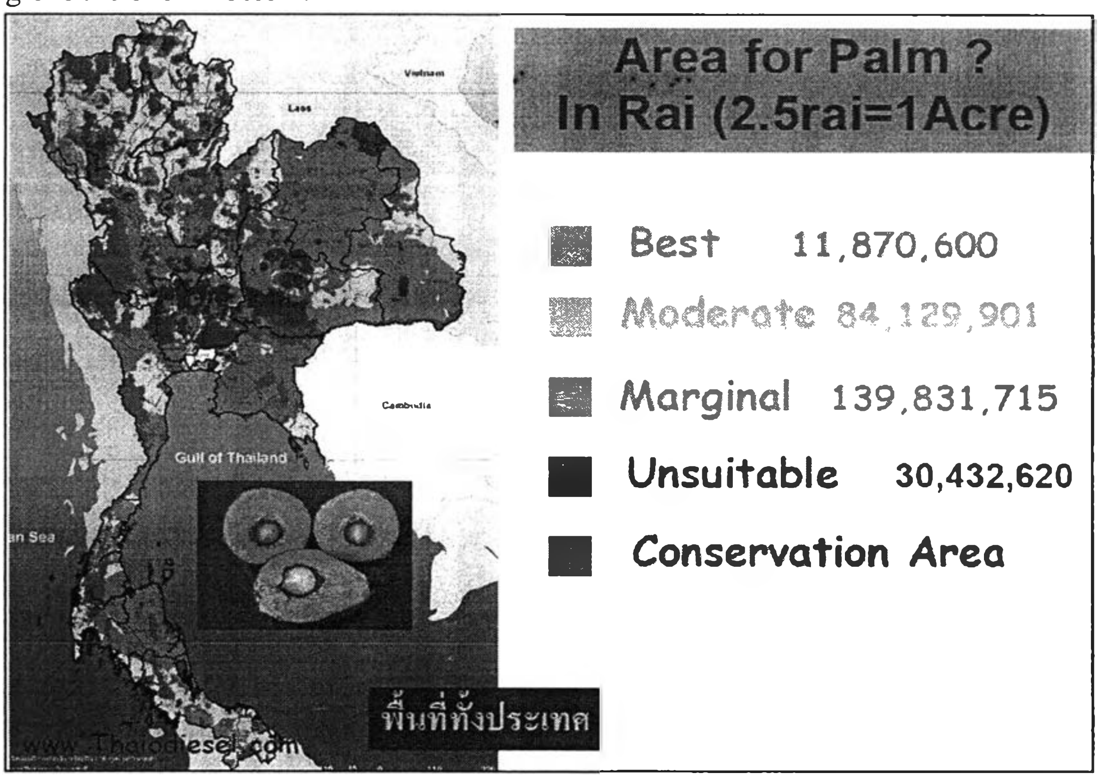


Figure 2.4 Distribution of oil palm plants in Thailand.
(Source: www.Thaidiesel.com)

2. The collaboration among government, scientists, companies and farmers is still not very efficient.

3. Water wastage also is a problem in the homogeneous catalyst process. In this process, the new technique to purify the main product is using vacuum distillation column, so the problem can be eliminated.

2.5 The Making of Biodiesel

2.5.1 Why Vegetable Oils Cannot be Used Directly

The main advantage of using vegetable oils as diesel fuels is its availability. However, the direct use of vegetable oils in diesel engines can lead to a number of problems such as poor fuel atomization, poor cold engine start-up, and gum and other deposit formation. Consequently, considerable effort has been made to develop an alternative diesel fuel that has the same properties and performance as petroleum-based diesel fuels. There are four major ways that have been studied extensively—i.e., pyrolysis, dilution and blending, microemulsification, and transesterification. The most commonly used method is transesterification.

2.5.2 Transesterification

Transesterification, also called alcoholysis, is the reaction of triglycerides with an alcohol (usually methanol) to form esters (most are mono-esters) and glycerol. This process has been widely used to reduce the viscosity of vegetable oils.

There are three kinds of transesterification reactions i.e. alkali-catalyzed, acid-catalyzed, and enzyme-catalyzed. The first two types are the most commonly used. Both alkali– and acid–catalyzed reactions can involve homogeneous or heterogeneous catalysts. In general, homogeneous catalysts such as mineral acids, metal hydroxide, and metal alkoxide are used. However, heterogeneous catalysts would have several advantages such as easy separation and reduction of environmental pollutants. A number of studies on transesterification have shown, however, that the use of a homogeneous catalyst yields a higher concentration of alkyl esters than that of a heterogeneous catalyst. As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two systems. Until now it has only been carried out on a laboratory scale. This project focuses only on the alkali-catalyzed.

2.5.3 Product

Fatty acid methyl esters (FAME), known as biodiesel, have received the most attention. FAME can be produced by the transesterification of vegetable oil with methanol and they have the proper viscosity and boiling point, and a high cetane number.

In many countries, different vegetable oils are used as a raw material for producing biodiesel; for example, soybean oil in the US, rapeseed and sunflower oil in Europe, and palm oil in Malaysia. In Thailand, coconut and palm oil are commonly used.

The composition of FAME diesel depends on the raw material used and the operational parameters.

2.5.4 Raw Material

Palm oil is an interesting vegetable oil to be used as an alternative to diesel in Thailand because it can give a large yield of oil per square unit equal to 5000 kg of oil per hectare compared to 375 of soybean, 800 of sunflowers, and 1000 of rapeseed. There are two types of palm oil; palm oil is oil extracted from palm fruits, and palm kernel oil is from its kernel. Because of their high viscosity, palm oils are refined to remove some impurities and are blended with diesel to decrease their viscosity. The type of raw material, palm oil used in this plant has the composition as listed in Table 4.1.

Table 2.2 Palm oil composition in Thailand

Palm Oils Composition in Thailand					
	C12	C14	C16	C18	C20
%wt	0.2	1.2	62	35	1.6
Name		Myristate	Palmitrate	Stearate	

Source: Veerasuwan Co., Ltd (Thailand).

2.6 Alkali-Catalyzed System

Recently, many research works on alkali-catalyzed transesterification have been carried out in laboratories and pilot plants. A reaction temperature near the boiling point of the alcohol (e.g., 60°C for methanol) and a 6:1 molar ratio of alcohol to palm oil were recommended. The kinetics of the alkali-catalyzed system were studied by Freedman, Noureddini and Zhu, and Darnoko and Chervan. From their results, a conversion of transesterification reaction approximately 90–98% was obtained within 90 minutes. In order to speed up the reaction, Boocock suggested the addition of tetrahydrofuran (THF) as a co-solvent to minimize mass transfer resistance. After the reaction, different separation techniques to purify the biodiesel product from the other products were investigated by Karaosmano. For the purity and yield of the biodiesel product, they concluded that using a hot water washing at 50°C was the best way to obtain high purity (99%-99.5%) and high yield (90%-95%) of the biodiesel product (this parameter also depends on other reasons, such as: raw material, operation parameter,etc.).

A commercial continuous alkali-catalyzed transesterification process to produce biodiesel on an industrial scale under high pressure (90 bars) and at high temperature (240°C) was demonstrated by Kreutzer. However, a high energy requirement, a significant increase in equipment cost, and also process safety, (with high pressure and high temperature), could make this process prohibitive. Krawczyk presented a flow diagram for producing biodiesel via transesterification on an industrial scale. The process has a transesterification reactor, a methanol/glycerol distillation column, and a methyl ester distillation column. A continuous deglycerolization process was introduced by Connemann and Fischer to produce bio-diesel from refined rapeseed oil by alkali-catalyzed transesterification at ambient pressure and 65–70°C. They were interested in successful commercial applications of this process in Europe. A distillation column was also used to separate methanol from biodiesel and glycerol. The methanol was recycled to the transesterification reactor and multi-stage water washing was employed to purify the biodiesel product. The information on biodiesel production formed the principle basis for the design of the alkali-catalyzed processes in all cases.

Unfortunately, the limitation of the alkali-catalyzed process is its sensitivity to the purity of the reactants; the alkali-catalyzed system is very sensitive to both water and free fatty acids (which is always present in the raw material). The presence of water may cause ester saponification under alkaline conditions. And free fatty acids will react with an alkali catalyst to produce soaps and water. Saponification not only consumes the alkali catalyst, but also the resulting soaps can cause the formation of emulsions. Emulsion formation creates difficulties in the downstream recovery and purification of the biodiesel. Thus, dehydrated vegetable oil with less than 0.5wt.% free fatty acids, an anhydrous alkali catalyst, and anhydrous alcohol are necessary for commercially viable alkali-catalyzed systems. This problem usually occurs with waste cooking oil as a low-cost feedstock. The free fatty acids contain in waste cooking oil is greater than 2wt.%. Reducing the free fatty acid contented via an esterification reaction with methanol in the presence of a sulfuric acid catalyst is recommended as a pretreatment step.

2.7 Design and Optimization of Biodiesel Plants

According to above information, it shows that although biodiesel is a product of great interest for many benefits it brings in, it still has deal with a lot of challenges in term of economy and technology. Research into the use of transesterified sunflower, and refining it to biodiesel, was initiated in South Africa in 1979. By 1983, the process for producing fuel-quality, engine-tested biodiesel was completed and published internationally. An Austrian company obtained the technology from the South African Agricultural Engineers; the company erected the first biodiesel pilot plant in 1987, and the first industrial-scale plant in 1989 (with a capacity of 30,000 tons of rapeseed per annum). In year 2007 Hamid successful designed a biodiesel process from the raw material which was rapeseed by using ICAS and PRO/II.

Design and optimization is the way to help investors to maximize its benefit and reduce disadvantages such as high cost. There are some software programs to assist the design and optimization phase, and in our project, the two following software: ICAS and PRO/II were chosen.

The aims of this project to improve the efficiency of a biodiesel production plant from palm oil in Thailand. Several factors such as technical, social, and economical aspects are taken into consideration. The methodology has been created in the order to assist companies in the selection of appropriate criteria for the implementation of biodiesel.