CHAPTER 2
LITERATURE REVIEWS

For more than two centuries, the world's energy supply has relied heavily on non-renewable crude oil derived (fossil) liquid fuels out of which 90% is estimated to be consumed for energy generation and transportation.

2.1 Conventional fuel

It is also known that emissions from the combustion of diesel fuels such as carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x) and sulphur-containing residues are the principal causes of global warming and many countries have passed legislation to arrest their adverse environmental consequences as present in Table 2.1 [5]. With populations increasing rapidly and many developing countries expanding their industrial base and output, worldwide energy demand is bound to increase. On the other hand, known crude oil reserves could be depleted in less than 50 years at the rate of consumption. This situation initiated and has sustained interest in identifying and channeling renewable (biomass) raw materials into the manufacture of liquid fuel alternatives because development of such biomass power would ensure that new technologies are available to keep pace with society's need for new renewable power alternatives for the future.

Table 2.1 Characteristics and emissions of diesel fuel No.2 ($C_{16}H_{34}$) [5].

Properties	Quantities
Specific gravity	0.83
Cetane number	44
Total HCNs as CH_4 (g.kW/h)	15.64
Carbon monoxide (g.kW/h)	23.89
Total oxides of N (g.kW/h)	9.94
Carbon dioxide (g.kW/h)	1316
Total particulates (g.kW/h)	1.36
Soluble fraction (g.kW/h)	1.04
Insoluble fraction (g.kW/h)	0.32

Studies to date based on biodiesel produced from palm oil have shown that biodiesel is environmentally friendly because there is substantial reduction of unburned hydrocarbons, CO and particulate matter emission when it is blended with 20% to conventional diesel fuel as shown in Table 2.2 [5]. Morever, biodiesel contains no sulphur, so the sulphate fraction in the fuel is eliminated; and since the oil originates from vegetable matter, the CO_2 produced is sequestered and the net CO_2 released into the atmosphere would be greatly reduced.

Table 2.2 Characteristics and emissions of diesel fuel No.2 blended with biodiesel [5].

Fuel blend characteristics	Properties
Biodiesel%	20
Cetane number	43.30
Total HCNs as CH_4 (g.kW/h)	5.83
Carbon monoxide (g.kW/h)	7.33
Total oxides of N (g.kW/h)	9.50
Carbon dioxide (g.kW/h)	1192
Total particulates (g.kW/h)	1.12
Soluble fraction (g.kW/h)	0.31
Insoluble fraction (g.kW/h)	0.82

For the searching of new energy sources, attention is naturally being focused on biomass, which can make a significant contribution to satisfying the needs of society for energy.

Palm oil and their derivatives in particularly of methyl esters or ethyl esters are being considered with respect to the substitution of classical liquid fuel. Thailand is an agriculture country and many of plant can produce oil. In Thailand, one of the most important in oilseed seems to be palm oil. However, palm oil is unsuitable for used as fuels in classic diesel engines (direct injection engines), since it is to viscous to be sprayed and their volatility is low due to high molar weight. Therefore, their burning is incomplete, leaving deposits in the engine.

On the way to accomplish the need of using palm oil is to reduce its viscosity. From the chemistry viewpoint, the basic route of reducing viscosity of palm oil is transesterification reaction of the oil with ethanol. A product of the reaction is called biodiesel. The biodiesel production reported in the literature can be categorized in to two groups: catalytic transesterification method, and noncatalytic transesterification method.

2.2 Biodiesel fuel

Biodiesel is a fuel manufactured from vegetable oils, recycled cooking grease, or animal fats. The fuel typically contains different types of fatty acids that are chemically transformed into fatty acid methyl esters or ethyl eaters. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression ignition (diesel) engines with no major modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel can be used as a pure fuel or blended with petroleum in any percentage. The production of biodiesel, or alkyl esters, is well known. There are four basic routes to ester production from oils and fats such as:

1. Base catalyzed transesterification of the oil with alcohol.
2. Direct acid catalyzed esterification of the oil with alcohol.
3. Conversion of the oil to fatty acids, and then to alkyl esters with acid catalysis.
4. Biodiesel fuel production by supercritical alcohol.

The majority of the alkyl esters produced today are done with the base catalyzed reaction because it is the most economic for several reasons:

1. Low temperature (65.56°C) and pressure (1.38 bar) processing.
2. High conversion (98%) with minimal side reactions and reaction time.
3. Direct conversion to methyl ester with no intermediate steps.
4. Exotic materials of construction are not necessary.

The general reaction of transesterification is depicted as Figure 2.1. A fat or oil is reacted with an alcohol, like methanol or ethanol, in the presence of a catalyst to produce glycerine and biodiesel. The alcohol is charged in excess to assist in quick conversion and recovered for a reuse. The catalyst is usually sodium or potassium hydroxide which has already been mixed with the alcohol.

Transesterification reaction is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except than an alcohol is used instead of water. This process has been widely used to reduce the viscosity of triglycerides. The transesterification reaction is represented by the general equation as in Figure 2.1. The transesterification reaction of the palm oil and rice-bran oil in the supercritical ethanol proceeds under the same reaction mechanism as that of using liquid ethanol, the reaction proceeds without any catalyst as in Figure 2.1 at the vigorous conditions. Where R^1, R^2, R^3 are alkyl groups with chain lengths ranging mainly from C_{16} to C_{18}. Theoretically, transesterification reaction is equilibrium reaction. In this reaction more amount of ethanol was used to shift the reaction equilibrium to the right side and produce more ethyl esters as the proposed product.

$$\begin{array}{l} CH_2COOR^1 \\ CHCOOR^2 \\ CH_2COOR^3 \end{array} + 3ROH \xrightleftharpoons{\text{Catalyst}} \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} + \begin{array}{l} R^1COOCH_3 \\ R^2COOCH_3 \\ R^3COOCH_3 \end{array}$$

100 pounds	10 pounds	10 pounds	100 pounds
Oil or Fat	Alcohol(3)	Glycerin	Biodiesel(3)

Figure 2.1 The chemical reaction for base catalyzed biodiesel production.

The most of conventional methods for biodiesel production use a basic or acidic catalyst. With acidic catalyst, a reaction of 1-45 hours was necessary for the formation of the respective esters and by basic catalyst [1], it is somewhat faster depending on the temperature and pressure, but it still takes 1-8 hours for a reaction [2]. In addition, a removal of both catalysts and the by-reaction saponified products after the reaction is very difficult.

It is, thus, of great interest from a practical point of view to study a practically possible process without using any catalyst. In this work, therefore, we have made a fundamental study on the transesterification of the palm oil in supercritical ethanol to investigate the possibility of converting the triglycerides of palm oil to ethyl esters as biodiesel fuels. The supercritical ethanol method, therefore, offers a potentially low cost method with simpler technology for producing an alternative fuel for compression ignition engines.

Two raw materials are ready needed for making biodiesel. Ethanol and vegetable oil are available readily in our nation. For the next section, the statuses of both raw materials will be given in detail.

2.3 Raw material

2.3.1 Ethanol

Ethanol (ethyl alcohol, grain alcohol, EtOH) is a clear, colorless liquid with a characteristic, agreeable odor. In dilute aqueous solution, it has a somewhat sweet flavor, but in more concentrated solutions it has a burning taste. Ethanol, CH_3CH_2OH, is an alcohol, a group of chemical compounds whose molecules contain a hydroxyl group, -OH, bonded to a carbon atom. In Thailand, ethanol can be produce by cassava roots and molasses. Recently, the government has shifted its focus to promote ethanol production by private companies for use as alternative fuel. The ethanol properties shown as Table 2.3 [6].

Table 2.3 Ethanol's properties [6].

Ethanol properties.	
Formular	C_2H_5OH
Molecular weight	46.07
Tc	242.65°C
Pc	63.60 bar
Density	0.79 g/ml

2.3.2 Palm oil

The oil palm, *Elaeis guineensis*, which originated from West Africa. Its use as a crop was not developed until 1917, when it was grown commercially. The modem expansion of the industry can be traced back to the 1960s when the Malaysian Government embarked on a massive programme of agricultural diversification. Palm oil and palm oil products are employed in numerous food and non-food applications. They can be used as frying media and for making margarines, shortenings, soap, oleochemicals and other products such as biodiesel. However, unlike fossil reserves, different regions of the world have their own vegetable oil resources that could be exploited for biodiesel production. Biodiesel has been produced from a variety of sources including refined and vegetable oil, and animal grease or tallow.

Thailand has a rich oil palm that generates excess crude palm oil (CPO), in vast quantities for consumption. CPO is one of the four leading vegetable oil traded on the world market. It is also cheaper than canola, rapeseed or soybean oil and would reduce the overhead cost of biodiesel production and generate a ready supply of diesel fuel substitute or blend. Table 2.4 [7, 8] shows that the status of palm oil in Thailand. Table 2.5 [9] shows the prices of palm oil in Thailand.

Table 2.4 Palm oil status in Thailand [7, 8].

Year	Productivity (million tons)
1992	0.25
1993	0.35
1994	0.35
1995	0.40
1996	0.48
1997	0.45
1998	0.35
1999	0.71
2000	0.60
2001	0.60

Table 2.5 Prices of palm oil in Thailand [9].

Year	Prices ($/kg)
1996	0.38
1997	0.40
1998	0.65
1999	0.46
2000	0.32
2001	0.22

Table 2.6 [10] shows that the fatty acid com position of CPO used in this study was within the range specified by the Palm Oil Research Institute of Malaysia (PORIM).

Table 2. 6 Quality characteristics of crude palm oil [10].

Parameters	PORIM specification
Moisture (%w/w)	ND
Acid value (mg KOH/g)	ND
Fatty acid composion	
Lauric	0-0.40
Myristic	0.60-1.60
Palmitic	41-47
Palmitoleic	0-0.60
Stearic	3.70-5.60
Oleic	38.20-43.50
Linoleic	6.60-11.90
Linolenic	0-0.50
Arachidic	0-0.80
Mean molecular weight (g)	847.30
Unsaturated fatty acids (%)	44.80-57.30
Saturated fatty acids (%)	45.30-55.40

2.3.3 Rice-bran oil

Rice bran which is obtained as a by-product in the milling of brown rice kernel to yield the familiar white rice, has an oil content that varies from 12 to 23%, depending on variety of rice and degree of milling. Table 2.7 [11] shows that the fatty acid composition of rice-bran oil used in this study

Table 2.7 Quality characteristics of rice-bran oil [11].

Parameters	Value
Specific gravity	0.92
Smoke point	490°C
Fatty acid composion	
Myristic	0.40-0.60
Palmitic	11.70-16.50
Stearic	1.70-2.50
Oleic	39.20-43.70
Linoleic	26.40-35.10
Lignoceric	0.40-0.90
Arachidic	0.40-0.60
Saponification value	186
Iodine value	99.60
Unsaponificable value	0.01% as oleic

2.4 Literature reviews

Some researchers reported kinetics for both acid and alkali-catalyzed transesterification reactions. Freedman and coworkers reported transesterification reaction of soybean oil with alcohol, and examined in their study were the effects of the type of alcohol, molar ratio, type and amount of catalyst and reaction temperature on rate constants and kinetic order. The reactions appear to be pseudo-first order or second order depending upon conditions used. At a molar ratio of methanol to soybean oil of 6:1, a shunt reaction was observed. The activation energy was determined as 83.64 kJ/mol [2]. Saka and Kusdiana reported the method involves uncatalyzed transesterification reaction and a kinetic study of rapeseed oil in supercritical methanol. Runs were made in a batch-type reaction vessel ranging form 200°C in subcritical temperature to 500°C at supercritical state with different molar ratios of methanol to rapeseed oil to determine rate constants by employing a simple method. As a result, the conversion rate of rapeseed oil to its methyl esters was found to increase dramatically in the supercritical state, and reaction temperature of 350°C was considered as the best condition, with the molar ratio of methanol in rapeseed oil being 42. The activation energy was determined as 69.29 kJ/mol [3, 4]. Diasakov and coworkers reported kinetics on uncatalytic transesterification reaction of soybean oil. The experimental have been carried out at 220 and 235°C with various molar ratio between methanol to soybean oil. It is observed that methyl ester content has surpassed 85wt% after 10 hour of reaction time at 235°C and 67wt% after 8 hour at 220°C. The calculated activation energy about 117 kJ/mol [12]. However, the kinetic study of palm oil with ethanol in and supercritical condition without catalyst has not yet been presented.