CHAPTER II

THEORIES AND LITERATURE REVIEW

2.1 Biofuel

Biofuel is a liquid or gaseous fuel that is predominantly produced from biomass and used in the transport sector. Biofuels are generally considered to offer many advantages: sustainability, the reduced greenhouse gas emissions, regional development, and a security of supply. In developing countries, such as Thailand, there is a growing trend towards employing modern technologies and bio-energy. Biofuel, in particular, is becoming a more attractive alternative to fossil fuels as it becomes more cost competitive.

Biomass has been recognized as a major world renewable energy source that can help to decrease the world's dependence on our limited fossil fuel resources. Renewable resources have the additional advantage of being more evenly distributed than fossil fuel resources (Demirbas, 2006). Biodiesel is one alternative renewable resource that can be used to replace fossil fuel. It is an environmentally friendly alternative fuel that can be used without engine modification.

There has been renewed interest in the use of vegetable oils as an alternative fuel. More than 100 years ago, Rudolph Diesel tested vegetable oil as fuel for a diesel engine. The use of vegetable oil has regained interest because of the environmental benefits and the fact that it is made from renewable resources (e.g., soy beans, peanuts, sunflowers, rape seeds, coconuts, karanja, cotton, mustard, jatropha, linseed, and coster) (Srivastava et al., 2000, Demirbas et al., 2003 and Murugesan et al., 2008).

2.2 Palm Oil

Palm oil is a form of edible vegetable oil obtained from the fruit of the oil palm tree. In 2004, palm oil was the second-most widely produced edible oil, after soybean oil; 28 million metric tons were produced worldwide. The better species is the one originating in Africa, named *Elaeis guineensis*.

The palm fruit is the source of both palm oil and palm kernel oil. Palm oil is derived from the mesocarp of the fruit (i.e., it is extracted from the fruit flesh),

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while palm kernel oil (PKO) is derived from the kernel of the fruit (i.e., it is extracted from the fruit seeds). Palm oil can be separated by physical processes into two fractions, solid (palm stearin) and liquid (palm olein), while palm kernel oil is a sharp melting fat at ambient temperatures. Palm oil consists mainly of palmitic acid, stearic acid, oleic acid, and linoleic acid. PKO has a higher content of shorter chain fatty acids; lauric acid, and myristic acid. The average fatty acid compositions in palm oil are shown in Table 2.1.

Table 2.1 Fatty Acid Compositions of Palm Oil

Fatty Acid (wt.-%)	Structure [a]	Formula	Palm Oil
Laurin acid	12:0	$C_{12}H_{24}O_2$	-
Myristic acid	14:0	$C_{14}H_{28}O_2$	0.6-2.4
Palmitic acid	16:0	$C_{16}H_{32}O_2$	32-46.3
Stearic acid	18:0	$C_{18}H_{36}O_2$	4-6.3
Oleic acid	18:1	$C_{18}H_{34}O_2$	37-53
Linoleic acid	18:2	$C_{18}H_{32}O_2$	6-12
Linolenic acid	18:3	$C_{18}H_{30}O_2$	-
Arachidic acid	20:0	$C_{20}H_{40}O_2$	-

[a] *xx: y* indicates *xx* carbons in the fatty acid chain with *y* double bonds.

Sources: Srivastava et al., 2000, BaJPAI et al., 2006, and The official of Site of the National Biodiesel Board, 2007

Palm oil is of interest both commercially and technically for the following reasons (Srivastava et al., 2000):

- It is readily available.
- It is economically priced. Refined palm oil is comparably much cheaper than partly hydrogenated soybean oil.
- It is a source of the solid fat needed for the functionality of many food fats, without the cost of hydrogenation and the concomitant formation of trans fatty acid.
- Palm midfraction is a major component of cocoa butter equivalent fat.

- Palm and palm olein have good stability at frying temperatures.
- The recent trend to minimize the trans fatty acid content in consumer products has led to increasing use of inter-esterification with palm stearin as the hard stock in the mixture.

2.3 Alternative Fuel for Diesel Production Processes

There are four techniques for using vegetable oil, animal fat oil, and waste oil as alternative fuels: the direct use or blending with fossil diesel, pyrolysis, transesterification, and microemulsion.

2.3.1. Direct Use or Blending

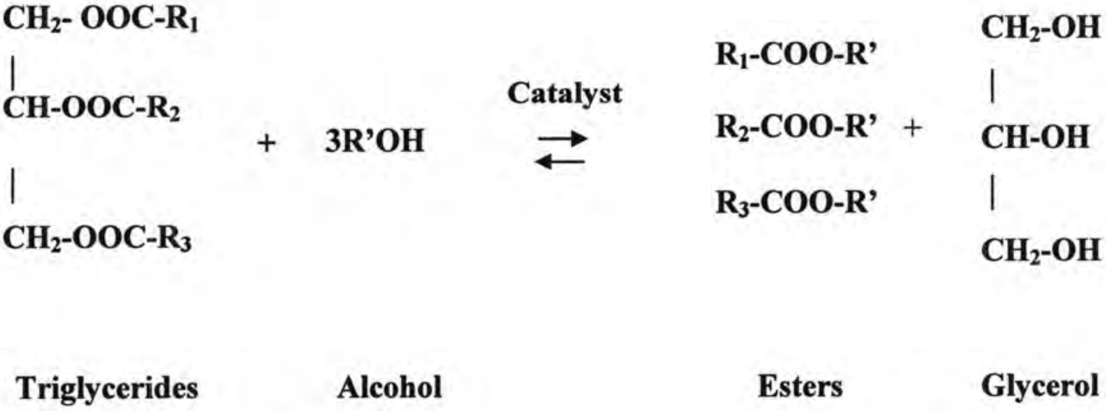
The direct use or blending process uses vegetable oil as the alternative fuel directly without any transformation or blend vegetable oils with petroleum diesel. In the 1980s, people began using vegetable oil as fuel. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blending of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up a 50/50 ratio (Ma and Hanna, 1999). The direct use of vegetable oils and its blends with diesel fuel as alternative fuels have been considered to be unsatisfactory for both direct and indirect diesel engines due to the high viscosity, acid composition, and free fatty acid content in the fuels as well as the gum formation during storage and combustion, carbon deposits, and lubricating oil thickening that occurs.

2.3.2 Pyrolysis Technique

Pyrolysis is the conversion of one substance into another by means of heat oxygen and the cleavage of chemical bonds to yield small molecules. The pyrolysis of triglycerides aims to obtain products suitable for diesel engines. The thermal decomposition of triglycerides produces alkanes, alkenes, alkadienes, aromatics, and carboxylic acids. However, pyrolysed vegetable oils process is found to be acceptable for the properties of amounts of sulphur, water content, and sediment and copper corrosion values, but unacceptable for the properties of amounts of ash and carbon residue and pour point. In addition, engine tests using pyrolysed oil have been limited to short-term tests (Srivastava and Prasad, 2000).

2.3.3 Transesterification Technique

Transesterification (also called alcoholysis) is the reaction of a fat or oil with alcohol to form esters and glycerol. The reaction is shown in Fig.2.1. A catalyst is usually used to improve the reaction rate and yield. The alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are used most frequently in the reaction. The stoichiometry of this reaction thus requires a 3:1 molar ratio of alcohol to triglycerides. In practice, the ratio needs to be higher to drive the equilibrium to the maximum ester yield. The reaction can be catalyzed by alkalis, acid, or enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium, and potassium alkoxides. Alkali-catalyzed transesterification is much faster than acid-catalyzed and is most often used (Ma and Hanna, 1999). Vegetables oils that are used in the production of alternative diesel engine fuel by transesterification include soy bean, palm, sunflower, peanut, and olive oils. These oils are gaining an interest due to the rapid decline of the crude oil reserve. Some properties of some vegetable oils produced using the transesterification technique closely resemble those of standard diesel fuel. Table 2.2 compares the properties of transesterification-produced palm kernel oil with those of petroleum diesel (Alamu et al., 2007).



$$\begin{array}{l} CH_2\text{-}OOC\text{-}R_1 \\ | \\ CH\text{-}OOC\text{-}R_2 \\ | \\ CH_2\text{-}OOC\text{-}R_3 \end{array} + 3R'OH \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} \begin{array}{l} R_1\text{-}COO\text{-}R' \\ R_2\text{-}COO\text{-}R' \\ R_3\text{-}COO\text{-}R' \end{array} + \begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array}$$

Figure 2.1 Transesterification of Triglycerides with Alcohol

Table 2.2 The Properties of Palm Kernel Oil Biodiesel and Petroleum Diesel

Fuel Properties and Parameters	Palm Kernel Oil Biodiesel Properties	Petroleum Diesel
Viscosity (@ 40 °C) (cst)	4.839	2.847
Specific gravity (@ 60 °F/60 °F)	0.883	0.853
Pour point (°C)	2	-16
Cloud point (°C)	6	-12
Flash point (°C)	167	74
Sulphated ash content (wt%)	0.018	0.038
Gross heat of combustion (MJ/kg)	40.56	45.43
Net heat of combustion (MJ/kg)	37.25	42.91

Source: Alamu et al., 2007

2.3.4 Microemulsion Technique

Microemulsion involves the isotropic, clear, or transparent stable dispersion of the oil, water, surfactant, and cosurfactant. Biofuel produced by microemulsion technique can be made of vegetable oil with an ester and dispersant (cosolvent), or of vegetable oils, an alcohol, and a surfactant, with or without diesel fuels in order to improve heating value because the alcohol content has a lower volumetric heating value than diesel fuels. However, alcohols have a high latent heat of vaporization and tend to cool the combustion chamber, which reduces nozzle coking (Srivastava and Prasad, 2000). This method can solve the problem of the high viscosity of vegetable oil (Ma and Hanna, 1999). In microemulsion formation, the stability of the emulsion is determined by the energy put into it and the type and amount of emulsifier. Microemulsion fuel can reduce air pollution, improve combustion efficiency and decrease the amount of fuel oil consumed by 5-10%. Moreover, microemulsified fuel can reduce the emission of smoke by 40-77% and reduce that of nitrogen oxide and carbon monoxide by 70-75% (Zhao et al., 2006).

2.4 Surfactant

Surfactants are among the most versatile products of the chemical industry, appearing in such diverse products as motor oils, pharmaceuticals, paint, cosmetics, detergents and so on. A surfactant, a contraction of the term "surface active agent," is made up of amphipathic molecules consisting of two dissimilar groups, a hydrophilic (water-loving) part and a hydrophobic (water-hating) part. The hydrophilic part is an ionic or highly polar group, while the hydrophobic part is usually a long chain hydrocarbon or a non-polar group. Figure 2.2 illustrates the basic structure of a surfactant. The hydrophilic part can be nonionic, ionic, or zwitterionic (a combination of the cationic and anionic groups) that has a strong attraction with polar environments, such as water, while the hydrophobic part comprises a long chain hydrocarbon that is attracted to nonpolar environments, for example oil (Rosen, 2004). Consequently, surfactants can dissolve either in water or oil and have the capability of solubilizing water or oil to create a homogeneous system. The surfactant that is used to form microemulsion fuel should not initiate soot formation and should not contain sulphur and nitrogen (Lif et al., 2006).

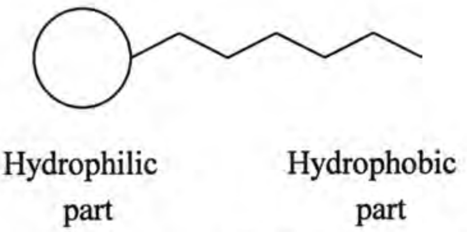


Figure 2.2 Structure of a Surfactant Molecule

2.5 Solubilization

Solubilization is the one of important properties of a microemulsion system. This property is directly related to the micelle formation of the surfactant. It may be defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by a reversible interaction with a micelle of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamically activity in the solubilized material (Rosen, 2004).

2.6 Microemulsion

Microemulsion is a transparent dispersion containing two immiscible liquids with size of 10-100 nm (0.01-0.1 μm) diameters that are generally obtained upon mixing the ingredients gently of oil and water in the presence of surfactants. They are thermodynamically stable isotropic dispersions of otherwise immiscible oil and water stabilized by a surfactant. Normally, microemulsion consists of at least three components: water, oil, and one or more surfactants or with a mixture of a surfactant and a cosurfactant (e.g., a polar compound of intermediate chain length).

A cosurfactant is another component which plays role on preventing the formation of rigid structures such as gels, liquid crystals, and precipitation. A cosurfactant can lower the system's viscosity, reduce interfacial tension, increase the fluidity of the interface, increase the entropy of the system, and influence the solubility properties of the aqueous and oleic phases due to its partition between the phases. As a consequence of these advantages, microemulsion has rapidly grown in use through its many applications such as in enhanced oil recovery, pharmaceuticals, cosmetics, and fuels (Bidyut and Satya, 2001).

2.7 Diesel Engine Operation

Engine performance with the different blends of diesel and biodiesel and their emission characteristics depend on how the engine related parameters (e.g., the combustion chamber and injector nozzle designs, injection pressure, air turbulence, air-fuel mixture quality, and actual start of combustion) interact with the properties of the fuels (Murillo et al, 2007). Moreover, since each parameter varies with the speed and load, the emissions are usually measured by using different operational parameters of utility for determining the overall emissions and performance of the engine with the various fuels.

The important characteristics of diesel fuel and biodiesel that were under consideration are listed in Table 2.3. Standard conventional diesel fuel and biodiesel that are suitable for running the diesel engine are listed in Table 2.4.

Table 2.3 Important Characteristics of Diesel Fuel

Fuel Characteristics	**Descriptions and facts**
Cetane number: a measure of the ignition quality of diesel fuels	(a) A high cetane number implies a short ignition delay. (b) Higher molecular weight normal alkanes have high cetane numbers. (c) It influences both gaseous and particulate emissions. (d) The cetane index which is very close to the cetane number is calculated based on 10, 50, and 90% distillation temperatures and specific gravity.
Heat of combustion: a measure of the energy available in a fuel	(a) A critical property of fuel intended for use in weight-limited vehicles.
Flash point: a measure of the tendency of oil to form a flammable mixture with air	(a) It indicates the presence of highly volatile and flammable materials. (b) It is used to assess the overall flammability hazard of a material.
Viscosity	(a) Proper fuel viscosity is required for the proper operation of an engine. (b) It is important for the flow of oil through pipelines and injector nozzles. (c) The effective atomization of fuel in the cylinder requires a limited range of viscosity of the fuel to avoid excessive pumping pressures.
Water and sediment	(a) They attribute to the corrosion of equipment.
Copper-strip corrosion: a measure to assess the relative degree of corrosivity	(a) It indicates the presence of sulphur compounds.

Table 2.3 Important Characteristics of Diesel Fuel (continued)

Fuel Characteristics	**Descriptions and Facts**
Cloud point, pour point cold-filter plugging point: a measure of the performance of fuels under cold temperature conditions	(a) It is used as a quality control specification or low temperature handling indicator for large storage tanks and pipelines at refineries and terminals.
Carbon residue	(a) It correlates with the amount of carbonaceous deposits in the combustion chamber. (b) Greater carbon deposits are expected for higher values of carbon residue.
Ash	(a) It results from oil, water-soluble metallic compounds or extraneous solids, such as dirt and rust. (b) It can be used to decide a product's suitability in a given application.
Sulphur	(a) It is controlled to minimize corrosion and wear and tear. (b) It causes environmental pollution from its combustion products. (c) It is corrosive in nature and causes physical problems in engine parts.

Source: Srivastava et al., 2000.

Table 2.4 Standard Properties of Petroleum Diesel and Biodiesel

Properties	**Diesel Fuel No.2 (Grade Low Sulphur)**	**Biodiesel**
Flash point, (°C), min	52	93
Water and sediment, % vol, max	0.05	0.05
Kinematic viscosity (mm^2/sec), at 40 °C	1.9-4.1	1.9-6.0
Ash, % mass, max	0.01	0.02
Sulphur, % mass, max	0.05	0.015
Copper strip corrosion rating max 3, at 50 °C	No. 3	No. 3
Cetane number	40	47
Cloud point	No report	No report
Carbon residue, % mass, max	0.35	0.05

Source: American Standard Testing Method (ASTM D975 and ASTM D6751)

2.8 Literature Review

Ali and Hanna (1994) reviewed four methods for preparing diesel like fuel from vegetable oil and animal fats. The four methods were transesterification, pyrolysis, dilution, and microemulsion. They found that the stability of the product prepared by the microemulsion technique is determined by the energy put into it and the type and amount of emulsifier or surfactant. The properties of the microemulsion fuel provided lower viscosity and heating values, but a higher cetane number when compared to diesel fuel No. 2.

Bidyut and Satya (2001) reported that one of microemulsion applications is fuel production. They found that microemulsion properties can reduce soot formation from water in the oil during combustion due to the stability of microemulsion. When water is vaporized during combustion, heat is released and the combustion temperature is lowered. As a direct consequence, the emissions of nitrogen gas and carbon monoxide also decrease.

Dantas and Neto (2001) studied a new microemulsion system containing diesel and different percentages of vegetable oils (i.e., soy bean, palm, and ricin) that can be used as alternative fuels in order to solve the combustion emissions problem. The main parameters that influence a microemulsion system were studied in this work such as the nature of the surfactant and cosurfactant, C/T ratio, and composition of the oil phase. The surfactants that were selected for this work were Texapon HBN (sodium laurylsulfate) and Comperlan SCD (coconut fatty acids diethanolamide). Ethyl, propyl, and isoamyl alcohol were used as cosurfactants. The results showed that it is possible to obtain microemulsion systems with different oil phase compositions (mixtures of diesel and vegetable oils) to create alternative fuels.

Lin et al. (2003) studied the fuel properties of three-phase emulsion as an alternative fuel for diesel engines. The aim of this experiment was to investigate the emulsification characteristics and fuel properties of three-phase emulsion for the possibility of using the resulting fuel as an alternative for diesel engines. Two commercial surfactants, Span 80 (a lipophilic surfactant with HLB = 4.3) and Tween 80 (a hydrophilic surfactant with HLB = 15), were used to prepare the three-phase emulsion: oil-in-water-in-oil, briefly denoted as O/W/O emulsions. The result showed that the drop size of the O/W/O emulsion was reduced by increasing the homogenizing the machine's revolution speed. HLB values of 6-8 produced more stable O/W/O three-phase emulsions, and thus are more suitable for use as diesel fuel.

In addition, they also studied the effects of the emulsification variable on fuel properties of two- and three-phase biodiesel emulsions. In this study, the emulsification technique was considered as a way of reducing the nitrogen emissions of fossil fuel. The biodiesel used in this experiment was prepared by a transesterification reaction with a peroxidation process, and was emulsified to form two-phase and three-phase emulsions. Tween 80 and Span 80 were the surfactants used in this work. The experiment result revealed that the HLB surfactant mixture of 13 was able to form stable emulsification. The fuel properties of the kinematic viscosity and specific gravity of the biodiesel emulsion were higher than those of neat biodiesel. In addition, the neat biodiesel had the least amount of carbon residue formation among the other kinds of fuel because of the incomplete burning of surfactants Span 80 and Tween 80, which are primarily composed of the elements C and H.

Zhao et al. (2006) studied the preparation and application of diesel microemulsion. They examined the formation of water in oil (W/O) in microemulsion with a water phase and a diesel oil phase by using cationic surfactants, oleinic and linoleinic acid, and an alcoholic cosurfactant. The factors that influenced the amount of solubilizing water in the microemulsion system were determined. The experimental results show that the quantities of ammonia, alcohol and the concentration of inorganic salt have effects on the formation of the microemulsion. Moreover, this studied found that the mixed surfactant was superior to the single surfactant. The amount of solubilizing water could be increased greatly by adding a small amount of the cationic surfactant into the anionic surfactant.

Lif and Holmberg (2006) reported that the presence of water in diesel emulsion has significant positive effects on the combustion of fuel: reduced nitrogen oxides (NO_x) emission, lower soot and particulate contents in the exhaust, and improved combustion efficiency. It has been reported that the presence of water in diesel at 15% can give a reduction in nitrogen oxides emission up to 35%. However, it relates to diesel with very low nitrogen content. Although the presence of 15-45% water content can reduce the NO_x and soot emissions, CO and hydrocarbon emissions also increase with the water content. The majority of water in fuel emulsion relates to diesel and other hydrocarbon fuels, but there are also a few papers that deal with the combustion characteristics and emissions from the emulsion of water in vegetable oils. In a case study on the water in biodiesel, palm oil emulsions were compared with diesel emulsion in engine performance, fuel consumption, and wear resistance. It was found that microemulsion biofuel containing 15% water gave lower NO_x and smoke emission than plain biodiesel, which is in line with a comparison of the emissions from water in diesel and neat diesel.

Kerihuel et al. (2006) studied the effectiveness of improving the combustion of low quality animal fat by making stable emulsions with water. An animal fat emulsion was prepared by mixing fat with water, a surfactant, and a cosurfactant. In this study, ethanol was the cosurfactant and SPAN 83 (Sorbitan Sesquiolate) was the surfactant. The investigated cosurfactant and surfactant ratios (C/S ratio) were C/S =1, C/S = 5, and C/S = 10. And the factors, such as the stirring speed, that affected the emulsion structure were also studied. They found that a number of parameters affect the emulsion's characteristics. The suitable stirrer speed was 500 rpm to make the animal fat emulsion, and a C/S ratio of 10 was optimal. The optimum emulsion was found to contain 36.4% of ethanol, 3.6% of SPAN 83, 10% of water, and 50% of animal fat by volume.

Kwanchareon et al. (2007) studied the phase diagram of diesel-biodiesel-ethanol blends at different levels of ethanol purity and different temperatures. Fuel properties were examined and compared to fossil diesel. Ethanol at 95%, 99.5%, and 99.9%; diesel fuel; and biodiesel (palm oil methyl ester) were used in this work. The composition of ethanol 99.5% was chosen to blend with diesel and biodiesel in order to study fuel properties. This composition was found to be close to the standard limit for diesel fuel. However, the flash point of blending containing ethanol was different from that of the diesel and the cetane value of the blended biodiesel was decreased by the presence of ethanol. With regard to the emissions from the prepared diesel's combustion, CO and HC emissions were found to be reduced, whereas NO_x were higher than the levels found for fossil diesel. They concluded that a blend of 80% diesel, 15% biodiesel, and 5% ethanol was the most suitable ratio for diesohol production.

Based on the literature review information, this research utilized the microemulsion technique to produce microemulsion biofuel. The previous works demonstrated the possibility of using this technique to produce biofuel and reduce combustion gas emissions. However, the utilization of the microemulsion technique with refined vegetable oil to produce biofuel has never been studied. The advantages of biofuel production by the microemulsion technique are its simple production and reduced exhaust emissions. Thus, this study aimed to prove that use of the microemulsion technique for biofuel preparation could be an acceptable alternative.