

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Diesel

Rudolph Diesel, a German engineer, introduced the diesel engine over a century ago. He designed the original diesel engine to run on vegetable oil. Since then a great deal of research and development has taken place, not only in the design area but also in finding an appropriate fuel. Diesel fuel, a hydrocarbon mixture obtained in the fractional distillation of crude oil between 250 and 350 °C at atmospheric pressure, plays an important role in the industrial economy of the country and frequently used on farms. This fuel runs a major part of the transport sector for its excellent drivability, thermal efficiency and cost effectiveness, and the demand is increasing steadily. At the same time, diesel engines are major contributors of various types of air pollutant emissions such as carbon monoxide (CO), oxides of nitrogen (NO_x), particulate matter (PM), and other harmful compounds.

Emission standards in Europe have forced oil refineries to dramatically reduce the level of mineral compounds and sulfur, resulting in a much cleaner-burning fuel that produces less air pollution. In the US, diesel fuel is controlled according to the American Society for Testing and Materials Standard D975-97. This standard describes a limited number of properties that diesel fuels must meet. Table 2.1 shows the property values for various grades of diesel fuel.

Table 2.1 Regular for diesel fuel oils (ASTM D 975-97)

	Grade	Grade	Grade	Grade	Grade
Property	LS #1	LS #2	No. 1-D	No. 2-D	No. 4-D
Flash point °C, min	38	52	38	52	55
Water and sediment, % vol, max.	0.05	0.05	0.05	0.05	0.50
Distillation temp., °C, 90%					
Min.	--	282	--	282	--
Max.	288	338	288	338	--
Kinematic Viscosity, mm ² /s at 40°C					
Min.	1.3	1.9	1.3	1.9	5.5
Max.	2.4	4.1	2.4	4.1	24.0
Ramsbottom carbon residue, on 10%, %mass, max.	0.15	0.35	0.15	0.35	--
Ash, % mass, max.	0.01	0.01	0.01	0.01	0.10
Sulfur, % mass, max	0.05	0.05	0.50	0.50	2.00
Copper strip corrosion, max 3 hours at 50°C	No. 3	No. 3	No. 3	No. 3	--
Cetane Number, min.	40	40	40	40	30
One of the following Properties must be met:					
(1) cetane index	40	40	--	--	--
(2) Aromaticity, % vol, max	35	35	--	--	--

Note: Grade No.1-D: A light distillate fuel for applications requiring a higher volatility fuel for rapidly fluctuating loads and speeds as in light trucks and buses.

Grade No.2-D: A middle distillate fuel for applications that do not require a high volatility fuel. Typical applications are high-speed engines that operate for sustained periods at high load.

Grade No.4-D: A heavy distillate fuel that is viscous and may require fuel heating for proper atomization of the fuel. It is used primarily in low and medium speed engines.

Low sulfur fuel is required for on-highway use with sulfur level $< 0.05\%$.

After the global fuel crises in the 1970s, many countries including Thailand have concerned their effects to oil prices and shortages. Many researches have been focused on the development of alternative fuel sources, with particular reference to the alcohols.

2.2 Alcohol

Practically, any of the organic molecules of the alcohol family can be used as a fuel. The alcohols that can be used for motor fuels are methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$) and butanol ($\text{C}_4\text{H}_9\text{OH}$).

2.2.1 Methanol

Methanol, or methyl alcohol, is the first alcohol with the molecular formula CH_3OH , a molecular weight of 32, and a boiling point of about $60\text{ }^\circ\text{C}$. Methanol can be used as one possible replacement for conventional motor fuels. The use of methanol as a motor fuel received attention during the oil crises of the 1970s due to its availability and low cost. Methanol is currently manufactured worldwide by conversion of derived from syngas (CO and H_2), natural gas, refinery off-gas, coal or petroleum. The production from these resources also produces toxic by-product, therefore, methanol is not recommended used for human consumption. In recent

years, a growing interest has been observed in the application of methanol as an alternative liquid fuel, which can be used directly for powering fuel cells. Biomass and coal can be considered as a potential fuel for gasification and further syngas production and methanol synthesis.

2.2.2 Ethanol

Ethanol, or ethyl alcohol, has the molecular formula C_2H_5OH , a molecular weight of 46.07, and a boiling point of 78 °C. There are essentially two methods used to produce ethanol. The first method manufactures from ethylene using steam. The end product is called "synthetic ethanol". The second method produces from a variety of biomass feedstocks such as sugars, starches and biomass wastes via anaerobic fermentation by yeast. The end product is called "bio-ethanol". Production of ethanol from biomass is one way to reduce both the consumption of crude oil and environmental pollution.

2.2.3 Butanol

Butanol, or butyl alcohol, is a four carbon alcohol with the molecular formula C_4H_9OH , a molecular weight of 74 and a boiling point of 116 °C. It has double the amount of carbon of ethanol which equal to a 25 percent increase in the energy content (Btu). Butanol can be produced via petrochemical route. Another method involves a biochemical process via butanol fermentation. This process can yield hydrogen - directly used for powering fuel cells - which ethanol fermentation cannot. In addition, butanol is far less corrosive than ethanol, and can be shipped and distributed through existing pipelines and filling station. Butanol when consumed in an internal combustion engine yields no SO_x , NO_x or CO all environmentally harmful byproducts of combustion.

2.3 Biodiesel

Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine. Biodiesel, a clear amber-yellow liquid, has properties similar to those of traditional fossil diesel fuel such that it can be substituted for diesel fuel with little or no engine modification (Nabi *et al.*, 2006). Biodiesel is non-flammable, and in contrast to diesel fuel it is non-explosive, with a flash point of 150 °C for biodiesel as compare to 64 °C for diesel fuel. Unlike diesel fuel, biodiesel is biodegradable and non-toxic, and it significantly reduces toxic and other emissions when burn as a fuel. It is clearly indicated that the use of biodiesel may potentially reduce the dependence on petroleum diesel fuel and improve air quality (Al-Widyan *et al.*, 2002 and Nabi *et al.*, 2006).

2.3.1 Raw Materials for Biodiesel Production

The choice of raw material depends on the yield and composition of oil in the plant, as well as the proper quantity of the plant that can be grown in a given location. There are two main types of feedstocks for biodiesel production: edible and inedible feedstocks. Biodiesel raw materials of current interest are also of the edible types, *e.g.*, palm and coconut oil. Table 2.2 summarizes the productivity of Thailand's six oil-yielding plants in a report prepared by the Office of Agricultural Economics, Ministry of Agriculture and Cooperatives. Biodiesel which is produced from food-grade vegetable oils, are more expensive than diesel fuel. Therefore, it would be useful to consider transforming inedible oils, *e.g.*, used cooking oil or *Jatropha* oil to replace palm and coconut oils, as this would yield biodiesel of lower production costs and greater benefit to the country. Using biodiesel derived from used cooking oil automatically cuts down on the reuse of cooking oil and prevents used cooking oil (which contains carcinogenic dioxin materials) from being used in animal feed preparation.

Table 2.2 Production of biofuels in Thailand (unit: thousand tons)

Year	Oil Palm	Coconut	Soybean	Peanut	Castor	Sesame
1995/1996	2,255	1,413	386	147	6	34
1996/1997	2,688	1,419	359	147	6	34
1997/1998	2,681	1,386	338	126	6	35
1998/1999	2,465	1,372	321	135	7	36
1999/2000	3,514	1,381	319	138	7	37
2000/2001	3,256	1,400	312	132	9	39
2001/2002	4,089	1,396	261	107	9	39
2002/2003	4,001	1,418	260	112	10	40

(The Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

Vegetable oil and animal fat are normally compounds of the family of triglyceride. Their structure consists of C_3H_6 molecules connected to fatty acids containing 10 to 30 carbon atoms. In general, most fatty acids in vegetable oil contain 12 to 18 carbon molecules, accounting for the different levels of saturated fatty acids in each type of oil. Biofuels are not stable, because they are easily oxidized by air and polymerize at high temperatures, resulting in a sticky substance. The iodine content is used to indicate the level of unsaturated fatty acids as well as the case of polymerization. Biofuels with high iodine contents are more likely to be polymerized. In contrast, biofuels with lower iodine contents are more suitable for use as fuels in order to prevent the formation of sticky substances in engines.

Table 2.3 Properties and compositions of fatty acids in biofuels

Oils	Oils Iodine Content	Composition of Fatty Acids						
		C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3
Palm	14.1-21.0	ND-0.5	0.5-2.0	39.3-47.5	3.5-6.0	36.0-44.0	9.0-12.0	ND-0.5
Palm Olein	>=56	0.1-0.5	0.5-1.5	38.0-43.5	3.5-5.0	39.8-46.0	10.0-13.5	ND-0.6
Palm Sterine	<=48	0.1-0.5	1.0-2.0	48.0-74.0	3.9-6.0	15.5-36.0	3.0-10.0	0.5
Palm Kernel	50.0-55.0	45.0-55.0	14.0-18.0	6.5-10.0	1.0-3.0	12.0-19.0	1.0-3.5	ND-0.2
Coconut	6.3-10.6	45.1-53.2	16.8-21.0	7.5-10.2	2.0-4.0	5.0-10.0	1.0-2.5	ND
Peanut	86-107	ND-0.1	ND-0.1	8.0-14.0	1.0-4.5	35.0-67.0	13.0-43.0	ND-0.3
Physic Nut	101	ND	ND	14.9	6	41.2	37.4	ND
Rape Seed	94-120	ND	ND-0.2	1.5-6.0	0.5-3.1	8.0-60.0	11.0-23.0	5.0-13.0
Soybean	124-139	ND-0.1	ND-0.2	8.0-13.5	2.0-5.4	17.7-28.0	49.8-59.0	5.0-11.0

ND =Not detected.

Note: The numbers denote the number of carbons and double bonds.

For example, C18:1 stands for 18 carbons and 1 double bond.

(The Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

Knothe (2005) studied the dependence of biodiesel fuel properties on the structure of fatty acid alkyl ester. He proposed that structure features that influence the physical and fuel properties of a fatty ester molecule are chain length, degree of unsaturation and branching of the chain. The results showed that cetane numbers decrease with increasing unsaturation and increase with increasing chain length.

2.3.2 Biodiesel Production via Trasesterification Process

Trasesterification is a process of using an alcohol (*e.g.* methanol, ethanol, propanol or butanol) in the presence of a catalyst usually a strong base, such as sodium or potassium hydroxide (NaOH, KOH), to chemically break the

triglyceride molecule into methyl (ethyl, propyl or butyl) esters of the renewable oil with glycerol as a by-product. The reaction is shown below:

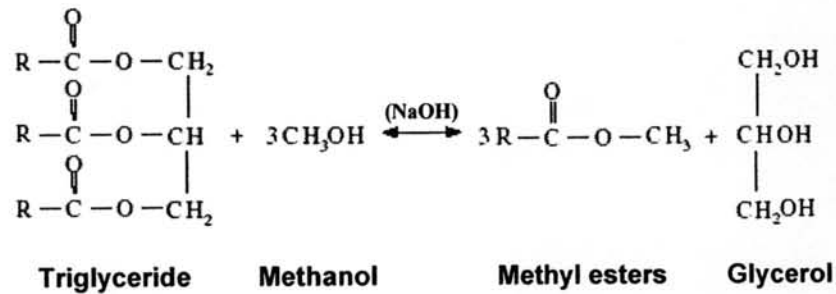


Figure 2.1 Transesterification of triglycerides and methanol results in methyl ester – the desired biodiesel fuel – with glycerol as the by-product (Vicente *et al.*, 2004).

where R is long hydrocarbon chain, sometime called fatty acid chain.

Biodiesel produced from cooking oil and methanol is called cooking oil methyl ester. The name will change along the type of oil and alcohol raw materials. For example, in Europe, biodiesel produced from rapeseed oil and methanol is called rapeseed oil methyl ester.

Methanol is the commonly used alcohol in this process, due to its low cost. The use of methanol is advantages as it allows the simultaneous separation of glycerol. The same reaction using ethanol is more complicated as it requires a water-free alcohol, as well as oil with low water content, in order to obtain glycerol separation (Demirbas, 2005). However, ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biodegradable.

Lang *et al.* (2001) prepared the methyl, ethyl, 2-propyl and butyl esters and characterized for their physical and fuel properties. They found that butyl esters showed reduced cloud points (-6 °C to -10 °C) and pour points (-13 °C to -16 °C) similar to those of summer diesel fuel having cloud and pour points of -8 °C and -15 °C, respectively.

2.3.3 Variable Affecting Transesterification Reaction

- *Effect of free fatty acid and moisture*

The free fatty acid (FFA) and moisture inhibit the vegetable oil transesterification process. The triglycerides should have lower acid value and all materials should be substantially anhydrous. When the reaction conditions do not meet the above requirements, ester yields are significantly reduced. Special processes are required if the oil or fat contains significant amounts of FFAs. Used cooking oils typically contain 2-7% FFAs and animal fats contain about 5-30% FFAs. When an alkali catalyst is added to these feedstocks, the FFAs react with the catalyst to form soap and water, as shown in the reaction below:

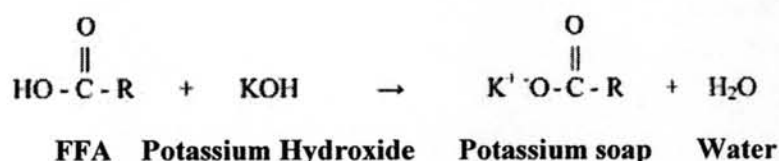


Figure 2.2 Saponification of free fatty acid and alkali catalyst results in alkali soap and water. (Gerpen, 2005)

Up to about 5% FFAs, the reaction can still be catalyzed with an alkali catalyst, but additional catalyst must be added to compensate for the catalyst lost to soap. The soap that is created during the reaction is either removed with the glycerol or is washed out during the washing step. When the FFA level is above 5%, the soap inhibits separation of the methyl esters and glycerol and contributes to emulsion formation during the washing step. For these cases, an acid catalyst, such as sulfuric acid, can be used to esterify the FFAs to methyl esters, as shown in the following reaction:

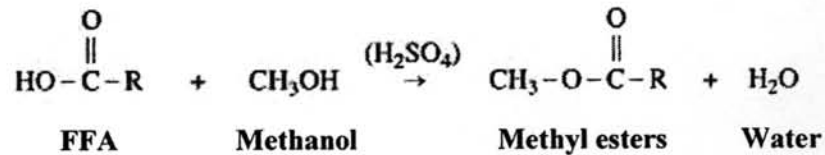


Figure 2.3 Esterification of free fatty acid with methanol results in methyl ester – the desired biodiesel fuel – with water as the by-product (Gerpen, 2005).

This process can be used as a pretreatment to convert the FFAs in high FFA feedstocks to methyl esters and thereby reduce the FFA level. Then the low FFA pretreated oil can be transesterified with an alkali catalyst to convert the triglycerides to methyl esters.

Zhang *et al.* (2003) have reviewed the commonly used procedures for producing biodiesel; including a process simulation using the commercial software package HYSYS. Their economic assessment indicated that the use of waste cooking oil feedstocks provided a higher rate of return than refined vegetable oils even after including the additional capital and operating costs of acid-catalyzed pretreatment.

The primary criterion for biodiesel quality is adherence to the appropriate standard. In the United States, this standard is ASTM D 6751-02. This standard gives the required extent of reaction through specifications for the total glycerol remaining in the fuel. The total glycerol is defined as the sum of the free and bound glycerol, and the bound glycerol is equal to the glycerol portion of the residual mono-, di-, and triglycerides. The amount of residual methanol, catalyst, soap, and glycerol is controlled by limits on the fuel's flashpoint, ash level, and free glycerol. When these limits are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine's durability and reliability.

- *Type and amount of catalyst*

In recent years, the use of several low molecular weight alcohols and homogeneous acid and basic catalysts for transesterification has been studied with success. A catalyst is usually used to improve the reaction rate and yield. Although, the acid catalyst has higher activity, the basic catalysts have surpassed the acid ones because the reaction is faster (only 30 min compares to 1-8 h for the acid catalysis)

(Felizardo *et al.*, 2006). The basic catalysts can be sodium or potassium hydroxide (NaOH, KOH), or sodium or potassium methoxide (NaOCH₃, KO CH₃). The amount of catalyst used in the process is another variable to take into account. In recent work (Tomasevic *et al.*, 2003), concentrations of 0.5%, 1.0% and 1.5% of KOH were studied and the optimum value found was 1% of KOH.

Felizardo *et al.* (2006) produced biodiesel (methyl ester) and investigated the effect of NaOH/frying oil mass ratio. As shown in Figure 2.4, the reaction yields after 1 h of reaction are maximized when the ratio of catalyst/oil ranges from 0.4% to 0.8%.

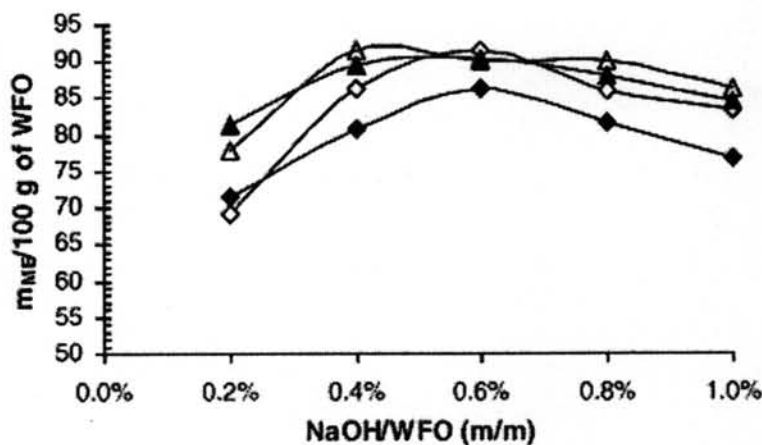


Figure 2.4 Influence of the catalyst/oil mass ratio on the yield of Biodiesel production. Experimental conditions: acid value of the oil: 0.42; reaction time: 1 h; methanol/oil molar ratio: ◆, 3.6; ◇, 4.2; ▲, 4.8; △, 5.4 (Felizardo *et al.*, 2006).

- *Molar ratio of alcohol to oil*

The alcohol/oil ratio is one of the most important variables in biodiesel production. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. Theoretically, transesterification reaction is an equilibrium reaction. In this reaction, however, more amount of alcohol was used to shift the reaction equilibrium to the right side and produce more biodiesel as the proposed product (Demirbas, 2005). On the other hand, an excessive amount of

alcohol makes the recovery of the glycerol difficult because there is an increase in solubility, so that the appropriate alcohol/oil ratio has to be established.

Freedman *et al.* (1984) prepared methyl ester and investigated the effect of alcohol/oil ratio on the %wt of product composition. They obtained a maximum conversion (98-99% of methyl esters) by transesterifying refined oil with methanol, for 1 h at 60 °C, using a molar ratio methanol/oil of 6:1 with 1% KOH or 0.5% NaOCH₃. The result is shown in Figure 2.5.

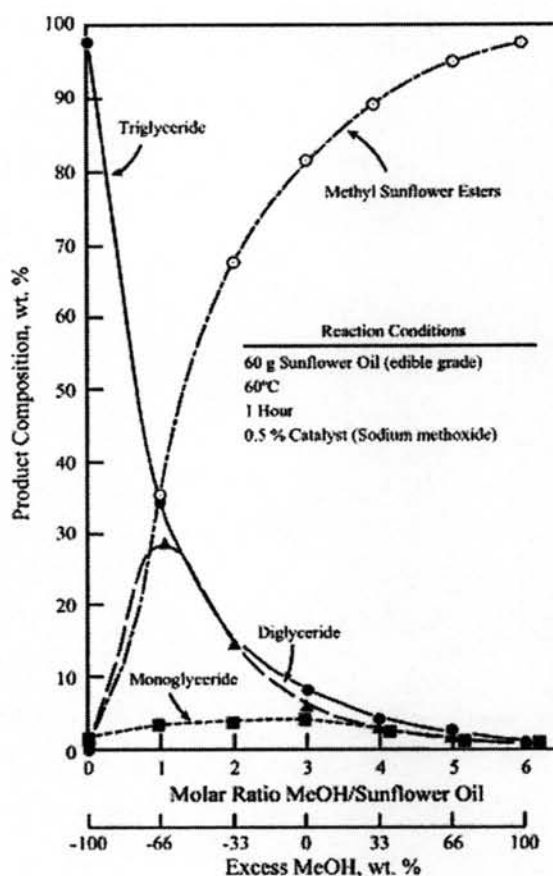


Figure 2.5 Effect of alcohol-to-oil ratio on product composition for transesterification (Freedman *et al.*, 1984).

2.3.4 Biodiesel Standard Test

In Europe and the U.S., biodiesel produced for commercial purposes is required to meet established standards. The European Union uses the BSEN 14214: 2003 standard, as shown in Table 2.4. ASTM PS 121-99 had been the standard for biodiesel quality in the US since 1999, until the endorsement of ASTM D 6751 was announced in December 2001 to govern the trade of fuel-grade biodiesel, as shown in Table 2.5. In Thailand, there is currently no established standard for biodiesel. Biodiesel produced at the Thailand Institute of Scientific and Technical Research (TISTR)'s pilot plant has been found to meet international standards, as shown in Table 2.6 (The Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004).

Table 2.4 Requirements and test methods of fatty acid methyl esters (FAME) according to BS EN 14214:2003

Property	Unit	Limits		Test method
		Min.	Max.	
Ester content	%(m/m)	96.5		EN 14103
Density at 15 °C	kg/m ³	860	900	EN ISO 3675 EN ISO 12185
Viscosity at 40 °C	mm ² /s	3.5	5	EN ISO 3104
Flash point	°C	120	-	prEN ISO 3679
Sulfur content	mg/kg	-	10	prEN ISO 20846 prEN ISO 20884
Carbon residue (on 10% transformation residue)	%(m/m)	-	0.3	EN ISO 10370
Cetane number		51		EN ISO 5165
Sulfated ash content	%(m/m)	-	0.02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg		24	EN 12662
Copper strip corrosion (3 h at 50 °C)	rating	class 1		EN ISO 2160
Oxidation stability, 110 °C	hours	6	-	EN 14112
Acid value	mg KOH/g		0.5	EN 14104
Iodine value	g iodine/100g		120	EN 14111
Linolenic acid methyl ester	%(m/m)		12	EN 14103
Polyunsaturated (≥4 double bonds) methyl esters	%(m/m)		1	
Methanol content	%(m/m)		0.2	EN 14110
Monoglyceride content	%(m/m)		0.8	EN 14105
Diglyceride content	%(m/m)		0.2	EN 14105
Triglyceride content	%(m/m)		0.2	EN 14105
Free glycerol	%(m/m)		0.02	EN 14105 EN 14106
Total glycerol	%(m/m)		0.25	EN 14105
Group I metals (Na+K)	mg/kg		5	EN 14108 EN 14109
Group II metals (Ca+Mg)	mg/kg		5	prEN 14538
Phosphorus content	mg/kg		10	EN 14107

Table 2.5 Biodiesel standard according to ASTM D 6751

Fuel properties	Requirements for biodiesel		
	Unit	Test method	Limits
1.Flash point (Closed cup)	° C	ASTM D 93	130 min
2.Water and sediment	%volume	ASTM D 2709	0.050 max
3.Kinematic viscosity at 40°C	mm/sec	ASTM D 445	1.9-6.0
4.Sulfated ash	%mass	ASTM 874	0.02 max
5.Sulfur	%mass	ASTM 5453	0.05 max
6.Copper strip corrosion		ASTM 130	No.3 max
7.Cetane No.		ASTM D 613	47 min
8.Cloud point	° C	ASTM D 2500	Report
9.Carbon residue	%mass	ASTM 4530	0.050 max
10.Acid No.	Mg KOH/g	ASTM 664	0.8 max
11.Free glycerin	%mass	ASTM D 6584	0.02
12.Total glycerin	%mass	ASTM D 6584	0.24
13.Phosphorus content	%mass	ASTM D 4951	0.001 max
14.Distillation temp.90%recovered	° C	ASTM D 1180	360 max

(The Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

Table 2.6 Properties of biodiesel from indigenous oils in Thailand

Fuel properties	Unit	Biodiesel from		
		Coconut oil	Palm kernel oil	Palm stearin
1. Flash point (Closed cup)	° C	116-120	122-134	171
2. Water and sediment	%volume	traces	traces	traces
3. Kinematic viscosity at 40 ° C	mm ² /sec	1.9-4.3	4.2-4.8	4.7
4. Sulfated ash	%mass	0.02	0.01-0.02	<0.001
5. Sulfur	%mass	0.0003	0.0004	0.0002
6. Copper strip corrosion		1a	1a	1a
7. Cetane No.		61.5-62.5	63.8	68.8
8. Cloud point	° C	1.9-4.3	-3	18
9. Carbon residue	%mass	0.01-0.03	0.021	0.03
10. Acid No.	Mg KOH/g	0.3	0.2	0.19
11. Free glycerin	%mass	ND	ND	ND
12. Total glycerin	%mass	0.07-0.23	0.01-0.08	0.13
13. Phosphorus content	%mass	ND	ND	ND
14. Distillation temp. 90% recovered	° C	343-345	342-350	352

(The Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

2.4 Diesohol

The blends between diesel and alcohol are diesohol which is ordinary diesel with 10 -15% added ethanol. Ethanol solubility in diesel is affected mainly by two factors, temperature and water content of the blends. At warm ambient temperatures dry ethanol blends readily with diesel fuel. However, below about 10 °C the two fuels separate. Prevention of this separation can be accomplished in two ways: by adding an emulsifier which acts to suspend small droplets of ethanol within the diesel fuel, or by adding a co-solvent that acts as a bridging agent through molecular

compatibility and bonding to produce a homogeneous blend. Emulsification usually requires heating and blending steps to generate the final blend, whereas co-solvents allow fuels to be “splash-blended”, thus simplifying the blending process (Hansen *et al.*, 2005).

Biodiesel is known to act as an additive for ethanol. Blending biodiesel and ethanol into a conventional diesel fuel dramatically improved the solubility of ethanol in diesel fuel over a wide range of temperature. The ethanol-biodiesel- diesel fuel blends had better properties of water tolerance and stability than ethanol-diesel blends (Shi *et al.*, 2005).

Makareviciene *et al.* (2005) studied the effect of ethanol moisture content on the solubility in tri-component systems (diesel-ethanol-rapeseed oil methyl ester and diesel-ethanol-rapeseed oil ethyl ester mixtures). As the results, the solubility limits of tri- component systems increased as the ethanol moisture content decrease. They observed that absolute ethanol (99.8%) should be used to form stable tri-component solutions.

2.4.1 Blend Properties

There are a number of fuel properties that are essential to the proper operation of a diesel engine.

- *Cold Flow*

Production of diesohol needs to evaluate dependence of intersolubility of biodiesel components upon temperature for determination of the ratio of components to obtain stable mixtures. At low temperatures components of mixtures must not separate. Two important parameters for low temperature applications of a fuel are cloud point (CP) and pour point (PP). CP is the temperature at which wax first becomes visible when the fuel is cooled. It is the temperature at which crystallization or phase separation occurs. PP is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow.

The blend between diesel and butanol could solve the problem with fuel instability at low temperature. Butanol is more soluble in diesel fuel since it has

double the amount of carbon of ethanol and lower crystallization temperature than ethanol.

- *Cetane index / cetane number*

Cetane number (CN) is a measure of ignition quality of diesel fuel. The higher the CN, the easier the fuel ignites when it is injected into the engine. Lower CNs mean longer ignition delays, allowing more time for fuel to vaporize before combustion starts. The CN is based on two compounds, namely hexadecane with a CN of 100 and heptamethylnonane with a CN of 15. The CN scale also shows that straight-chain, saturated hydrocarbons have higher CN compared to branched-chain or aromatic compounds of similar molecular weight and number of carbon atoms.

Normal diesel has a cetane number around 50. Adding 15% ethanol causes a shift down in cetane number. Incidentally high cetane number fuels have low octane numbers and vice versa. Ethanol has a low cetane number (8, and therefore a high octane number). Adding it to diesel lowers the cetane number and decreases the propensity to autoignite. Nevertheless, it is preferable to add an ignition improver such as ethylhexylnitrate or di-tert-butyl peroxide to raise the cetane number of ethanol-diesel blends.

- *Heat of combustion*

The heat of combustion of a fuel has a direct influence on the power output of the engine. The energy content of ethanol-diesel blends decreases by approximately 2% for each 5% by volume of ethanol added.

- *Emissions*

The use of ethanol in diesel fuel can yield significant reduction of exhaust emission in terms of CO and NO_x (Ajav *et al.*, 1999) and particulate matter (PM) emissions for motor vehicles (He *et al.*, 2003, Xing-cai *et al.*, 2004 and Hansen *et al.*, 2005). In Thailand, a national ethanol program to promote blending 10% of

ethanol, produced from sugarcane and cassava, in unleaded gasoline -called gasohol- without significant modification to engines has shown encouraging results.

- *Safety*

The flammability of alternative fuels during handling and storage is of particular concern when considering their introduction into existing facilities. Flammability of a fuel is typically described in terms of its flammability limits and its flashpoint. Flammability limits are the minimum and maximum concentrations of combustible vapor in air, and the temperature at which the vapor occurs, that will propagate a flame after sufficient ignition energy is provided. Flash point is the lowest temperature at which the vapor pressure of a liquid is sufficient to produce a flammable mixture in the air above the liquid surface within a vessel.

2.5 Literature Review

Lang *et al.* (2001) studied the production of biodiesel (methyl, ethyl, 2-propyl and butyl esters) from various bio-oils. Two-step transesterification was adapted for methyl and ethyl esters preparation in which glycerol formed during the first step was separated from the reaction mixture before the second step. This facilitated the reaction to nearly complete conversion in the second step. In both KOH and NaOCH₃ catalyst cases, the yields of methyl esters were 95-97% relative to the theoretical yields. However, only NaOCH₃ catalyst gave high conversion for ethyl ester. This is because ethanol ($pK_a=15.9$) and other primary alcohols are weaker acids compared to water ($pK_a=15.7$), while methanol ($pK_a=15.5$) is a slightly stronger acid. Therefore, the reaction of KOH with methanol may favor the formation of methoxide ion (the active catalytic species); the reactivity between KOH and other alcohols to form respective alkoxide anion would be very low. Although KOH was an excellent base catalyst for methyl esters, it became less effective for ethyl, butyl and 2-propyl esters.

Hansen *et al.* (2005) studied the properties and specifications of ethanol blended with diesel fuel include blend properties such as stability, viscosity and lubricity, safety and material compatibility. Ethanol solubility in diesel is affected mainly by two factors: temperature and water content of the blend. Ternary liquid-liquid phase diagrams illustrated the relative effects of moisture content and temperature on blend stability and also the increasing amounts of co-solvent required with increasing moisture and temperature to maintain a single phase liquid. The aromatic content of diesel fuel also affects the solubility of ethanol in diesel. The polar nature of ethanol induces a dipole in the aromatic molecule allowing them to interact reasonably strongly, while the aromatics remain compatible with other hydrocarbons in diesel fuel. Hence aromatics act as bridging agents and co-solvents. Reducing the aromatic content of diesel fuels will influence the miscibility of ethanol in diesel fuel and will affect the amount of additive required to achieve a stable blend. The percentage of additive required is affected by the lower limit of temperature to which the blend must be stable. Accordingly ethanol-diesel blends require fewer additives in summer conditions as compared to winter.

Makareviciene *et al.* (2005) studied the influence of the ethanol purity in the mixture of diesel fuel-ethanol-biodiesel. 94%, 98.5% and 99.8% ethanol was used. They found that intersolubility of two pairs of components, diesel fuel-biodiesel and ethanol-biodiesel, was not limited. Intersolubility of the tri-component system was limited and depended on water content. It was found that the higher purity of ethanol gives better solubility. Therefore, they recommended that ethanol with low water content should be used in diesohol production.

Sendzikiene *et al.* (2006) investigated the intersolubility of mixtures of rapeseed oil methyl esters, diesel fuel and ethanol; determined the dependence of solubility upon temperature and finally evaluated emissions of exhaust gases of these stable fuel mixtures. One of the most important parameters of diesel fuel is its stability at low temperature. The solubility of tri-component system at -10, 0 and 20 °C was investigated. The intersolubility of two pairs of components, diesel fuel-methyl ester and ethanol-methyl ester, was not limited at any of the temperatures examined. The intersolubility of diesel fuel and ethanol, however, decreased on

lowering the temperature. At -10 °C the field of solubility of the tri-component system was less than a half of that at 20 °C.

Kwanchareon *et al.* (2006) investigated the intersolubility of mixtures of palm oil methyl ester, diesel fuel and ethanol. They found that the ethanol solubility in diesel was affected by 2 factors. The first one is water content of the blends. In the case of ethanol 95%, diesel and ethanol were insoluble in each other. Therefore, it was not suitable for diesohol production. In the cases of ethanol 99.5 and 99.9%, they showed the same result. Ethanol and diesel could be mixed into a homogeneous solution at any ratio. However, since ethanol 99.5% was much cheaper than ethanol 99.9% and could be produced in our country, ethanol 99.5% was therefore chosen to blend with diesel and biodiesel. Another factor that affected the solubility is temperature. When the temperature decreased, the intersolubility of the components of diesel-biodiesel-ethanol system decreased. However, at temperatures above 20 °C there was not any problem about phase separation. They also investigated the fuel properties of the stable blends and found that the blend of 80% diesel, 15% biodiesel and 5% ethanol was the most suitable ratio for diesohol production because of the acceptable fuel properties.