CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Diesel

Diesel is a product used as a fuel in a diesel engine invented by Rudolf Diesel, and perfected by Charles F. Kettering. Diesel can be obtained from petroleum, which is called petrodiesel to distinguish it from diesel obtained from other sources. As a hydrocarbon mixture, it is obtained in the fractional distillation of crude oil between 250 and 350 °C at atmospheric pressure. Diesel is generally simpler to refine than gasoline and often costs less. However, diesel fuel often contains higher quantities of mineral compounds and sulfur. Emission standards in Europe have forced oil refineries to dramatically reduce the level of these impurities, resulting in a much cleaner-burning fuel that produces less soot. The United States has worked to reduce the emissions from gasoline-powered vehicles in the last few decades, but diesel engines have not been regulated as heavily. Diesel fuel in the U.S. is generally much less pure than European diesel, though the transition to ultra-low sulfur diesel (ULSD) will begin in 2006. Reducing the level of sulfur in diesel is better for the environment, and it allows the use of more advanced catalytic converters to reduce emissions of oxides of nitrogen (NOx). However, this also reduces the lubricity of the fuel, meaning that additives must be put into the fuel to help lubricate engines. Diesel contains approximately 18% more energy per unit of volume than gasoline, which along with the greater efficiency of diesel engines contributes to fuel economy (distance traveled per volume of fuel consumed).

In the U.S., diesel fuel is controlled according the American Society for Testing and Materials Standard D975-97. This standard describes a limited number of properties that diesel fuels must meet. It should be noted that the requirements are all performance-based. They do not mandate the composition of the fuel, only the specific performance related requirements demanded of a fuel for a diesel engine.

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

Property	Grade LS #1	Grade LS #2	Grade No. 1-D	Grade No. 2-D	Grade 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%.

ASTM D975 specifies the property values shown in Table 2.1 for these grades of diesel fuel. The surprising aspect about ASTM D 975 is how few requirements are actually included. The standard says nothing about the composition of the fuel or its source. It only defines some of the property values needed to provide acceptable engine operation and safe storage and transportation (ASTM D 975 Standard Specifications for Diesel Fuel Oils, 1997).

2.2 Ethanol

Ethanol, or ethyl alcohol, is an organic compound with the molecular formula C_2H_5OH, a molecular weight of 46.07, and a boiling point of about 78 °C. A colorless liquid, ethanol is highly flammable, giving off a smokeless, blue flame, and thoroughly mixes with water, ether, or chloroform at any proportion.

There are two processes for the production of ethanol. The first method involves a chemical process to synthesize ethanol with ethylene as the raw material. The end product is called "synthetic ethanol". The second method uses a biochemical process with agricultural products – containing starch, sugar or cellulose as the raw material. The end product is called "bio-ethanol".

Ethyl alcohol produced via a biochemical process is called bio-ethanol – or ethanol in short. Every part of agricultural products and residue can be used as raw material for ethanol. However, the production technology and yield of ethanol vary with the type of raw material, as shown in Table 2.2.

Table 2.2 Comparison of ethanol yields (by volume) from various raw materials

Raw Material (one ton)	Ethanol Yield (liters)
Molasses	260
Sugarcane	70
Fresh Cassava	180
Sorghum	70
Grains (e.g., rice, corn)	375
Coconut Juice	83

(Taken from the Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

Although a large variety of raw materials can be used to produce ethanol, only a few are suitable based by the abundance, low prices, and year-round availability. Moreover, the high yield of ethanol per unit of raw material feed and per unit area of cultivation is necessary to be concerned as well as the positive net energy balance. Finally, the raw materials should not being a rival for human food.

Based on these criteria, the choice of raw materials for producing ethanol varies from country to country. For example, in Brazil, the world's largest ethanol producer, sugarcane is the primary raw material. In the U.S., on the other hand, corn is the preferred plant. In Thailand, the National Ethanol Committee (NEC) selected three types of raw materials regarded as suitable for ethanol production: sugarcane, molasses, and cassava (The Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004).

2.3 Biodiesel

Biodiesel has been defined as the monoalkyl esters of long-chain fatty acids derived from renewable feed stocks, such as vegetable oils or animal fats, for using in compression-ignition (diesel) engines. The biodiesel is considered as a possible substitute or extender of conventional diesel fuel and commonly composed of fatty acid methyl esters that are prepared from the triglycerides in vegetable oils by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics. Biodiesel is compatible with conventional diesel and can be blended in any proportion. A number of units are manufacturing biodiesel worldwide. These units are using sunflower oil, used-frying oil, jatropha oil, etc. as a source of triglycerides (Srivastava and Prasad, 2000).

2.3.1 Biodiesel Raw Materials

Biodiesel can be produced from many kinds of raw materials, such as vegetable oil and animal fat. In the case of vegetable oil, the suitable choice of raw material depends on the composition and yield of oil in the plant, as well as the quantity of the plant can be grown in a given area. Being an agricultural country, Thailand has many kinds of oily plant such as soybean, oil palm, peanut, coconut, castor and sesame. As stated by Biodiesel Development and Promotion Strategy (18 January 2005), the main feedstock for biodiesel production is oil palm, because oil palm is a plant with high competitive potential due to its lower costs in production and marketing than other plants. Besides, palm can be utilized diversity in consumption goods. Moreover, oil palm has the highest annual yield of 4.0 million tons, followed by coconut at 1.4 million tons. Table 2.3 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. Apart from the plants mentioned, there are other sources of oil, such as the physic nut, jatropha oil, animal oil, and used fried oil, all of which can be used for biodiesel production (The Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004).

Table 2.3 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

(Taken from the Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

Although the production of oil palm is highest among Thailand's oil-yielding plants, Thailand contributes only 2.3% toward the world's production of oil palm, ranking as the fourth largest producer in 2003. Malaysia is the world's largest oil palm producer with nearly 50% of the world's production, as shown in Table 2.4.

Table 2.4 World major producers of palm oil

Country	Palm oil production during 1998-2003 (x 1000 tons)					
	1998	1999	2000	2001	2002	2003
Malaysia	8,319	10,554	10,842	11,804	11,909	13,354
Indonesia	5,361	6,250	7,050	8,030	9,200	9,750
Nigeria	690	720	740	770	775	785
Colombia	424	501	524	548	528	543
Thailand	475	560	525	620	600	630
Others	1,900	2,040	2,196	2,175	2,224	2,321
TOTAL	17,169	20,625	21,877	23,947	25,236	27,383

(Taken from 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. Vegetable oil and animal fat are composed of many kinds of fatty acids, accounting for 94-96% of the molecular weight of the triglycerides. Consequently, the chemical and physical properties of each types of oil depend on the properties of such fatty acids. 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 2.5 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.

(Taken from the Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

Biofuel usually has a heating value equivalent to 83-85% of that of diesel oil. Biofuel and animal oil have viscosity 10 times higher than diesel oil. As the temperature falls, the viscosity of biofuels increases until it forms a waxy-like substance. This phenomenon creates an obstacle when using it as fuel at low temperature. Due to the low volatility, biofuel is more difficult to ignite in the combustion chamber, thus leaving more carbon residue than the combustion of diesel oil. However, biofuel from different sources has different properties. The properties and heating value of various biofuels appear in Table 2.6.

Table 2.6 Properties and heating value of biofuels varieties, compared with diesel

Variety of Oil	**Specific Gravity (at 21 °C)(g/ml)**	**Viscosity (at 21 °C) (cp)**	**Heating Valve (kJ/kg)**
Soybean	0.918	57.2	39,350
Sunflower	0.918	60.0	39,490
Coconut	0.915	51.9	37,540
Peanut	0.914	67.1	39,470
Palm	0.898	88.6	39,550
Palm Kernel	0.904	66.3	39,720
Physic Nut	0.915	36.9 (at 38 °C)	39,000
Diesel Oil	0.845	3.8	46,800

(Taken from the Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

2.3.2 Biodiesel Fuel Properties

In general, biodiesel has fuel properties better than that of biofuel. Biodiesel, also known as methyl ester or ethyl ester, made from biofuels and animal oil, has comparable viscosity with diesel oil and is highly stable even during temperature changes. Due to a higher flash point than diesel oil, biodiesel is safer for transport and other uses. On top of this, biodiesel is easier to autoignite than diesel oil, as indicated by a higher cetane rating.

2.3.3 Biodiesel Production

Biodiesel refers to the fuel that comes in the form of esters resulting from the chemical reaction between biofuels or animal oil with methanol or ethanol. This chemical reaction is called "transesterification" and appears in Figure 2.1. Transesterification, also called alcoholysis, 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 (Srivastava and Prasad, 2000).

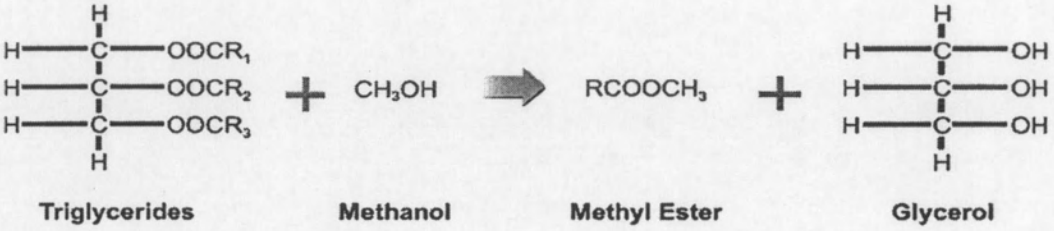

Figure 2.1 Transesterification of triglycerides and methanol results in methyl ester – the desired biodiesel fuel – with glycerol as the by-product.

(Taken from the Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

In developed countries, the production and consumption of biodiesel is highly popular – for household use, in pilot plants, and on a commercial scale for distribution. Biodiesel is widely accepted by automobile manufacturers and oil distributors in the U.S. and the European Union. Within the last 15 years, 28 countries worldwide have continuously studied and developed biodiesel production technology. And within the last decade, the eight largest commercial producers of biodiesel are Austria, the U.S., the Czech Republic, France, Germany, Italy, Nicaragua and Sweden. For Thailand, the Thai government has recently approved a budget of 1.3 billion Baht (or about 32.5 million US$) for biodiesel development during 8 years' period, from 2005 to 2012. A target is set to produce 8.5 million liters of biodiesel by 2012.

For biodiesel production, there are three production processes for biodiesel. The first one is transesterification of oil and alcohol with an acid or base as catalyst. The second is transesterification of oil and alcohol at high pressures without the use of catalysts, a method used by a company called Henkel. The last one is conversion of biofuels or animal fat into fatty acids, and the subsequent reaction of fatty acids with alcohol to form esters.

In developed countries, there are two types of biodiesel production processes: batchwise and continuous. Although the former allows for low-cost production, it lags in process safety and uniform product quality. Henkel's technology, on the other hand; yields light-colored biodiesel with high quality and purity, as well as high-quality glycerine. A high investment process with high-energy consumption, this technology can be adapted to produce FAME esters (Fatty Acid Methyl Esters) – raw materials for the production of oleochemical cosmetics.

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 2.7. 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 2.8. 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 2.9 (The Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004).

Table 2.7 Requirements and test methods of fatty acid methyl esters (FAME) according to BS EN 14214:2003

Property	Unit	Limits		Test method
		Minimum	Maximum	
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/100 g		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 2.8 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

Table 2.9 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

(Taken from the Department of Alternative Energy Development and Efficiency Ministry of Energy, 2004.)

2.4 Diesohol

Diesohol is ordinary diesel with 10 -15% added ethanol by volume and an additive known as an emulsifier. It is also known as E-diesel in the U.S. The fuel mixture is known as a micro-emulsion and is prepared by splash blending, a process that requires no special equipment or temperature control. The use of ethanol in conventional fuels increases the renewable portion of the fuel; it also significantly lowers polluting emissions from the use of the fuel.

2.4.1 Solubility of Ethanol in Diesel

A number of different terms are used when discussing ethanol-diesel blends, and it is important to properly understand the definitions to avoid confusion. These are described below:

Solution is a single-phase liquid system, homogeneous at the molecular level. Some diesohol formulations may be a solution of ethanol, plus additives, in diesel fuel;

Solvent is a liquid substance capable of dissolving one or more other substances. A cosolvent is a solution component that imparts solvent behavior to a system where solubility does not exist or is limited otherwise;

Miscible means that two or more components are capable of being mixed in any ratio without separation into two phases. Two liquids that are immiscible cannot be blended to make a solution (like oil and water). Ethanol and diesel fuel are not accurately described as either miscible or as immiscible. Some ethanol can be dissolved in diesel fuel at room temperature, but as the temperature is lowered the solution will separate into two phases;

Emulsion is a system consisting of a liquid dispersed with or without an emulsifier in an immiscible liquid as very small droplets (as fat in milk). Emulsions tend to look cloudy or milky. Diesohol is not an emulsion. Stability of emulsions is always a concern, and emulsions may separate into two phases during storage;

Micro-emulsion is a chemically and thermodynamically stable ultra-fine (or colloidal) dispersion of a dispersed liquid phase in an immiscible host phase. A micro-emulsion is clear, like a solution, but actually consists of droplets or micelles dispersed in the host phase. The micelle size is roughly one micron. A surfactant additive called an emulsifier and a small amount of water are typically required for formation of a micro-emulsion. Diesohol formulations are most likely micro-emulsions.

Ethanol-diesel micro-emulsions appear to have been first described by Boruff and coworkers in 1982. They used a mixture of unsaturated fatty acids and N,N-dimethylethanolamine as the emulsifier at a concentration excess 10 volume percent. Since that time, emulsifier technology has advanced and today less than 1 volume percent is required in some cases. Stability is much less of a concern for micro-emulsions as these have proven stable for extended periods. However, stability of diesohol micro-emulsions under a range of storage conditions will need to be demonstrated (McCormick and Parish, 2001).

Gerdes and Suppes (2001) presented a detailed study of the solubility of ethanol in various diesel fuels as a function of temperature and ethanol blending level (with no emulsifier). Their results showed that the phase separation temperature for up to 5% ethanol in conventional No. 1 and No. 2 diesel is identical to the cloud point of the pure fuel. Thus, blending of up to 5% ethanol places no additional temperature restrictions on these fuels (if no water is present). Lowering diesel aromatic content reduces the solubility of ethanol. For example, blending ethanol with a zero aromatic Fischer-Tropsch diesel increased cloud point by nearly 25 °C at 5% ethanol. Thus, diesel fuel chemical properties can have a large effect on ethanol solubility. They also demonstrated that ethanol-diesel blends are even less tolerant of water than ethanol-gasoline blends, in the absence of emulsifier.

2.4.2 Emulsifiers/Additives

Ethanol readily blends with gasoline at any ratios (miscible) but will only blend up to around 20% with diesel if the ethanol is anhydrous (partially miscible). However, at temperatures of 10°C and below diesel ethanol blends of 20% of more ethanol start to separate into two immiscible phases. The use of additives allows stable blends to be achieved. There are two types of additives: the first are emulsifiers or surfactants (soap-like chemicals) that produce microemulsions and the second are cosolvents.

Emulsifiers are generally known to extend the stability of ethanol-diesel blends to lower temperatures at ethanol blending levels as high as 15% or even 20% in conventional No. 2 diesel. Different additive packages are presently available from several different suppliers, and the known emulsifiers or emulsifier manufacturers are listed in Table 2.10.

Table 2.10 Emulsifier manufacturers and blending levels (percent by volume) non exhaustive

Emulsifier Producer	Preferred Ethanol Level	Emulsifier Level
O2 Diesel (formerly AAE Technologies, Inc.)/Octel Starreon, LLC	7.7 or 10	0.5 (product is AAE05/Octimax 4930)
Akzo-Nobel	10 to 15	1 to 4 (Beraid ED10)
GE Betz (formerly Betz-Dearborn, Inc.)	5, 10 or15	0.25, 0.35-0.75, or 1
Pure Energy Corporation	5 to 15	1 to 5
Lubrizol		Unknown, (PuriNOx fuel system (20% water))
Apace	15 (hydrous)	1-3 (DALCO -PEOPS copolymer)
Biodiesel (cosolvent)	10	10

(Adapted and enhanced from NREL reports, Advanced Petroleum based fuels program and renewable diesel program, Milestone report November 2001, and Safety and performance assessment of ethanol/diesel blends, September 2003).

2.4.3 Ethanol/Diesel Blend Properties

2.4.3.1 Flash Point & Flammability of Vapor

The flash point is the minimum temperature at or above the fuel will ignite (flash) when an ignition source is applied. The flash point varies inversely with the volatility of a fuels vapor. Diesel fuel has a higher flashpoint than gasoline and is therefore safer to handle from a temperature point of view. Diesohol has a lower flash point than ordinary diesel because of the ethanol vapor and so requires safer handling when filling up a vehicles fuel tank and also not to lose the ethanol portion of the fuel. Effectively it must be handled like gasoline.

2.4.3.2 Cold Flow

This is the performance of the fuel at lower temperatures and can be quantified by the cloud point and pour point of the fuel. Cloud point is the temperature at which crystallization or phase separation occurs (solidification), and as diesohol has a range of components it freezes over a range of temperatures, usually higher than ordinary diesel (thought to be an increase in the size of the micelles or droplets in the microemulsion and not an issue in fuel performance of diesohol). However, the pour point, temperature below which the fuel will not pour, is lower than ordinary diesel and therefore has better cold flow properties than ordinary diesel.

2.4.3.3 Cetane Index / Cetane Number

This is a measure of the propensity of the fuel to autoignite under compressed engine conditions relative to a chemical that burns badly (2,2,4,4,6,8,8-heptamethylnonane (sometimes called isocetane) although originally 1-methylnaphthalene was used) and has a low cetane number and chemical that burns very well (n-hexadecane, also called cetane) and has a cetane number of 100. Therefore, the higher the cetane number, the shorter the delay interval from injection to autoignition. Normal diesel has a cetane number around 50. Adding 15% ethanol as a microemulsion 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. Therefore, a cetane enhancing additive such as ethylhexylnitrate or ditertbutyl peroxide can be added.

2.4.3.4 Energy Content

The lower heating value of ethanol is 42% lower than that of a typical diesel fuel on a volume basis, as shown in Table 2.11. Blending ethanol with diesel lowers the volumetric energy density in proportion to the ethanol content of the fuel as shown in the calculated heating values in Table 2.11. The lower fuel energy content will translate directly into lower miles per gallon fuel economy, and a lower maximum horsepower. At some blending level modification to the fuel injection system to allow injection of larger quantities of fuel is likely to be required for engine performance and for fuel injector/pump durability.

Table 2.11 Lower heating value of ethanol, diesel, and theoretical ethanol- diesel blends

Fuel	LHV, btu/gal (MJ/L)	% Decrease from Diesel
Typical Diesel	132,000 (36.6)	--
5% Ethanol/Diesel	129,222 (35.8)	2.1
10% Ethanol/Diesel	126,443 (35.1)	4.2
15% Ethanol/Diesel	123,665 (34.3)	6.3
Ethanol	76,431 (21.3)	42

(Taken from NREL report, Advanced Petroleum based fuels program and renewable diesel program. Milestone report November 2001).

2.4.3.5 Emissions

There are clear reductions in particulate matter (PM) emissions, as much as by 40% compared to ordinary Diesel in some studies. It is also likely that carbon monoxide emissions are reduced in line with PM emissions. There are increased hydrocarbon emissions.

2.4.3.6 Materials Compatibility

Ethanol reacts differently to elastic and metal surfaces and may need some durability testing for engine components.

Fernando and Hanna (2004) found that biodiesel, which is a renewable fuel, can be used successfully as an amphiphile (a surface-active agent) to stabilize ethanol and diesel. There work also has revealed that ethanol-biodiesel-diesel (EB-diesel) fuel blend microemulsions are stable well below sub-zero temperatures and have shown equal or superior fuel properties to regular diesel fuel. Microemulsions of certain component concentrations have shown substantially increased lubricity without compromising the cetane numbers and energy values. Despite ethanol having a considerably lower energy value, cetane number, and lubricity value than biodiesel or diesel fuel alone, the heat of combustion and cetane numbers of the EB-diesel blends remained steady, without significant reduction.

Makareviciene *et al.* (2005) investigated the solubility of biodiesel fuel components in fossil diesel fuel–methanol–rapeseed oil methyl ester, fossil diesel fuel–ethanol–rapeseed oil methyl ester and fossil diesel fuel–ethanol–rapeseed oil ethyl ester systems. The solubility of components in the fossil diesel fuel–ethanol–rapeseed oil methyl ester system at 20 °C was substantially higher than in the fossil diesel fuel–methanol–rapeseed oil methyl ester system. The solubility of components in the fossil diesel fuel–ethanol–rapeseed oil ethyl ester system was slightly lower than in the fossil diesel fuel–ethanol–rapeseed oil methyl ester mixture. The moisture content of ethanol had a great influence on mixture solubility. With decrease of temperature, the solubility of components in the fossil diesel fuel–ethanol–rapeseed oil methyl ester system decreased.

Hansen *et al.* (2005) studied the properties and specifications of ethanol blended with diesel fuel. Special emphasis is placed on the factors critical to the potential commercial use of the blends. The factors include blend properties such as stability, viscosity and lubricity, safety and materials compatibility. The effect of the fuel on engine performance, durability and emissions is also considered. The formulation of additives to correct certain key properties and maintain blend stability is suggested as a critical factor in ensuring fuel compatibility with engines. They reported that the properties of ethanol–diesel blends have a significant effect on safety, engine performance and durability, and emissions. An increase in fuel consumption approximately equivalent to the reduction in energy content of the fuel can be expected when using ethanol–diesel blends. With ethanol percentages of 10%

or less, operators have reported no noticeable differences in performance compared to running on diesel fuel. It is accepted that the addition of ethanol to diesel fuel will have a beneficial effect in reducing the PM emissions at least. The amount of improvement varies from engine to engine and also within the working range of the engine itself. While there is considerable value in being able to use the fuel directly in an unmodified engine, small adjustments to fuel injection characteristics may result in further gains in reducing emissions. The flammability of ethanol–diesel blends indicates that, according to the NFPA in the USA they should be treated as Class I liquids as they have flashpoints below 37.8 °C, in contrast to diesel fuel, which is a Class II liquid. Therefore, appropriate measures need to be implemented to meet the storage, handling and dispensing requirements that are stipulated for Class I liquids.

De-gang *et al.* (2005) studied the effects of different ethanol–diesel blended fuels on the performance and emissions of diesel engines. The purpose of their project is to find the optimum percentage of ethanol that gives simultaneously better performance and lower emissions. They conducted the experiments on a water-cooled single-cylinder Direct Injection (DI) diesel engine using 0% (neat diesel fuel), 5% (E5–D), 10% (E10–D), 15% (E15–D), and 20% (E20–D) ethanol–diesel blended fuels. With the same rated power for different blended fuels and pure diesel fuel, the engine performance parameters (including power, torque, fuel consumption, and exhaust temperature) and exhaust emissions [Bosch smoke number, CO, NOx, total hydrocarbon (THC)] were measured. The results indicate that: the brake specific fuel consumption and brake thermal efficiency increased with an increase of ethanol contents in the blended fuel at overall operating conditions; smoke emissions decreased with ethanol–diesel blended fuel, especially with E10–D and E15–D. CO and NOx emissions reduced for ethanol–diesel blends, but THC increased significantly when compared to neat diesel fuel.

According to the literature reviews mentioned above, diesel – ethanol blended fuel was found to have a promising future in order to use as an alternative fuel. Moreover, some earlier researches have suggested biodiesel as an effective additive to improve intersolubility of diesel – ethanol and also improve some fuel properties of the fuel blend. However, biodiesel from different sources has different properties. Therefore, this work is focused on studying the use of biodiesel as an additive for diesohol production. The phase behavior, fuel properties, and emissions of the blended diesohol will be investigated by the experiment described in the next chapter.