



CHAPTER II

THEORETICAL AND LITERATURE REVIEWS

2.1 Diesel Engine

2.1.1 Introduction

The diesel engine is more efficient than gasoline counter part. This has resulted in growing popularity for diesel cars because of the lower fuel costs and the compression ratio of a diesel engine is much higher when compared to a gasoline engine. This results in a higher thermal efficiency gasoline engines are on order of 24% whereas diesel engines can reach as high as 43% thermal efficiency, thus a better fuel efficiency and lower CO₂ emission. High thermal efficiency is the primary reason why almost all commercial vehicles in the medium to heavy-duty range are powered by diesel engines all over the world.[3]

Diesel engines use less volatile, heavier liquid fuels than gasoline engines. Gasoline engines must use a more volatile fuel because only a fuel which will evaporate at low temperature will form a uniform mixture with the rapid current of air flowing through the carburetor. Furthermore, diesel engines use fuel pumps and injection nozzles to inject the oil into the cylinder in the form of a fine spray. Gasoline engines, on the other hand, mix the fuel and air in a carburetor.

Diesel engines have come into general use for all these applications. The principal reason is the saving in cost of fuel –the diesel engines use fewer gallons of a less costly fuel the gasoline engine does. True, the diesel engine costs more to begin with, but if it is used in a class of service which keeps it busy most of the time, the saving in cost of fuel soon pays back the extra investment. Another advantage of the diesel is greater pulling or lugging power when it slow down under a heavy load. In other words, the diesel loses less power at reduced speed than the gasoline engine.

Locomotive and railcars

Almost all railroad locomotives now being built are powered with diesel engines, and steam locomotives have been replaced with diesels. Locomotives for pulling trains and for switching service are mostly diesel-electric, that is the diesel

engine drives an electric generator which supplies electric power to electric motors connected to the wheels. The reason why the railroads have almost universally adopted the diesel engine is to save money. Compared to steam locomotives, diesels save money by using much less fuel and by being available for service for much more for the time.

Locomotives for mines and tunnels

Diesel locomotives are now preferred to electric locomotives for mine haulage and for tunnel construction because they are less expensive in both first cost and operating cost. Their exhaust gases contain little poisonous monoxide gas, which is an important objection to gasoline engines in mines.

Marine uses

Diesels are now widely used in marine service of many kinds, such as sea-going vessels, motor boats, ferry boats, tugs, naval vessels, and icebreakers. The main reason for these uses of diesels is, again, lower cost of fuel compared to steam.

Stationary power plants

Diesel engines are employed in a great many kinds of stationary power plants. The reasons are many; the chief ones are saving in cost of fuel compared to small steam or gasoline power plants, and lower total cost than that of purchased electric power.

Additional advantages enter into certain special applications such as isolated service stations, railway water stations, vacation resorts, lumber camps, mine power plants, oil-well drilling, and emergency power plants. Here the following advantages of the diesel are important: independence of water supply, lightness and compactness, freedom from fire hazard, and ability to start quickly. [6]

2.1.2 Diesel engine and combustion process [7]

The basic engine components are illustrated in Figure 2.1. The single-cylinder engine consists of a cylinder (engine block), a movable piston inside this cylinder, a connecting rod attached at the top end to the piston and at the bottom to offset portion of a crankshaft, a camshaft to operate the two valves (intake and exhaust), and a cylinder head. A flywheel is attached to one end of the crankshaft. The other end of the crankshaft has a gear to drive the camshaft gear. The camshaft

gear is twice as large as the crankshaft gear. This drives the camshaft at half the speed of the crankshaft on four-stroke-cycle engines. On two-stroke-cycle engines, the crankshaft and camshaft run at the same speed.

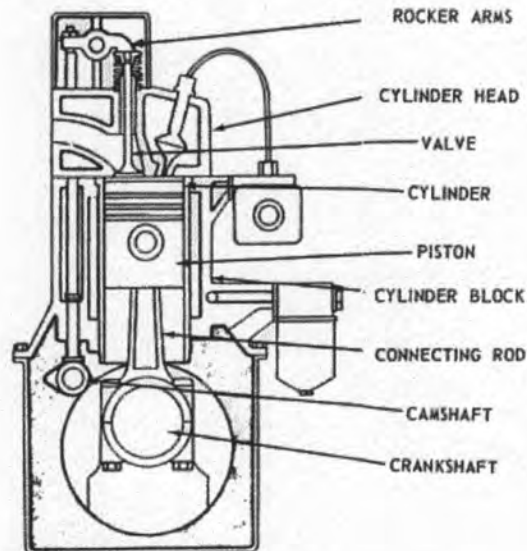


Figure 2.1 Basic diesel engine components.

Typical diesel engines is reciprocating engines that operate with four strokes and two strokes of the piston in the cylinder, but the majority falls into four strokes category

1.) Four-stroke-cycle engine operation

The movement of the piston from its uppermost position to its lowest position is called a stroke. Many engines operate on the four-stroke-cycle principle. A series of events involving four strokes of the piston completes one cycle. These events are: the intake stroke, the compression stroke, the power stroke and the exhaust stroke. Two revolutions of the crankshaft and one revolution of the camshaft are required to complete one cycle. The four stroke-cycles are illustrated in Figure 2.2

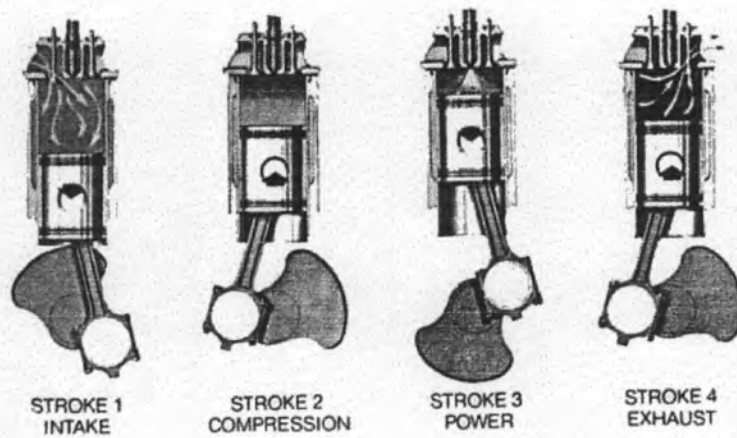


Figure 2.2 Four-stroke combustion cycles.

2.) Two-stroke-cycle engine operation

The two-stroke-cycle diesel engine completes all four events (intake, compression, power and exhaust) in one revolution of the crankshaft or two strokes of the piston. A series of port or openings is arranged around the cylinder in such a position that the ports are open when the piston is at the bottom of its stroke. A blower forces air into the cylinder through the open ports, expelling all remaining exhaust gases past the open exhaust valves and filling the cylinder with air. This is called scavenging. The two-stroke cycle are illustrated in Figure 2.3.

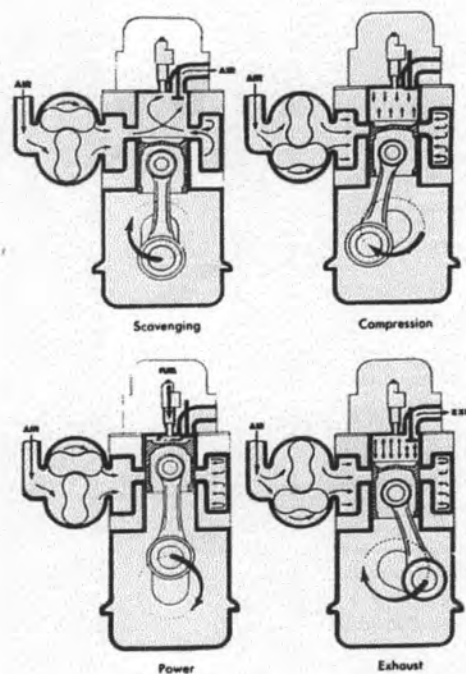


Figure 2.3 Two-stroke combustion cycles.

2.1.3 Type of diesel engines [8]

Diesel engines are divided into two basic categories according to their combustion chamber design:

1.) Direct-injection engines (DI)

The engines which have a single open combustion chamber into which fuel is injected directly and have the largest-size engines, where mixing rate requirements are least stringent, quiescent direct-injection systems of the type are required. The combustion chamber shape is usually a shallow bowl in the crown of the piston, and central multihole injector is used.

2.) Indirect-injection systems (IDI)

The chamber is divided into two regions and the fuel is injected into the “prechamber” which is connected to the main chamber via a nozzle. IDI engine design are only used in the smallest engine sizes.

2.2 Diesel fuel

2.2.1 Introduction

Fuel for diesel engine is obtained from fractional distillation of the crude oil to separate it into fractions with boiling ranges appropriate to the major fuel application.

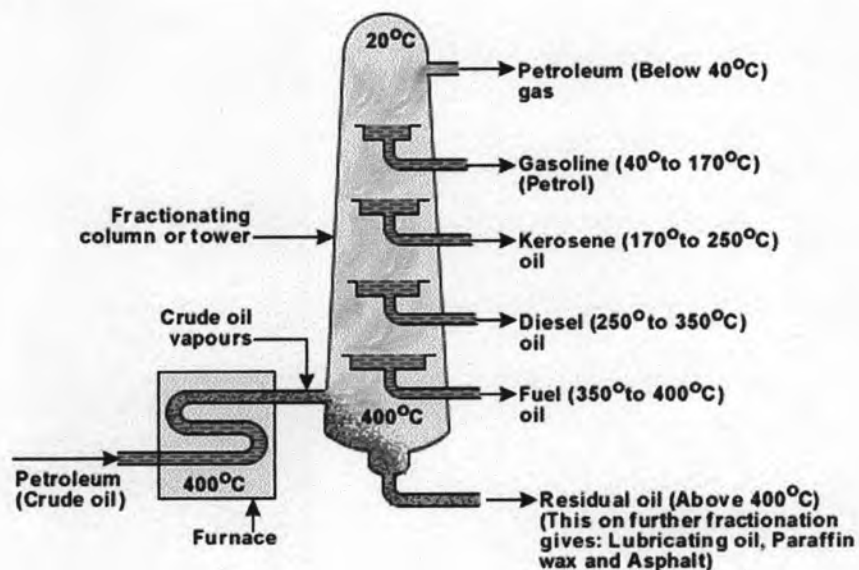


Figure 2.4 Fractional distillation of petroleum.

The boiling range of distillate fuel is approximately 250-350°C (450-700°F). It is a general property of hydrocarbons that the more volatile they are the higher temperatures for spontaneous ignition. It is for this reason that the less volatile middle distillate fractions of petroleum crude and even residues are more readily applicable to diesel engines than gasoline or lighter fractions.

The more common designation is that portion of the distillation curve from 25 to 65 percent of the crude-oil barrel, or within the temperature ranges of 475-725 °F. Other properties are evaluated and characteristics are determined which influence the fuel performance value in a specific application. In the diesel fuel classification many properties are considered significant by the American Society for Testing Materials, such as cetane number, viscosity, carbon residue, sulfur content, flash point, pour point, ash, and copper-strip corrosion.

The properties of commercial fuel oils depend on the refining practices employed and the nature of the crude oils from which they are produced.

2.2.2 Composition of diesel fuels [10]

The composition of fuels derived from petroleum may be considered under two classes, differentiation fuel properties from fuel impurities. In the first class consideration is given to the compounds comprising only carbon and hydrogen in varying proportion in the molecules. The compounds in the second class are those comprising carbon and hydrogen together with sulfur, nitrogen or oxygen in the molecule. Highly unsaturated molecules of carbon and hydrogen, which are quite reactive and tend to polymerize (react with each other) or to react with other components to form gums or products of extremely low volatility, are also considered in the second class.

2.2.2.1 Class I Components [3]

Diesel fuels consist mainly of saturated (paraffin and naphthenes) and aromatic hydrocarbons. Their relative distribution depends on the feedstocks and fuel processing schemes.

Saturate hydrocarbons.

Generally long-chain alkanes with carbon numbers in the range of C_{10} - C_{20} are the major paraffinic components. The corresponding lower and upper boiling points for the n-alkanes are 174 °C (n - C_{10}) and 344 °C (n - C_{20}) respectively. The boiling range in the distillation curve of a diesel fuel could cover the range from about 160 to 380 °C. There can be some lighter (C_9) and heavier (C_{20}^+) components, but they exist in small quantities in most high-way diesel fuels. The contents of heavier components in fuel oils for low-speed diesel engines are higher than those in automotive diesel fuels. Long-chain paraffins have excellent cetane numbers and show good combustion performance, but higher-boiling n-alkanes tend to have higher cloud points and do not have good cold-flow properties.

Alkylated cycloalkanes are also present in diesel fuels. Alkylcyclohexanes, decahydronaphthalenes and perhydrophenanthrenes are typical examples of 1-ring to 3-ring cycloalkanes in diesel fuels, and in hydrotreated light cycle oil. The contents of naphthenic components depend on both the nature of the crude and the blending stocks as well as processing parameters. If a naphthenic crude is used or if heavily hydrotreated light cycle oil from fluid catalytic cracking is used as a blending stock for diesel pool, then the content of cycloalkanes will increase.

Aromatic components

The aromatic compounds in diesel fuels include alkylated benzenes, indanes, naphthalenes, tetralins, biphenyls, acenaphthenes, phenanthrenes, chrysenes, and pyrenes. Diaromatic hydrocarbons with naphthalene-type structure are more abundant aromatic components in diesel fuels.

2.2.2.2 Class II components [3], [10]

The compounds considered in this class which are present in diesel fuel fractions derived from crude oil are those that reflect not so much fuel characteristics as they reflect characteristics indicative of potential problems in handling or storage of fuels and problems of diesel engine maintenance. Included in this category are those derivatives of hydrocarbons containing sulfur, nitrogen or oxygen together with such compounds of the diolefin type which are quite reactive to form high molecular weight materials of extremely low volatility, or by reactions with other materials

such as oxygen, to form insoluble compounds that separate from the fuel mixture and are generally referred to as gums.

Sulfur derivatives

In the most simple forms sulfur exists as mercaptans, sulfides, and disulfides. The combustion of sulfur compounds gives oxides of sulfur which appear in the product gases. These oxides may take up water to form the well known sulfur acid. Therefore the petroleum refining industry is facing a major challenge to meet the limited sulfur in diesel fuel.

On the other hand, it should be noted that ultra-low sulfur diesel fuels lack the lubricity because the treatments to reduce sulfur also remove some components in fuels that can serve as natural lubricating compounds. Therefore, lubricity additives are required for using such fuels.

Nitrogen derivatives

Nitrogen is present in some crudes, and considered to be basic in nature but very little more is known as to the actual structural form in which they are present in crude oils. It is known that when crude-oil fractions containing nitrogen are subjected to high temperatures, such as in cracking with or without a catalyst, some nitrogen is found in the products in the form of ammonia or low molecular weight amines. During the oxidation that takes place in the internal combustion engine, nitrogen compounds may be expected to form oxides of nitrogen that, in the presence of moisture, form the well known nitrogen acids.

Oxygen derivatives

Hydrocarbon derivatives containing oxygen are also present in some crudes, such as naphthenic acids are found. Naphthenic acids are carboxyl acids containing a naphthene ring in the molecule.

Highly unsaturated hydrocarbons

The breaking down of high molecular weight hydrocarbons to molecules of lower molecular weight produces an increase in the unsaturation of lower molecular weight products. Thus there is a tendency to form molecules of a higher degree of unsaturation of the products unless countersteps are taken to resaturate the products. In such operations these higher unsaturated products do not appear except in very low concentrations, and are usually associated with low stability of the

product mixture or with high gum contents. These compounds, because of their highly reactive nature, may normally be removed by various types of treatment.

2.2.3 Type of diesel fuels [3], [11]

Compositions of fuels for diesel engines are generally different from those for gasoline. There are three classes of diesel engine, those for high-speed diesels trucks, cars, locomotives; those for medium-speed diesels marine auxiliaries, stationary power generators, and those for low speed diesels (marine diesels) ships, fishing boats, farm tractors, and electric power generators. The fuels for high speed diesel engines are mainly lighter and higher-quality diesel fuel. The low speed diesel engines can operate on fairly-poor quality fuel such as marine diesel, heavy fuel oil and home heating oils. In some cases they can even operate on crude oils. Typical ranges of diesel engines are listed in Table 2.1.

Table 2.1 Typical range of diesel engines

Type	Range	Conditions and applications
High Speed	> 1000 rpm	- Frequent variation in load and speed - Road transportation vehicles - Diesel locomotives; Construction equipment
Medium Speed	300- 1000 rpm	- Fairly high load, relatively constant speed - Marine auxiliaries; Pumping units - Stationary power generation
Low Speed	< 300 rpm	- Heavy load, constant speed; Marine main propulsion; Electric power generation

There are several types of diesel fuel specified in the ASTM D975-91, that is grades 1D, 2D and occasionally 4D. Grades 2D diesel fuel has a wide boiling range and lower volatility than 1D, and it is similar to 2D fuel oil. It usually contains

cracked stocks and may be blended from naphtha, kerosene, and light cracked oil from the coker and the fluid catalytic cracking unit. Grades 2D fuels are transportation diesel fuels. They are used for applications that do not require a high-volatility fuel. They can also be used for engines in industrial and heavy mobile services. Grades 4 diesel fuels are generally low-quality fuels for low-and medium-speed engines in non-automotive applications. The focus of this article is on automotive diesel fuels.

Table 2.2 Properties of ASTM grades of diesel fuels [11]

Grade ^a	Flash Point, °F [°C]	Pour Point, °F [°C]	Water and sediment, vol %	Carbon Residue on 10% residuum, %	Distillation Temperatures, °F [°C]		Viscosity at 100 °F [37.8°C] kinematic, centistokes, (or saybolt universal sec)		Sulfur, wt %	Cetane Number ^b
	Min.	Max.	Max.	Max.	Min.	Max.	Min.	Max.	Max.	Min.
1D	100 or Legal [37.8]	c	Trace	0.15		550 [287.8]	1.4	2.5 [34.4]	0.50	40 ^f
2D	125 or Legal [51.7]	c	0.10	0.35	540° [287.8]	640 [338]	2.0 ^g [32.6]	43 [40.1]	0.70 ^f	40 ^f
4D	130 or Legal [54.4]	c	0.50	0.15			5.8 [45]	26.4 [125]	2.0	30 ^f

Source: Chevron Research Company

^a To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and supplier.

^b Where cetane number by Method D613 (Test for ignition quality of diesel fuels by the cetane method) is not available, ASTM Method D 976 (Calculated cetane index of distillate fuels) may be used as an approximation. Where there is disagreement, Method D 613 shall be the reference method.

^c For cold weather operation, the pour point should be specified 10°F [5.6°C] below the ambient temperature at which the engine is to be operated except where fuel oil heating facilities provided.

^d Low atmospheric temperatures as well as engine operation high tudes may require use of fuels with high cetane ratings.

* When pour point less than 0°F[-17.8°C] is specified, the minimum viscosity shall be 1.8 cSt (32.0 SSU) and the minimum 90 percent point be waived.

† For all products outside the United States, the maximum sulfur limit be 1.0 wt.%

2.2.4 Properties of diesel fuels [10], [11]

Cetane number

Cetane number is a test designed to measure ignition quality. It is generally recognized that ignition quality is of considerable importance in cold starting of diesel engines. As the engine becomes heated up the significance of cetane number is not so important as other properties necessary for good combustion. If we then consider that cetane number is of importance only during starting operation, very serious consideration should be given to minimizing this requirement when it is in conflict with other desirable properties. In general, cetane number can be increased by increasing the average boiling point of the fuel mixture. The cetane number of paraffins increases with increase in boiling point. There appear to be practically no cetane number data available on naphthene hydrocarbons. In one case, that of cyclohexyl cyclohexane, which is a 100% naphthene hydrocarbon, the cetane number has been reported to be 53.

Viscosity

The viscosity of diesel fuels is usually expressed in term of Saybolt Universal seconds at 100°F. Control of viscosity appears to be a function only of the average boiling point of the fuel mixture and the concentration of naphthene hydrocarbon. On this basis, viscosity requirements, if any, should not be defined until all the other properties which are functions of boiling range are firmly established.

Pour point

The pour point of a fuel can be broadly defined as a measure of the percentage of high-melting-point components in the mixture. In order to reduce pour point for any particular stock mixture a reduction in paraffin content is usually required, inasmuch as paraffin hydrocarbons have higher melting points than all other hydrocarbons boiling at the same temperature and are usually present in sufficient concentrations to be effective.

Flash point

Flash point is considered as having no significance in diesel engine performance. It is used primarily as a safety measure since it represents temperatures at which the fuel will flash in the presence of some igniting hot spot or flame. When considered in connection with the distillation range of the fuel it gives some measure as to the degree of fractionation applied in separating the diesel fuel fraction lower boiling materials. For example, in fuels having the same initial boiling points but with different flash points, the lower flash represents poorer fractionation.

Water and sediment content

Water and sediment content reflects for the most part the care taken in the finishing and handling operations employed in preparing the fuel for the engine. It is quite easy to suspend water in hydrocarbon mixtures boiling in the range of diesel fuels, and it should be emphasized that in the handling of such fuels, where agitation is involved, potential contact with water and rust must be kept at a minimum. During agitation in the presence of water and rust particles such diesel fuels can easily become contaminated and, if such contaminated fuels are then held at low temperature in storage, the contamination may remain suspended for a considerable length of time. Such fuels would eventually cause trouble when charged to the diesel engine.

Ash content

The ash content is usually quite small. Large values reflect improper finishing in the production of fuels, particularly where treating steps are involved. In some cases it is known that ash-forming contaminants may be introduced to fuel mixtures through entrainment or otherwise in the distillation step employed to separate the diesel fuel from heavier stocks.

Carbon residue

Carbon residue reflects the presence of high boiling or rather extremely low volatility components present in a fuel; they crack down to a carbonaceous residue at the distillation temperatures of the fuels. These materials usually result from entrainment during separation of the diesel fuel by fractionation from higher boiling fractions. A carbon residue value on diesel fuels is always determined on the 10% residue in order to increase the accuracy of the test. The components causing high

carbon residues may be expected to increase engine deposits due to high carbon residues may be expected to increase engine deposits due to their inability to vaporize.

Sulfur content

The sulfur content is associated with the corrosion and deposit forming tendencies of the fuel. A considerable amount of work has been done in an attempt to evaluate the harmful effects of sulfur in diesel fuels as a function of the percent sulfur contained in the fuel. The presence of excessive (more than 0.5 percent) sulfur content in the fuel will eventually damage the engine unless the intervals between oil changes are shortened. If the oil is not changed frequently enough, the cylinder liner, pistons and rings, exhaust valves, and the fuel injection system components will rapidly deteriorate. Such deterioration is brought about by oxidation of the sulfur during combustion. As the sulfur combines with the moist intake air, it produces sulfuric acid. This acid collects in the engine's lubrication system, becomes suspended in the oil, and thus causes the damage. Diesel engines using direct injection are more affected than engines using a precombustion chamber, a turbulence chamber, or power cells. Direct-injection engine components are also more subject to acid attack when the coolant temperature is low.

Sulfur corrosion

Sulfur corrosion is a test which primarily determines the amount of free sulfur present in the fuel and reflects the corrosive tendency of the unvaporized and unburned fuel mixture.

Volatility

Any substance that may be readily vaporized at relatively low temperatures is said to have volatility. Volatility affects power output, performance, starting, warm-up, and exhaust smoke.

2.2.5 Diesel fuel additives [3]

Additives are chemicals introduced in very small proportions to the fuel to improve performance, enhance its desirable characteristics and to reduce the undesirable ones. Additives can correct deficiencies and extend the boiling range of blendstocks. Some additives function by physical interactions with fuel components,

while others are involved in chemical reactions Additives represent not only potential added benefit but also added cost of the fuels. Consequently, unless they are truly cost-effective, there is no incentive for the oil companies to use them.

Table 2.3 lists some major types of additives by their applications, including those for improving certain properties of diesel fuels during storage, precombustion, and combustion. There are various additives designed to improve certain properties of diesel fuels, such as cold flow improvers, cetane improvers, antioxidants, metal deactivators, corrosion inhibitors, dispersants, detergents, lubricity agents, and demulsifiers.

Table 2.3 List of some representative diesel fuel additives.

Group	Type and Purpose	Description
Storage, transport and fueling	Storage stability additives to retard gum formation	Anti-oxidants such as 2,6-di-tert-butyl-4methyl-phenol, and secondary amines, 20 ppm
	Corrosion inhibitor	Alkyl phosphate, 15 ppm
	Pipeline anti-corrosion additives	Esters or amine salts of alkenyl succinic acids, alkyl phosphoric acid, or aryl sulfonic acids surfactants, 5 ppm
	De-emulsifiers	Anti-moisture agent to break fuel and water emulsions, 50 ppm
	Anti-foam additives	Silicon surfactant, 10-20 ppm
Pre-combustion	Cold flow improver (Wax anti-settling additives)	Ethylene vinyl acetate, polyolefin ester, polyamide, 100-500 ppm

Table 2.3 (continued) List of some representative diesel fuel additives.

Group	Type and Purpose	Description
Pre-combustion	Dispersant, to restrict the size of the particles formed in fuel	Polyamides, amines, 60-80 ppm
	Detergents, to remove carbonaceous and gummy deposits from fuel injector	Amines, amides, and imidazones, 100-200 ppm
	Lubricity agents	Polyalphaolefins, alkylated aromatics, polybutenes, aliphatic diesters, polyolesters, phosphate esters
Combustion	Cetane Improver	Alkyl nitrate such as iso-octyl nitrate, 300 ppm; low-or non-N cetaners
	Combustion improver	Organic compounds of metals such as Ca, Mn, or Fe
	Deposit modifiers	Minimize non-combustion and fuel deposits
Emission reduction or control	Diesel emission reducer	Metal compounds for burning of PM in trap Polyethers (high concentration, like a blend component)

2.3 Lubricity of diesel fuels

2.3.1 Introduction [12]

Since the introduction of low sulfur diesel fuel in 1993, there has been a considerable amount of effort by the automotive industry, users, and the petroleum industry to incorporate a “lubricity requirement” in commercial diesel fuel; namely ASTM D975, Because lubricity is the primary factors in determining diesel engine wear which describes the ability of a fluid to minimize friction between, and damage to, surfaces in relative motion under loaded conditions.

The lubrication mechanism is a combination of hydronamic lubrication and boundary lubrication. In hydronamic lubrication, a layer of liquid prevents contact between the opposing surfaces. For diesel fuel pumps and injectors, the liquid is the fuel itself, and viscosity is the key fuel property. Fuels with higher viscosity will provide better hydronamic lubrication. When high load and/or low speed have squeezed out much of the liquid that provides hydronamic lubrication, boundary lubrication becomes important. Now, small areas of the opposing surfaces are in contact. Boundary lubricants are compounds that form a protective anti-wear layer by adhering to the solid surfaces.

Many diesel are good boundary lubricants. This is not due to the hydrocarbons that constitute the bulk of the fuel. Instead it is attributed to trace amounts of oxygen and nitrogen containing compounds and certain classes of aromatic compounds. However, when hydrotreating process is used on petroleum refineries, it removes not only sulfur but also it removes nitrogen, oxygen, and polyaromatic compound. The removal of these components might be responsible for lubricity of fuels. The use of fuels with poor lubricity can increase fuel pump and injector wears. The majority of low sulfur automotive diesel fuels marketed today are treated with an additive to enhance the lubricity of the base fuel. It is necessary to prepare the surface of the metal accordingly. It is possible to create a lubricant that forms a surface film over the surfaces, strongly adhering to the surface. These films are thick but they provide enough of a protection to prevent metal-to-metal contact. This type of boundary protection is known as boundary lubrication. The boundary lubrication is shown Figure 2.5

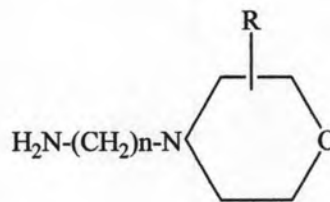


Figure 2.5 Boundary lubrication.

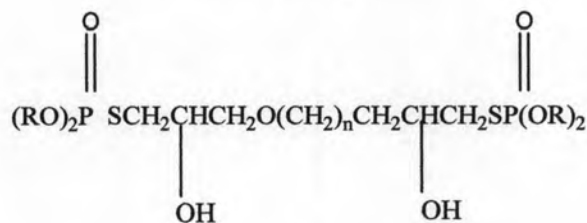
2.3.2 Lubricity additives [12,13]

The need for diesel fuel lubricity has been recognized for many years. As previously described, lubricity additives are generally long slender molecules. They normally have a straight hydrocarbon chain consisting of at least ten carbon atoms. Hydrocarbons derived from natural products are ideal for such applications. The polar head group is the dominant factor in the effectiveness of the molecule as a lubricity additive. Such polar groups consist of Figure 2.6

1. Carboxylic acids or derivatives (including their salts)
2. Phosphoric or phosphonic acids, and their derivatives
3. Amines, amides, imides, and their derivatives



Aminoalkylmorpholine



Dithiophosphoric diester-dialcohol

Figure 2.6 Lubricity additives

Field experience has shown that in order to achieve the full benefits of the low sulfur diesel fuel, the lubricity additive must not only provide sufficient lubricity performance to protect sensitive diesel fuel pumps but must have no undesirable side effects. These potential side effects include:

1. Degrading the properties of the base fuel,
2. Interacting with crankcase lubricating oils,
3. Reducing the effects of other fuel additives present.

The oil and additive industries have developed a wide range of tests to evaluate the no-harm performance of lubricity packages and components.

Generally, the best additives are active organic compounds with long chain molecules and active end groups such as fatty acid, fatty acid ester, and fatty acid amide. These compounds bind tightly and intricately with each other, forming a film that builds up on the metal.

2.3.3 Synthetic esters [14]

Esters are now used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils and grease formulations. The inherent biodegradability of ester molecules offers added benefits to those of performance.

The direct effect of the ester group on the physical properties of a lubricant is to lower the volatility and raise the flash point. This is due to strong dipole moment, called the London forces, binding the lubricant together. The presence of the ester group also affects other properties such as:

- thermal stability
- hydrolytic stability
- solvency
- lubricity
- biodegradability



2.3.3.1 Lubricity

Ester groups are polar will therefore affect the efficiency of anti-wear additives. When a too polar base fluid is used, and not the anti-wear additives, will cover the metal surfaces. This can result in higher wear characteristics. Consequently, although esters have superior lubricity properties compared to mineral oil, they are less efficient than anti-wear additives.

Esters terminated by normal acids or alcohols have better lubricities than those made from branched acids/alcohols, while esters made from mixed acids-alcohols have lubricities intermediate between esters of normal acids/ alcohols and esters of branched acids/ alcohols.

2.3.3.2 Thermal stability

The ester linkage is an exceptionally stable one; bond energy determinations predict that it is more thermally stable than the C-C bond. The advantage in thermal stability of polyol esters compared to diesters is well documented and has been investigated on a number of occasions. It has been found that the absence of hydrogen atoms on the beta-carbon of the alcohol portion of an ester leads to superior thermal stability.

2.3.4 Biodiesel [15-18]

Biodiesel, which is defined as the monoalkyl esters, mainly methyl esters of long-chain fatty acids derived from renewable biological sources, such as vegetable oils or animal fats, is considered as a possible substitute or extender of conventional diesel fuel. Because of its good lubrication properties, biodiesel is also used as an additive to improve the lubricity of diesel fuels. Much research has been done to blended biodiesel to the range of 1% to 3% with base diesel fuel that could enhanced the fuel's lubricity number and could improve operation of diesel include with extend life of their components.

Most vegetable oils are triglycerides. Chemically, triglycerides are the triacylglyceryl esters of various fatty acids with glycerol is shown in Figure 2.7

Some physical properties of the most common fatty acids occurring in vegetable oils and animal fats are well as their methyl esters. Besides these fatty acids, numerous other fatty acids occur in vegetable oils and animal fats, but their abundance usually is considerably lower.

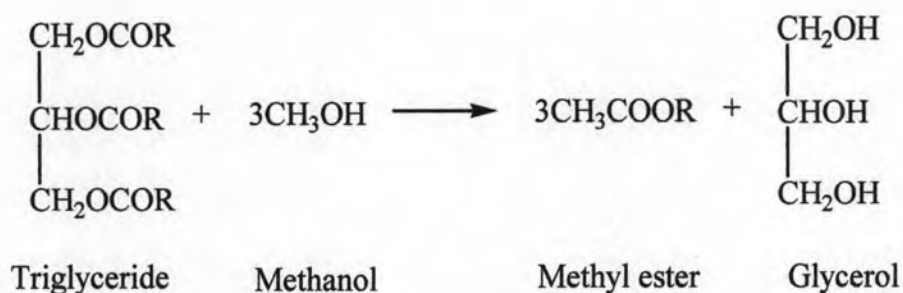


Figure 2.7 Structure of triglycerides and principle of the transesterification reaction

The most common derivatives of triglycerides for fuels are methyl esters. These are formed by transesterification of the triglyceride with methanol in presence of usually a basic catalyst to give the methyl ester and glycerol. Other alcohols have been used to generate esters, for example, the ethyl, propyl, and butyl esters.

2.3.5 Sulfonation [19]

Sulfonation is chemical method for introducing the SO_3 group into an organic molecule, to give a product with $-\text{SO}_3-$ linkage in the form of a sulfonic acid ($-\text{SO}_3\text{H}$), a sulfonate salt ($-\text{SO}_3^-$). There are several methods to prepare them which have shown in table 2.4.

Table 2.4 Reagents for sulfonation.

Reagents	Chemical formula	Physical form	Principle uses
Sulfur trioxide	SO ₃	liquid gas	- wildely used for organic compounds
Oleum, 20%, 30%, and 65%	SO ₃ ·H ₂ SO ₄	liquid	for alkylaryls for detergent dyes
Chlorosulfuric acid	ClSO ₃ H	liquid	for alcohol, dyes
Sulfuric acid (96-100%)	H ₂ SO ₄	liquid	sulfonation of acetylene group
Sulfur dioxide plus chlorine gases	SO ₂ +Cl ₂	gas mixture	chlorosulfonation of paraffinic hydrocarbons
Sodium sulfite	Na ₂ SO ₃	solid	sulfonation of alkyl chloride, epoxy compound
Sodium bisulfite	NaHSO ₃	solid	sulfonation of lignin
Hydroperoxide + bisulfite	ROOH + NaHSO ₃	gas and solid	sulfonation of paraffinic petroleum fraction

SO₃ is an aggressive electrophilic reagent that rapidly reacts with any organic compound containing an electron donor group. Sulfonation is difficult reaction to perform on an industrial scale because the reaction is rapid and high reacted. Most organic compounds are made from black char on contact with pure SO₃ due to the rapid reaction and heat evolution. Additionally, as shown in Table 2.5, the reactants increase in viscosity between 15 and 300 times as they are converted from the organic feedstock to the sulfonic acid. This large increase in viscosity makes heat removal difficult. The high viscosity of the formed products reduces the heat transfer coefficient from the reaction mass. Effective cooling of the reaction mass is essential

because high temperatures promote side reactions that produce undesirable by-products. Also, precise control of the molar ratio of SO_3 to organic is essential because any excess SO_3 , due to its reactive nature, contributes to side reactions and by-product formation.

Table 2.5 Viscosity increase on sulfonation. [20]

Feed stock	Feed viscosity (cp)	Acid viscosity . @ 40°-50°C
Linear alkyl benzene	5	400
Branched alkyl benzene	15	1000
Ethoxylated alcohol	20	500
Tallow alcohol	10	150
Alpha olefins	3	1000

Sulfonation reaction is commonly used as detergent and dispersants additives for development of modern engine oils for gasoline and diesel combustion motors. Detergents and dispersants additives keep oil-insoluble combustion products in suspension and also prevent resinous and asphalt-like oxidation products from agglomerating into solid particles to keep surface engine clean

Mechanism of detergent and dispersants additives. [21-23]

Detergent and dispersants polar substrate types consist of four major classes: sulfonates, phenates, salicylates, and phosphonates. Sulfonates are the most widely-used detergent additives followed by phenates, salicylates, and phosphonates.

Additives which are known detergents and dispersants contain polar groups, and are considered to function by mechanisms which include:

1. Surface action due to the polar group promoting the formation of a barrier film on critical surfaces
2. Dispersant action due to the polymeric additives preventing agglomeration of particulate matter and keeping it dispersed
3. Solvent action due to additives dissolving pre-formed deposits

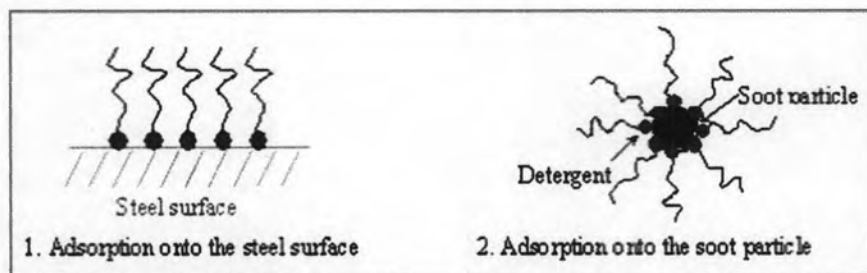


Figure 2.8 The mechanism of detergent and dispersants.

In this study, sulfonation reaction was carried out by reacting with unsaturated methyl ester and oleum. This reaction was observed in Figure 2.9.

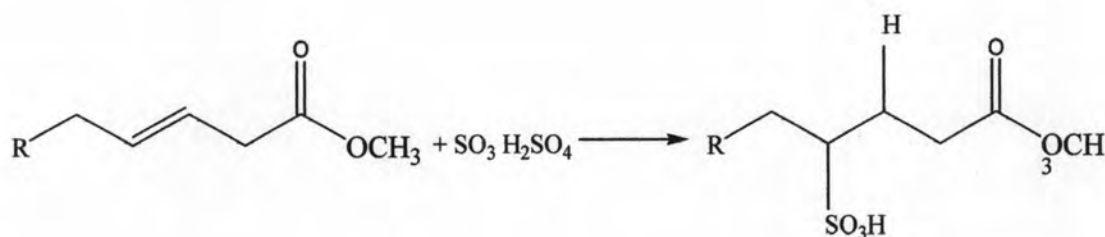


Figure 2.9 Sulfonation reaction.

2.3.6 Measurements of lubricity performances [5]

There are two methods that are commonly used to measure lubricity. One is the HFRR (High Frequency Reciprocating Rig) and another is BOCLE (Ball-on-Cylinder Lubricity Evaluator). The HFRR has been accepted by ISO and SAE. It was developed in Europe for testing diesel fuel lubrication. The drawback to this test is that there are currently only a few of these testing machines in the country. The BOCLE has been used for some time and there are several of these machines in labs throughout the country. Some as the test of choice is forwarding at the HFRR test, but others would also like to include the Scuffing BOCLE because it appears to have good correlation to the HFRR and BOCLE equipment is widely available.

Using the HFRR test procedure, according to ASTM D6079-02 out all measurement. The temperature was 60°C and the volume of fuel sample used was 2 ml. The relative humidity was kept between 50 and 55 % while the mean ambient temperature in the laboratory was approximately constant at 23°C . The HFRR test also uses a steel ball that is placed on a flat surface. The ball is then rapidly vibrated back and forth with a stroke distance of one millimeter while 200 grams of weight is applied. After a given time the flat spot that has been worn into the ball is measured, the size of the spot gives the lubrication qualities of the fuel being tested. The lubricating efficiency of the fuels was estimated by measuring the average wear scar diameter (WSD) of the spherical segment by using a photomicroscope. The wear scars quoted are corrected to give 1.4 WS values. The HFRR WS 1.4 parameter is the mean wear scar diameter normalized to a standard vapor pressure of 1.4 KPa.

In Europe lubricity is measured by HFRR method where an acceptable result is below $460\ \mu\text{m}$ wear scar.

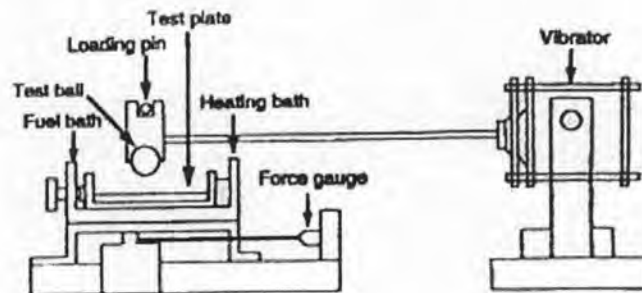


Figure 2.10 High Frequency Reciprocating Rig Test

2.4 Soapstock

2.4.1 Introduction [25],[26]

The main co-product of the vegetable oil refining industry is soapstock. Sodium soaps are formed during the initial refining of the crude oil by reaction of extracted free fatty acids with sodium hydroxide which is shown in Figure 2.14

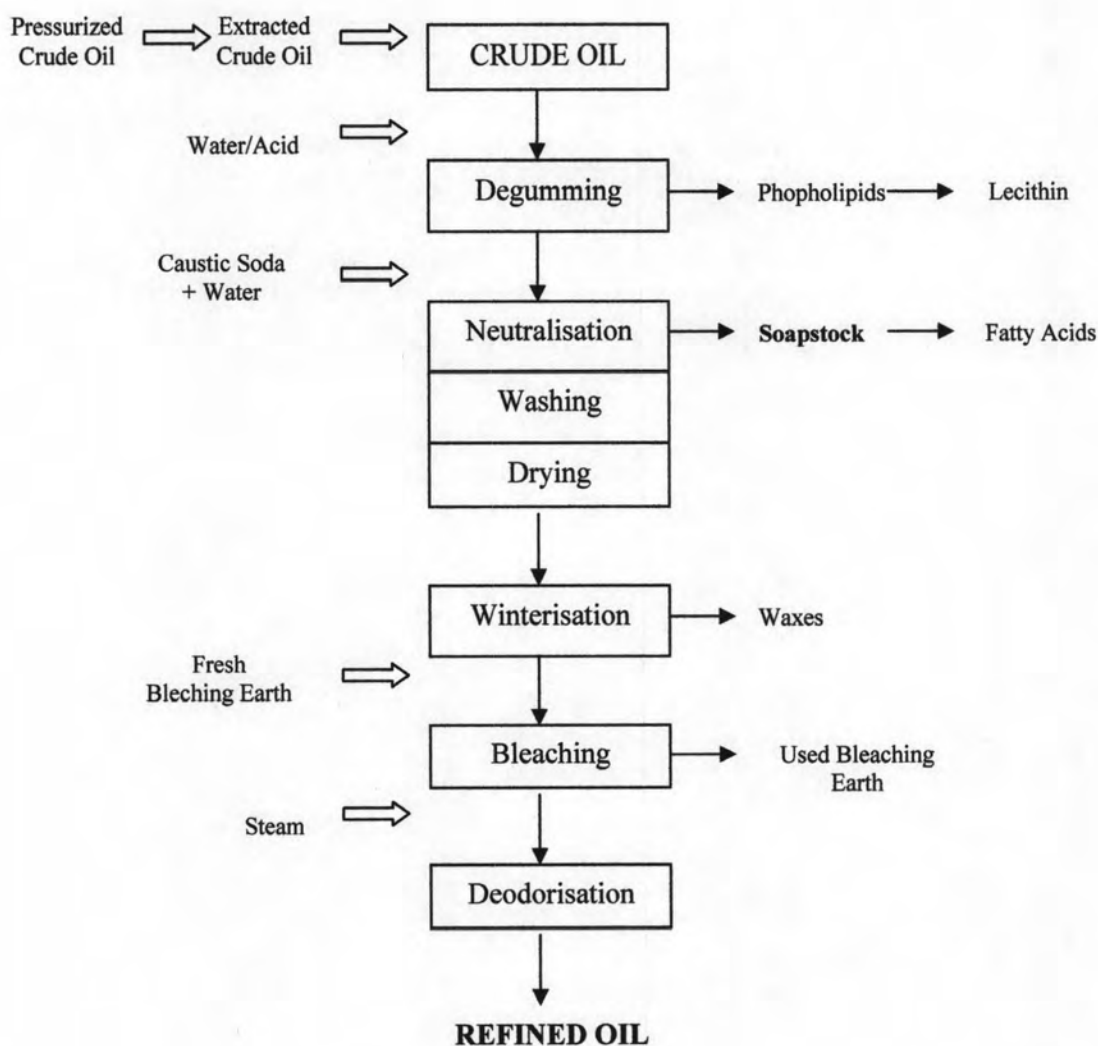


Figure 2.11 Chemical oil refining

2.4.2 The composition of soapstock [27]

Soapstock is a relatively inexpensive byproduct, that is rich in the fatty acids that are the precursors of biodiesel. Soapstock consist largely of water, acylglycerides, phosphoglycerides, and free acids. The total fatty acid content, including both free and lipid-linked acids, is 25-30% (weight basis). The price of soapstock can be as low as one tenth or less that of refined vegetable oil.

2.5 Literature reviews

Dmytryshyn *et al.* [16] studied the trans-esterification of vegetable oils and waste fryer grease by base catalyzed. The methyl esters of the corresponding oils were separated from the crude glycerol, purified, and characterized by various methods to evaluate their densities, viscosities, iodine values, acid numbers, cloud points, pour points and gross heat of combustion, fatty acid and lipid compositions, lubricity properties, and thermal properties. The fatty acid composition suggests that 80-85% of the ester was from unsaturated acids. The lubricity of the methyl esters, when blended at 1 Vol% treat rate with ISOPAR[®] reference fuel, showed that the canola methyl ester enhanced the fuel lubricity number.

Kinast *et al.* [17] studied the effect of mixing biodiesel and diesel from multiple feedstocks and testing the properties of these. The properties selected for studied as part of these effect support feedstock neutral specifications for biodiesel. The physical and chemical tests for biodiesel blends were viscosity, pour point, cloud point, cold filter plugging point, cetane number, lubricity and oxidation stability. The fractions of biodiesel that were tested were: 0.25%, 0.5%, 1%, 3%, 5%, 10%, 20%, 35% and 50%. In terms of lubricity, the significant increase that occur with even concentrations at 3% or less of the biodiesels appears to confirm that biodiesel additives could improve operation of diesels and extend life of their components.

Foster *et al.* [20] studied the sulfonation and sulfation industrial process to make a diverse range of products, such as dyes organic intermediate and detergent additives. The agents to reduce sulfonation reaction were sulfamic acid, chlorosulfonic acid, oleum and air/SO₃. Sufamic acid is an expensive reagent,

chlorosulfonic acid is an expensive of SO_3 although it is approximately one half the cost of sulfamic acid and it is also corrosive and a hazardous chemical to handle and liberates HCl as a by-product during the reaction. Sulfuric acid and oleum are inexpensive SO_3 and widely used as sulfonating agents. However, it has the disadvantage of being an equilibrium process which left large quantities of unreacted sulfuric acid. The air/ SO_3 is the lowest SO_3 cost of any sulfonation process and is extremely versatile, producing very high quality products, but it requires expensive precision equipment and highly trained operating personnel.

Hass *et al.* [27] synthesized the biodiesel fuel from soybean soapstock. The fatty acid composition of soybean soapstock and quite similar to that of commercial biodiesel produced from refined soybean oil. The ester product met the provisional biodiesel specifications of American Society for Testing and Materials with regard to all variables examined: flash point, water and sediment, carbon residue, sulfated ash, density, kinematic viscosity, sulfur, cetane number, cloud point, copper corrosion, acid number, free glycerin, and total glycerin, and had density and iodine number values comparable to those of commercial soy-based biodiesel.

Galler *et al.* [28] studied the effect of specific fatty acid methyl esters on diesel fuel lubricity. These studies sought to examine the effects of individual component fatty acid methyl esters on diesel lubricity. Additive levels of 0-1.0% of specific fatty acid methyl esters were added to diesel fuel and the resulting lubricity was measured using the High Frequency Reciprocating Rig method. The lubricity enhancing effects of the single fatty acid methyl esters were compared to those of other pure fatty acid methyl esters. An attempt was made to correlate fatty acid methyl ester chain length, saturation and hydroxylation to lubricity enhancement. The individual fatty acid esters did not have as dramatic an effect on lubricity as did methyl esters derived from vegetable oils composed of a mixture of several fatty acids.

Charaensuk. [29] synthesized biodiesel from vegetable oil soapstocks such as palm oil, rice bran oil, and soybean oil. The base diesel fuel blended with 5% weight of biodiesel was tested for lubricating performance. The product from palm oil soapstock has good lubricity enhancing capabilities and showed properties similar to base diesel fuel.

Sroisopee. [30] produced fatty acid methyl ester by transesterification of vegetable oils with various alcohols such as ethanol, 1-butanol, and 1-hexanol in the presence of sulfuric acid. The diesel fuel blended with 0.2% weight of fatty acid methyl ester was tested for lubricating performance and showed properties similar to diesel fuel.