

## CHAPTER II

### THEORY AND LITERATURE

#### 2.1 The Diesel Engine

Diesel engines provide high thermal efficiency – in excess of 50 percent. Better than the best gasoline engines, which are only 30 percent to 35 percent efficient at wide throttle openings. Diesel engines also provide high torque output and power under a wide range of conditions.

Diesel fuel powers the trucking, construction, and farming industries; stationary power generation and marine propulsion; and most public transportation around the world. However, diesel power is not limited to heavy-duty application. Motor vehicles with modern diesel engines comprise a large portion of the private fleet in the most European and many Asian countries, and their use is growing in the U.S. consumer market, make diesel an appealing option for the popular sports utility vehicles.

The diesel engine has now extended over a much wider range of applications than any other engines currently in use. Within the past eighty years diesel engines have been used wherever engine power has been required. They are found driving small and large electric power generating and pumping units; in the main propulsion of ships and their auxiliaries; in large and small road vehicles; they are used for off road agricultural and civil engineering vehicles and machinery and also for railway locomotives. Whilst few examples now exist, diesel engines usually power the lighter than air airship and in the past have seen application in winged aircraft. They find no

favour today for this latter purpose because other engine types have far higher power to weight ratios. It must also say that diesel engines are not unique to any one part of the world. They will be found everywhere where man needs to augment his own work capability. Therefore, diesel fuels have a universal market.

The power producing capabilities of diesel engines vary from 1 or 2 kW to about 20000 kW and may be used for stand-by or continuous duty, so that individual units may vary in annual fuel consumption from a few hundred liters to many thousand tons. Although diesel engines are regarded, justifiable, as the most rugged and reliable of engines, maintenance is necessary and the extent of the maintenance needed may depend in part of the quality of fuel used. There are instances where maintenance needs must be minimal and this is achieved at some economic cost, by using selected highly refined fuel, but in general diesel engines will find most favour where operating economy in terms of fuel cost is paramount. In recognition of this interest many designs aim to be relatively insensitive to fuel quality and indeed, within the scope of petroleum fuels diesel engines have operated over the range from gasoline to neat crude oil. Whilst this wide range of adaptability does exist it has to be recognized that it is not inherent in any one engine type to be so omnivorous. Detailed design changes are necessary to utilize all petroleum fuels and if, as is projected for the future, fuels are extended to coal and vegetable oils, then even wider variants of the basic design must be contemplated [1].

However, much of the debate on target or tailpipe emissions and effectiveness of after treatment devices centers on ability of the refining industry to produce and supply diesel fuels at required ultra low-sulfur levels – levels not previously or easily achieved. To remain a key fuel to global applications, the refining industry is challenged to implement ultra-low diesel fuel technologies.

The diesel engine differs from the Otto engine in the heterogeneous combustion of its mixture and the self-ignition of the fuel. The temperature necessary for self-ignition is produced in the compression stroke, in which compression of air to ca. 3.0-5.5 MPa leads to temperatures of 700-900°C. Fuel is injected into the heated air shortly before the end of the compression stroke, where it self-ignites. In principle the diesel engine can be either of the four- or two-stroke type. In practice, four-stroke engines are found in the vast majority of vehicles, whereas the two-stroke process is used in large ship or simpler truck engines. In the diesel engine, air is generally taken in unthrottled and the fuel-air ratio varies with the quantity of fuel injected (quality governing) thus leading to a very lean fuel-air mixture.

The diesel engine must achieve compression temperatures and pressures, which are adequate to enable starting from cold and to give acceptable smooth combustion when running. In high-speed automotive diesel engines, this is obtained by the use of compression ratios of between 12:1 and 23:1, depending on cylinder size, combustion system and whether the engine is turbocharged. It is the typically high compression ratio of the diesel engine, which dictated the need for its general mechanical robustness and also leads to its high-indicated efficiency characteristics.

After compression ratio, the main factors affecting combustion in the diesel engine are combustion chamber design and fuel injection characteristics. The time from start of fuel injection to end of combustion is very small, and during this a fuel-air mixture has to be formed which will ignite within a reasonable delay period. Good mixing of fuel and air is essential and adequate oxygen has to be available for combustion to be completed early in the expansion stroke.

Diesel engines are similar to gasoline engines in many ways. Both are internal combustion engines and most versions of both use a four-stroke cycle. Diesel engine works by igniting the air-gas mixture without a spark, but the gasoline engine ignites the fuel-air mixture with a spark. The main advantage of a diesel engine is its high thermal efficiency. Diesel engines can achieve thermal efficiencies in excess of 50%. The best gasoline engines are only about 30% to 33% efficient, and then only at wide throttle openings. As a result, diesel engines have better fuel economy than gasoline engines.

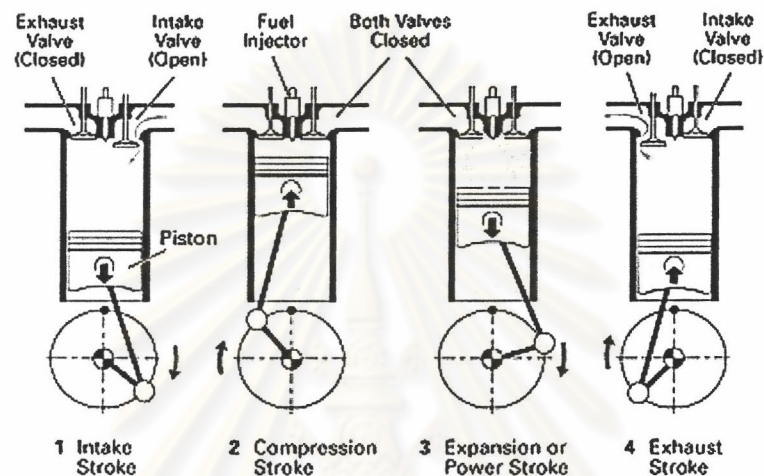
Diesel engines are more efficient than gasoline engines, because

1. Diesel engines employ direct fuel injection in which fuel is injected directly into the engine cylinder rather than indirectly through a carburetor system.
2. A diesel engine takes in air, compresses it, and then injects fuel into the compressed air. Compressing air creates heat, which ignites the fuel spontaneously and eliminates the need for a spark plug.
3. A diesel engine uses a much higher compression ratio than a gasoline engine. A diesel engine compresses at a ratio of 14:1 to as high as 25:1, while a gasoline engine compresses at a ratio of 8:1 to 12:1. The higher compression ratio of the diesel engine leads to better efficiency.

There are both four-stroke and two-stroke diesel engines, but the majority falls into the four-stroke category.

### 2.1.1 Four-stroke cycle

Almost all cars currently use what is called a four-stroke combustion cycle. The four-stroke approach is also known as the Otto cycle, in honor of Nikolaus Otto, who invented it in 1867. The four-stroke are illustrated in Figure 2.1



**Figure 2.1** four-stroke combustion cycles [4].

They consist of:

1. Intake stroke: in the first stroke or intake stroke, the inlet valve opens while the piston moves down from its highest position in the cylinder (closest to the cylinder head) to its lowest position, drawing air into the cylinder in the process.
2. Compression stroke: in the second stroke, the intake valve closes and the piston moves back up the cylinder. This compresses the air and, consequently, heats it to a high temperature, typically in excess of 1,000 °F (540°C).
3. Expansion or power stroke: near the end of the compression stroke, fuel is injected into the cylinder. After a short delay the fuel ignites spontaneously, a process called auto-ignition. The hot gases produced by the combustion of the fuel further increase the pressure in the cylinder, forcing the piston down.

4. Exhaust stroke: the exhaust valve opens when the piston is again near its lowest position, so that as the piston once more moves to its highest position, most of the burned gases are forced out of the cylinder.

### **2.1.2 Two-stroke cycle**

Two-stroke cycle diesel engines are very similar to four-stroke cycle engines, except that they do not have separate intake and exhaust strokes. Instead, exhaust occurs at the end of the expansion, or power, stroke and continues into the early part of the compression stroke. Intake occurs during the end of the expansion stroke and the early part of the compression stroke. To assist the intake process, the intake air is almost always boosted above atmospheric pressure, using supercharging or turbo charging. Airflow into the cylinder and exhaust gas flow out of the cylinder are controlled by conventional puppet valves in the cylinder head, ports in the cylinder wall, or a combination of both.

The advantage of the two-stroke cycle is that it generates more power for a given engine size, since power is generated on every other stroke, rather than every fourth stroke. The disadvantages are that emissions are higher with a two-stroke cycle than with a four-stroke cycle. However, they are still common in uses such as large marine engines, where poor emissions performance is not currently an issue.

### 2.1.3 Diesel Advantages

Today's diesel-powered vehicle owners recognize the advantages of diesel engines-lower emissions, durability, reliability, friction loss and fuel safety.

1. Emission: efficient, lean operating diesel engines emit much smaller amounts of unburned hydrocarbon and carbon monoxide emissions than spark ignition engines; however, Nitrogen oxide (NO<sub>x</sub>) and particulate matter (PM) emissions are slightly higher. Low-sulfur, diesel-fuel technological developments are expected to lower the PM and NO<sub>x</sub> emissions to levels no higher than those from a gasoline engine.

2. Durability: because diesel engines have compression ratios that almost twice as high as gasoline engines, the heat released and the amount of torque produced from diesel engines occurs at lower speeds. As a result, diesel engines may last up to four times longer with heavy-duty diesel engines in semi-tractors routinely lasting well over 900,000 miles.

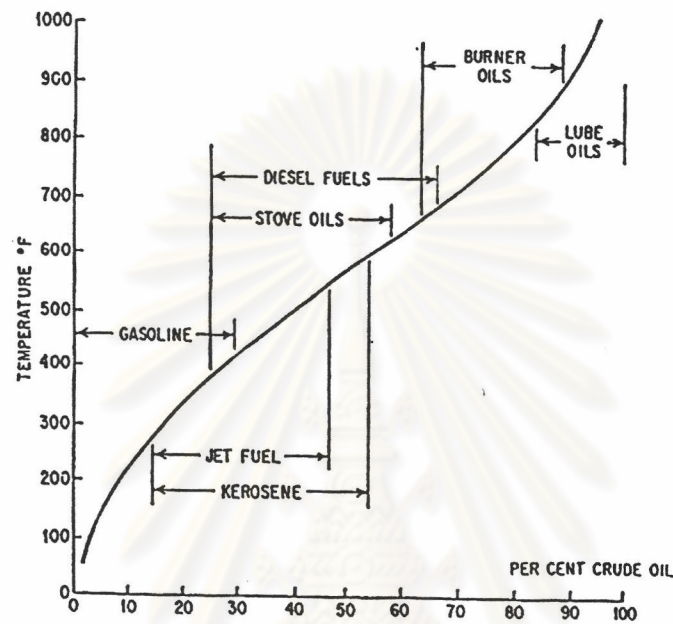
3. Reliability: because diesel engines lack spark plugs, distributors, and ignition systems, breakdowns occur much less frequently.

4. Friction losses: diesel engines produce their power at lower engine speeds. Consequently, diesel-engine friction losses are also lower, which improves the brake horse power and the service life of engines.

5. Safety: because the volatility of diesel fuel is lower than that of gasoline, diesel fuel is safer to handle and store. Its lower volatility also diminishes the probability of releasing hydrocarbon vapors into the atmosphere during handling and transfer.

## 2.2 Diesel Fuel

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 2.2** Proportion of diesel fuel and other petroleum products processed from crude petroleum [5].

The boiling range of distillate fuel is approximately 150-370°C (300-700°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 375-725°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.

### **2.2.1 Composition of Fuel Derived from Petroleum**

The composition of diesel fuels derived from petroleum may be considered under two classes [5];

1. The first class, consideration is given to the compounds comprising on carbon and hydrogen in varying proportions in the molecule.

2. The second class, consideration is given to the compounds 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 or to react with other compounds to form gums or products of extremely low volatility.

#### *Class I Component*

Diesel fuels are mixtures comprising these hydrocarbons boiling within the range from about 350°F to about 700°F. It is possible to further classify such hydrocarbon mixtures into four main types: paraffins, olefins, naphthenes and aromatics.

1. Paraffins, both straight chain and moderately branched, Generally, one may consider that for diesel fuel, in the formula varies from 9 to 20 carbon atoms.

2. Olefins structurally undefined.
3. Naphthenes consisting of major proportions of five and six carbon rings with multiple and short paraffinic side chains.
4. Aromatics consisting of major proportions of mononuclear compounds and multiple and short paraffinic side chains.

### Class II Components

Those derivatives of hydrocarbons containing sulfur, nitrogen or oxygen, together with such compounds of the diolefin type, which are quit reactive to form high molecular weight.

Sulfur derivatives – In the simplest forms sulfur exists as mercaptans, sulfides, and disulfides. These compounds are produced in the conventional treating operations. Other sulfur compounds are known to exist in diesel-fuel fractions from petroleum.

Nitrogen derivatives – These nitrogen compounds are 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.

Oxygen derivatives – Hydrocarbon derivatives containing oxygen are also present in some crudes such as naphthenic acids.

Highly unsaturated hydrocarbons – The breaking down of high molecular weight hydrocarbons to molecules of lower molecular weight produces an increase in the unsaturation of the products.

### 2.2.2 Specification for Diesel Fuels

Although diesel engines vary widely in size speed, power output, and mechanical design, their fuel requirements are quite similar in many respects. Performance features desired of all diesel fuels, and the physical properties most directly related to them are summarized below. Fuel properties are presented in the order in which they are seen by the engine as the fuel flows from the storage tank, through the fuel system, to the combustion chamber, No attempt is made in the table to indicate relative importance.

<u>Performance Feature Desired</u>	<u>Indicated By</u>
1. Safety in handling	Flash point
2. Pumpability at low temperature	Pour or cloud point, viscosity
3. Freedom from all suspended matter	Storage stability, suspended sediment tests
4. Readily atomized	Viscosity
5. Readily ignitable	Cetane number
6. Clean burning	Volatility, Cetane number
7. Good fuel economy	$^{\circ}$ API gravity
8. Major effects on engine wear and deposit	Sulfur

The properties generally considered to be most indicative of diesel fuel quality, however, are (a) cetane number, (b) volatility, (c) viscosity, (d) sulfur content, and (e)  $^{\circ}$ API gravity. This section discussed the more important fuel characteristics as they relate to engine performance.

## **Cetane Number**

Cetane number is an index of a fuel's ignition quality. It is measured in a single cylinder, variable compression ratio diesel engine under fixed conditions of speed, load, jacket temperature, inlet air temperature, etc. The ignition quality of the test fuel is compared with mixtures of two reference hydrocarbon fuels, namely, cetane, which is assigned a rating of 100, and alpha-methyl-naphthalene which is assigned a rating of zero.

## **Volatility**

A simple laboratory distillation test indicates the volatility or boiling range of a fuel. Important distillation points for determining fuel volatility are the 10%, 50%, 90%, and final boiling point. The higher than 50% and/or final boiling points, the more difficult it is to vaporize the fuel completely. High speed engines in particular require volatile fuels high boiling products cannot be vaporized in the short time available for combustion, and sooty, incomplete burning results. It is very important in high speed engines to have volatile, readily vaporized fuels; the importance of fuel volatility decreases as speed decreases or, stated another way, as the time available for combustion increases.

## **Viscosity**

Viscosity is a time measure of a fuel's resistance to flow, and is directly related to the ease with which the fuel is atomized in the combustion chamber. Too high a viscosity will result in the fuel spray penetrating too far into the combustion chamber; it wets the piston and cylinder walls, and then carbonizes on the hot combustion

chamber surfaces. If fuel viscosity is too low, injector plungers and barrels, which depend on the fuel for lubrication, will tend to wear excessively.

### Gravity

The gravity of petroleum oil is an index of the weight of a measured volume of the product. There are two scales in use in the petroleum industry; API gravity and specific gravity, the former being most widely used in the United States. The specific gravity of a petroleum oil or of mixtures of petroleum products with other substances is the ratio of the weight of a given volume of the material at a temperature of 60°F. to the weight of an equal volume of distilled water at the same temperature, both weights being corrected for the buoyancy of air. The temperature requirements are shown by the expression, "Specific Gravity 60/60°F." For heavier products such as asphalt and liquid road materials a reference temperature of 77°F. is used instead of 60°F.

The API gravity of petroleum oil is based on an arbitrary hydrometer scale, which is related to specific gravity in accordance with the formula:

$$\text{Degree API} = \frac{141.5}{\text{Sp. Gr. } 60/60^\circ\text{F}} - 131.5 \quad (1)$$

### 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. There is evidence that high sulfur fuels cause more corrosion or deposits than low sulfur fuels. The problem that remains open, however, is how much

does this corrosion or deposit formation cost in relation to added fuel costs to reduce the sulfur content.

### **Pour and Cloud Points**

Pour point, or the minimum temperature, at which a fuel remains liquid, is of importance in mobile installations where the fuel must be handled at or near atmospheric temperatures. If the fuel is to be pumped through filters, the cloud point, or that temperature at which crystals begin to form, is the minimum temperature at which engine operation is permissible. Operation below the cloud point will result in clogging of the fuel filters by wax.

### **Flash Point**

Fuel flash point is useful only as an index of fire hazard. Although flash point is an indication of the “readiness” of a fuel to ignite when exposed to a flame, it cannot be used for estimating auto-ignition temperature of diesel fuels.

### **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. Sediment in fuel leads to filter clogging and injector fouling, while water is harmful because it promotes rusting of critical steel injection equipment.

## **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 content is an index of the carbonizing tendencies of a fuel. It 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 fuel. 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% distillation residue in order to increase the accuracy of the test. The higher the carbon residue value, the greater will be the tendency for deposits to form on the fuel injector tip or in other parts of the combustion chamber.

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

**Table 2.1** Properties of various hydrocarbon groups with regard to their suitability as diesel fuels [6].

Hydrocarbon groups	Properties
Paraffins	High cetane number, low combustion heat per gallon, high pour point, and low mixed fuel-air combustion characteristics.
Olefins	Low combustion heat per gallon and low pour point. The characteristics are not too well defined.
Naphthenes	Intermediate cetane number, intermediate combustion heat per gallon, and low pour point.
Aromatics	Low cetane number and pour point, with high combustion heat per gallon and high mixed fuel-air combustion characteristics.

The ASTM Classification D975 of diesel fuel oils is intended as a statement of permissible limits of significant fuel properties used for classifying the wide variety of commercially available diesel fuel oils. These grades and their general applicability for use in diesel engines are broadly indicated as follows.

Grade No. 1-D comprises the class of volatile fuel oils from kerosene to the intermediate distillates. Fuels within this classification are used in high-speed engines in services involving frequent and relatively wide variations in loads and speeds and also for use where abnormally low fuel temperatures are encountered.

Grade No. 2-D includes the class of distillate gas oils of lower volatility. These fuels are applicable for use in high-speed engines in services involving



relatively high loads and uniform speeds, or in engines not requiring fuels having the higher volatility or other properties specified for No. 1-D.

Grade No. 4-D covers the class of more viscous distillates and blend of these distillates with residual fuel oils. These fuels are applicable for use in low- and medium-speed engines employed in services involving sustained loads at substantially constant speed.

**Table 2.2** Properties of ASTM grades of diesel fuels [6].

Grade <sup>a</sup>	Flash point, °F [°C]	Pour point, °F [°C]	Water and sediment vol %	Carbon residue on 10% residuum, %	Ash wt %	Distillation temperatures, °F [°C]		Sulfur, wt%	Copper strip corrosion	Cetane number <sup>e</sup>
	Min.	Max.	Max.	Max.	Max.	Min.	Max.	Max.	Max.	Min.
1D	100 or Legal [37.8]	b	Trace	0.15	0.01		550 [287.8]	0.50	No.3	40 <sup>f</sup>
2D	125 or Legal [51.7]	b	0.10	0.35	0.02	540 <sup>c</sup> [282.2]	640 [338]	0.7 <sup>d</sup>	No.3	40 <sup>f</sup>
3D	130 or Legal [54.5]	b	0.50		0.10			2.0		30 <sup>f</sup>

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

<sup>b</sup> 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 are provided.

<sup>c</sup> 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 shall be waived.

<sup>d</sup> For all products outside the United State, the maximum sulfur limit shall be 1.0 wt%.

<sup>e</sup> Where cetane number by method D613 ( Test for Ignition Quality of Diesel Fuels by the Cetane Method) is not available. ASTM Method D976 (Calculated Cetane index of Distillate Fuels) may be used as an approximation. Where there is disagreement, Method D613 shall be the referee method.

<sup>f</sup> Low-atmospheric temperatures as well as engine operation at high altitudes may require use of fuels with high cetane ratings.

Source : Chevron Research Company

## 2.3 Ignition Quality

Ignition quality is the most important property of diesel fuel. It is generally recognized that ignition quality is of considerable importance in cold starting of diesel engines.

Fuel ignition in diesel engines is achieved through the heat generated by air compression, as a piston in the cylinder move to reduce the cylinder volume during the compression stroke. In the engine, the air is first compressed, and then the fuel is injected into the cylinder; as the fuel contacts the heated air, it vaporizes and finally begins to burn as self-ignition temperature is reached. Additional fuel is injected during the compression stroke and the fuel burns almost instantaneously, once the initial flame has been established. Thus, a period of time elapses between the beginning of fuel injection and appearance of a flame in the cylinder. This period is commonly called "ignition delay "and must be relatively short in order to avoid "diesel knock ".

Fuel that have poor ignition characteristic, that is, relatively high spontaneous ignition temperature will exhibit an unduly large ignition lag between the time fuel is injected into a zone of combustion and the time when the fuel ignites. In diesel engines, for example, a large ignition lag will result in combustion of the fuel and the development of pressure over an improper portion of the crank angle period and piston stroke, resulting in knocking, rough engine operation, incomplete combustion in the combustion zone, power losses, and ultimately detriment to the engine.

### 2.3.1 Physical Chemistry Factors Affecting Ignition Delay

The magnitude of ignition delay is affected by significant physical and chemical factors, such as;

### Effect of Temperature

It will be observed that ignition delay decreases as the temperature increases on this are shown in Fig. 2.3.

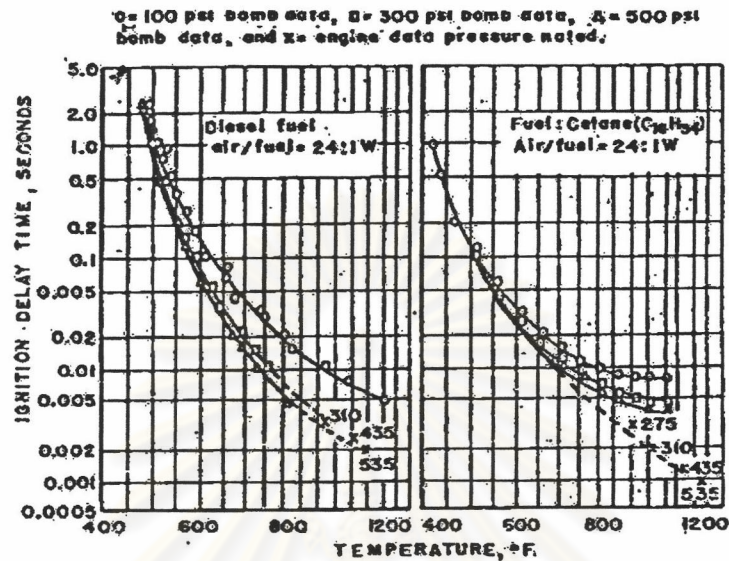


Figure 2.3 Effect of temperature on ignition delay of diesel fuel and cetane in a CFR engine and in a bomb [6].

### Effect of Pressure

The effect of pressure on ignition delay determined by Wolfer is show in Figure 2.4, which shows that ignition lag is reduced by increasing the pressure, the dependence on pressure being much greater at lower pressure.

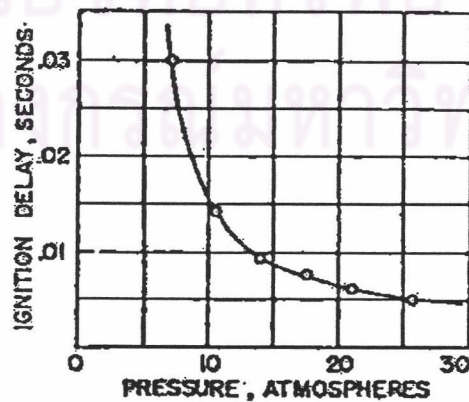


Figure 2.4 Effect of pressure on ignition delay of diesel fuel [6].

### Concentration of Fuel

Under the heterogeneous conditions in the diesel engine at the time of ignition, we probably have in the combustion chamber local-air ratios ranging from zero to infinity. Ignition takes place in some region where the fuel-air ratio is optimum. The determination of this optimum fuel-air ratio should be done under conditions such that all the fuel is vaporized and completely mixed with air. This optimum fuel-air ratio is analogous to the lower limit of inflammability. It is important in diesel-engine combustion because, under the heterogeneous conditions existing during combustion, local regions will be present in which the concentration of fuel is less than the minimum or lower limit. Partial oxidation will occur in these regions, but because of the lower fuel concentration and lower temperatures, the regions will not ignite or inflame. Consequently, products of partial oxidation giving rise to odor and possibly deposits will appear in the exhaust.

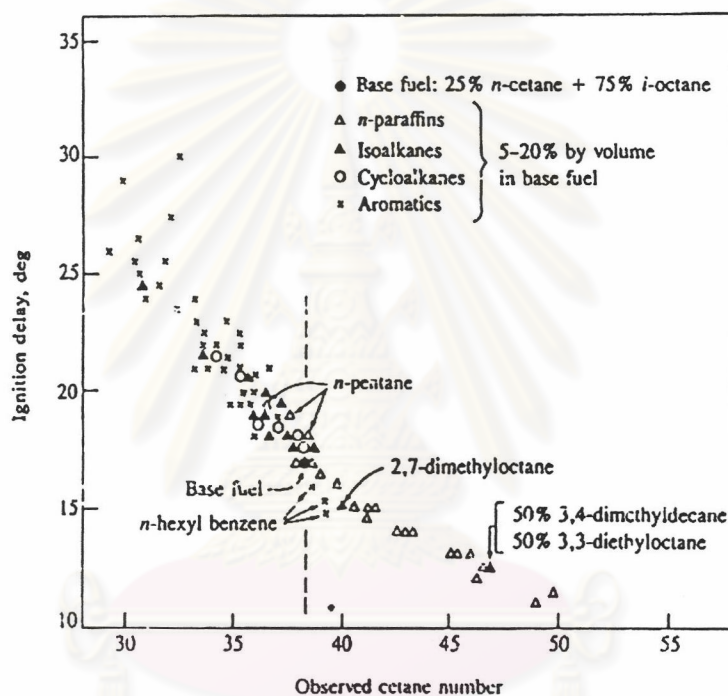
### Effect of Turbulence

The effect of turbulence on ignition delay should be mentioned, although it is very difficult to establish a satisfactory criterion of turbulence. Data available indicate that, in some instances, turbulence reduced delay and, in other instances, the delay is increased by turbulence. In an engine, turbulence has a marked effect on increasing the rate of inflammation and combustion, and this effect probably far outweighs any effect on ignition delay.

### Effect of Fuel Properties

Some both physical and chemical processes take place during the ignition delay, the effects of changes in the physical and chemical properties of fuel on the

delay period have been studied. The chemical characteristics of the fuel are much the more important. The dependence of ignition delay on fuel molecular structure is as follows. Straight-chain paraffinic compounds (normal alkanes) have the highest ignition quality, which improves as the chain length increases. Aromatic compounds have poor ignition quality as do the alcohol (hence, the difficulties associated with using methanol and ethanol, possible alternative fuels, in compression-ignition engines). Figure 2.5 illustrates these effects.



**Figure 2.5** Effect of type of hydrocarbon structure on ignition quality of fuels DI diesel combustion process at constant compression ratio and engine operating conditions [6].

A base fuel was blended with pure paraffinic (normal, iso-, and cycloalkanes), aromatic, and olefinic hydrocarbons of various carbon numbers, by up to 20 percent by volume. The base fuel, a blend of 25 percent n-hexadecane and 75 percent isooctane, had a cetane number of 38.3. The figure shows that the resulting ignition

delays correlate well as a function of cetane number at constant compression ratio and engine operating conditions. Addition of normal alkanes (excluding n-pentane and lower carbon number alkanes) improves the ignition quality. As the chain length of the added paraffin gets longer (higher carbon number) the cetane number improvement increases. Isoalkanes, depending on the degree of branching, degrade ignition quality (unless the branching is concentrated at one end of the molecule, when these types of isoalkanes improve ignition quality). Cycloalkanes and aromatics generally reduce the cetane number, unless they have a long n-alkane chain attached to the ring [6].

## **2.4 Diesel Ignition Improvers**

### **2.4.1 Cetane Number**

As previously stated, the most universally accepted measure of the ignition quality of diesel fuels is cetane number. The standard method for determining the cetane number of a diesel fuel is the ASTM D613 CFR engine technique. In this procedure the cetane number of a diesel fuel is determined by comparing its ignition quality with two reference fuel blends of known cetane numbers under standard operating conditions. This is done by varying the compression ratio for the sample and each reference fuel to obtain a fixed delay period between the start of injection and ignition. The compression ratio for the sample is bracketed by reference fuel blends, which differ, by less than five cetane numbers, and the rating of the sample is calculated by interpolation.

The cetane number scale is based on two primary reference fuels. One, normal cetane (n-hexadecane), has excellent ignition qualities and, consequently, a very short

ignition delay. A cetane number 100 was arbitrarily assigned to this fuel. The second fuel, alphas-methylnaphthalene, has poor ignition qualities and was assigned a cetane number of 0. In 1962, alphas-methylnaphthalene was replaced as a primary reference fuel by heptamethyl nonane, which has a cetane number of 15 as determined by use of the two original primary reference fuels.

The cetane number of a diesel fuel is defined as the whole number nearest to the value determined by calculation from the percentage by volume of normal cetane (Cetane No. = 100) in a blend with heptamethylnonane (Cetane No.15) which matches the ignition quality of the test fuel when compared by this method. The matching blend percentages to the first decimal are inserted in the following equation to obtain the cetane number:

$$\text{Cetane No.} = \% \text{ n-cetane} + 0.15 (\% \text{ heptamethylnonane}) \quad (2)$$

When fuel is injected into the combustion chamber of a diesel engine, ignition does not occur immediately. The interval between the beginning of the fuel injection and its self-ignition is known as the ignition delay period. This delay period depends on the fuel, the engine and its design, and on the operating conditions.

High-speed diesel engines normally are supplied with fuels in the range of 45 to 55 cetane number. The actual cetane number required in any given service depend on engine design and size, speed and load variations, and on starting and atmospheric conditions. Exhaust smoking and odor are affected only indirectly by cetane number.

Diesel fuels of high cetane number differ from those of lower cetane number by having a shorter ignition lag when injected into the diesel-engine cylinder. High-cetane fuel also is ignited at a lower compressed-air temperature than low-cetane fuel.

These characteristics result in the differences in the performance of high-cetane and low-cetane fuels in operating engines as described below [7]:

**Starting.** The higher the cetane number, the lower the temperature at which the engine can be started, but the range of starting temperatures differs for different engines. Furthermore, there is a lower limit for each engine below which starting cannot be achieved by using higher cetane fuel alone. A practical example: if a given engine would start on 35 cetane fuel with intake at 60°F, it might start at 30°F on 60 cetane fuel, but it could not be expected to start at 0°F with 85 cetane fuel.

**Warm-up.** After starting at low temperatures, engines can be brought to a state of steady running, without misfiring or emitting white smoke, more quickly on high-cetane fuel than on low-cetane fuel.

**Combustion Knock.** Combustion roughness, or diesel knock, as well as shock loading of pistons, bearings and other engine parts, results when a fuel having too low cetane number is used for the size and type of engine and conditions under which it is being operated. Use of higher-cetane fuel will give smoother combustion and reduce the noise and stress on the parts. The small, high-speed engines in automotive service usually require fuel of higher than 40 cetane number, although large-bore, slow-speed engines can utilize fuel of lower-cetane quality.

**Engine Deposits.** Low-cetane fuels may cause more rapid accumulation of varnish and carbonaceous deposits while the engine is idling at light-load operation than high-cetane fuels of the same grade. Such deposits are probably the result of the



fuel composition per se rather than the result of poor combustion due to late ignition or low cetane number.

**Smoke, Fumes and Odor.** High-cetane fuel will help reduce the production of acrid odor and fumes (cold smoke) during light-load, cool-running conditions; but ignition quality has only a minor effect on black (hot) smoke. In some types of engine very high cetane fuel, 60 or higher, causes more smoke than fuel of lower cetane number.

**Power and Fuel Consumption.** Ignition quality has a negligible influence on output and economy. Low-cetane fuels, however, as long as they satisfy the cetane requirement of the engine, tend to give slightly more power at maximum output or lower fuel consumption than high-cetane fuels. This is because low-cetane fuels generally are heavier and, therefore, contains more heat units per gallon.

In the majority of diesel engines, the ignition delay period is shorter than the duration of injection. Under such circumstances, the total combustion period can be considered to be divided into the following four stages:

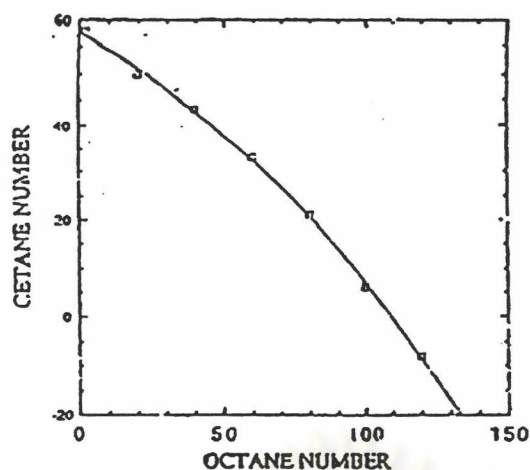
1. Ignition delay
2. Rapid pressure rise
3. Constant pressure or controlled pressure rises
4. Burning on the expansion stroke

The rapid pressure rise results from the large number of ignition points and the accumulation of fuel during the ignition delay period. Following this stage, the rate of combustion can be controlled to a much greater degree by controlling the injection rate, since the fuel is being injected into flame. Because the rapid pressure rise represents uncontrolled and inefficient combustion resulting from the burning of fuel accumulated during the ignition delay period, it is desirable to limit ignition delay to

minimum. This limitation can be accomplished mechanically by the development and selection of a spray pattern configuration properly tailored to the combustion chamber. The use of high fuel injection pressures and high fuel/air turbulence to promote rapid fuel jet break-up and through fuel distribution can reduce ignition delay.

Although the reduction of ignition delay by mechanical means is important, the nature of the fuel is the primary factor in reducing the time consumed by ignition delay. Physical characteristics, such as viscosity, gravity, and mid-boiling point are influential. On the other hand, hydrocarbon type is important only as it affects the physical characteristics of the fuel. Since the ignition delay characteristics of diesel fuels directly influence the interval of uncontrolled combustion during injection and as a result, the overall engine performance, this property is of primary importance, thus becomes desirable to have a numerical basis for evaluating the fuel ignition delay and for measuring and predicting this property.

The hydrocarbon composition of diesel fuel is believed to influence ignition quality and combustion characteristics, the depending on the degree of fuel-air mixing obtained before complete combustion. For ignition quality or low-temperature ignitability, long chain normal paraffins have a high cetane number. Highly branched chain paraffins and aromatics (compact structure) have a low cetane number. Olefins and naphthenes are intermediate. It is obvious that fuels having a high cetane number have a low octane number. We have also seen that aromatics in gasoline have very high octane numbers. This reversal of desirable fuel properties when comparing diesel and gasoline suggests an inverse relationship between cetane and octane numbers, as illustrated in Figure 2.6.



**Figure 2.6** The inverse relationship between cetane and octane numbers [8].

The cetane numbers of a variety of compounds are shown in Table 2.3. As a rule, for compounds having the same number of carbon atoms, the cetane number drops in the order  $n$ -alkane > alkene > cycloalkane > alkyl aromatic.

**Table 2.3** Cetane number for pure organic compounds [9].

Chemical Structure	Compounds	Cetane Number
Normal Paraffins	Hexadecane	100.0
	Tetradecane	96.1
	Dodecane	87.6
	Decane	76.9
	Octane	63.8
	Heptane	56.3
Olefins	1-Octadecene	90.0
	1-Hexadecene	84.2
	1-Tetradecene	82.7
	1-Dodecene	71.3
	1-Decene	60.2
	1-Octene	40.5

**Table 2.3(continued)** Cetane number for pure organic compounds.

Chemical Structure	Compounds	Cetane Number
Naphthenes	Dicyclohexyl	47.4
	Decalin	42.1
	Methylcyclohexane	20.0
Aromatics	n-Nonylbenzene	50
	n-Hexylbenzene	26
	n-Amylbenzene	8
	n-Diisopropylbenzene	-12

#### 2.4.2 Cetane Index

Since the determination of cetane number by engine testing requires special equipment, as well as being time consuming and costly, alternative methods have been developed for calculating estimates of cetane number. The calculation is based upon equations involving values of other known characteristics of the fuel.

One of the most widely used methods is based on the Calculated Cetane Index formula. The formula represents a means for directly estimating the ASTM cetane number of distillate fuels from API gravity and mid-boiling point [19]. The index value as computed from the formula is termed the Calculated Cetane Index. The Calculated Cetane Index is not an optional method for expressing ASTM cetane number. It is a supplementary tool for predicting cetane number with considerable accuracy when used with due regard for its limitations. It may be conveniently employed for approximating cetane number where the quantity of sample is too small for an engine rating. In cases where the cetane number of a fuel has been initially

established, the index is useful as a cetane number check on subsequent samples of that fuel, provided its source and mode of manufacture remain unchanged.

Calculated Cetane Index is determined by 2 methods.

1. It may be conveniently determined by means of the alignment chart in Figure 2.7.

2. It is determined from the following formula [5]:

2.1 When it is not applicable to fuels containing additives for raising cetane number.

$$\begin{aligned} \text{Calculated Cetane Index (CCI)} &= -420.34 + 0.016G^2 + 0.192G \log M \\ &+ 65.01 (\log M)^2 - 0.0001809 M^2 \end{aligned} \quad (3)$$

2.2 When it is applicable to fuels containing additives for raising cetane number. The calculated cetane index improver is determined from the equation 2 plus equation 3.

$$\text{Improver value} = 0.1742 (0.1G)^{1.4444} (0.01M)^{1.0052} \{\ln (1+17.5534D)\} \quad (4)$$

Where:

G = API gravity, determined by Test Method D287 or D1298.

M = Mid-boiling temperature (°F), determined by Test Method D86 and corrected to standard barometric pressure.

D = Percent weight of cetane improver, %weight.

Therefore;

$$\text{CCI improved} = \text{CCI} + \text{Improver value} \quad (5)$$

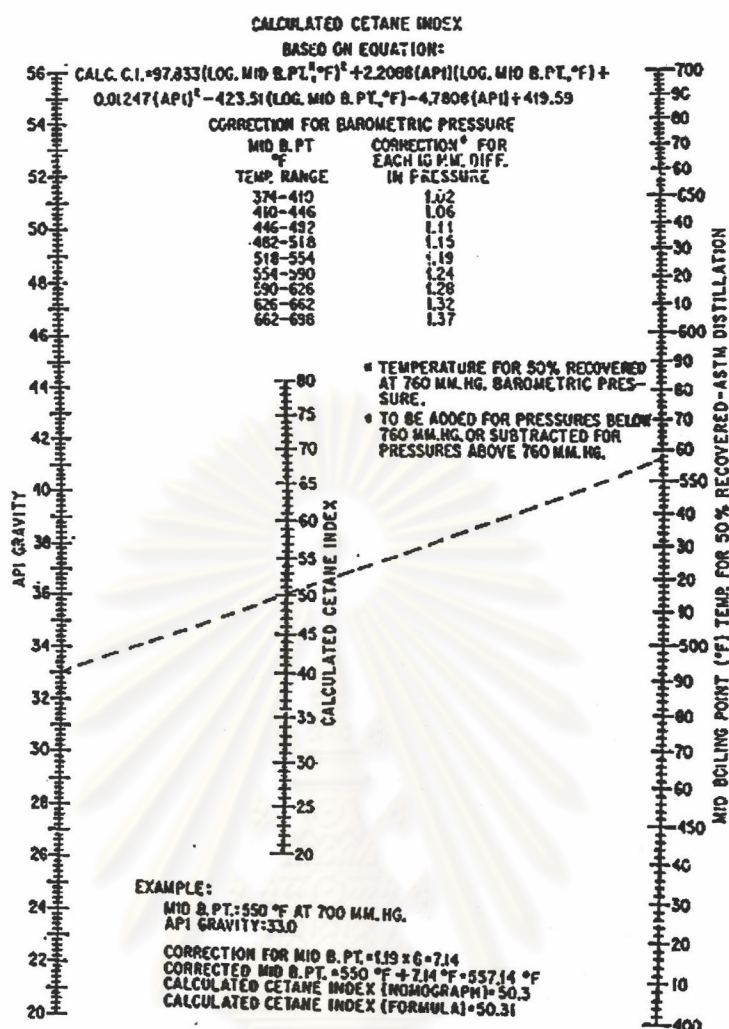


Figure 2.7 Nomograph for calculated cetane index [5].

The Calculated Cetane Index formula possesses certain inherent limitations, which must be recognized in its application. These are:

It is not applicable to fuels containing additives for raising cetane number. It is not applicable to pure hydrocarbons, synthetic fuels, alkylates or coal-tar products. Substantial inaccuracies in correlation may occur if used for crude oils, residuals or products having a volatility of below 500°F end point. Correlation of index values with ASTM cetane number is dependent to a great extent upon the accuracy of determination of both API gravity and mid-boiling point. A difference of 2°F in the mid-boiling point represents a difference of approximately 0.4 in index value. Within

the range of 30 to 60 cetane number, the expected correlation of the calculated cetane index with the ASTM cetane number will be somewhat less than  $\pm 2$  cetane numbers for 75 percent of the distillate fuels evaluated. Errors in correlation may be greater for fuels whose cetane numbers are outside this range.

### 2.4.3 Cetane Improver

Cetane improvers are compounds, which readily decompose to give free radicals and thus enhance the rate of chain initiation in diesel combustion. They promote fast oxidation of fuels and thus improve their ignition characteristics. They are specialty chemicals which, when added to diesel, improve diesel's cetane number similar to the way ethanol and ETBE improve the octane rating of gasoline. At concentrations less than 0.15%, cetane improvers can reduce ignition delay times of diesel fuel. Fundamentally, the cetane improver concentration is another degree of freedom in designing a diesel fuel. In practice, this degree of freedom is often capable of simultaneously decreasing  $\text{NO}_x$ , hydrocarbon and particulate emissions. Cetane improvers are considered a key technology to provide cleaner burning diesel fuel. They are key additives for making premium diesel. Chemical compounds such as alkyl nitrates, ether nitrates dinitrates of polyethylene glycols and certain peroxides are known cetane improvers [10].

The isooctyl nitrate product, in view of its good response and low production costs, is the most cost-effective additive and is now almost exclusively used in all commercial applications with hydrocarbon-based fuels. The weak  $\text{RO-NO}_2$  bond in isooctyl nitrate provides the available source of the free radicals required enhancing diesel combustion.

## 2.5 Diesel Fuel Additives

Apart from a few exceptions treatment of diesel fuel with additives has only recently become important. For this relatively late development in diesel fuels, compared with gasoline, two main reasons exist; First a significant progress occurred in diesel engine technology from about the mid-1970s, which made improved diesel fuel quality seem desirable, especially with respect to lower exhaust emissions. Second an anticipated change in the middle distillate quality became apparent at the same time and made the use of additive very attractive.

Commercial diesel fuel may contain a variety of additives to enhance or impart certain desirable properties. Among those which may be found in current fuels are ignition quality improvers, oxidation inhibitors, biocides, rust preventives, metal deactivators, pour point depressants, demulsifiers, smoke suppressants, detergent-dispersants, conductivity improvers, dyes and de-icers.

Diesel fuel additives are shown by class and function in Table 2.4. As with any system in which a variety of additives may be used, care should be taken to avoid incompatibilities among additives and unanticipated interactions which may produce undesirable fuel effects.

**Table 2.4** Commercial diesel fuel additives-function and type [5].

Class or Function	Common Additive Type
1. Ignition Quality Improvers: Raise Cetane Number thereby promoting faster starts and less white smoke.	-Alkyl nitrates
2. Oxidation Inhibitors: Minimize oxidation and gum and precipitate formation, improve storage life	-Alkyl amines and amine-containing complex materials



**Table 2.4(continued)** Commercial diesel fuel additives-function and type.

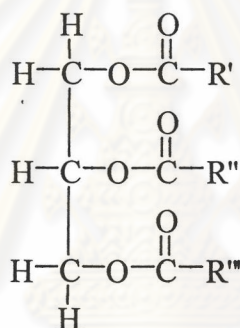
Class or Function	Common Additive Type
3. Biocides: Inhibit the growth of bacteria and fungi which feed on hydrocarbons, help prevent filter-clogging caused by these organisms.	-Boron compounds, ethers of ethylene glycol, quaternary amine compounds
4. Rust Preventives: Minimize rust formation in fuels systems and storage facilities.	-Organic acids and amine salts
5. Metal Deactivator: Deactivates copper ions which are powerful oxidation catalysis.	-N,N-disalicylidene-1,2-propane diamine
6. Pour Point Depressants: Reduce the pour point and improve low-temperature fluidity properties by modifying the wax crystal growth, structure, and/or agglomeration.	-Generally consist of polymeric materials such as polyolefins, polyacrylates and ethylene-vinyl chloride copolymers
7. Demulsifiers and Dehazers: Improve the separation of water from distillate fuels and prevent haze.	-Surface-active materials which increase the rate of water/oil separation
8. Smoke Suppressants: Minimize exhaust smoke by catalyzing more complete combustion of carbonaceous materials or by helping to maintain fuel spray patterns.	-Catalyst types are generally overbased barium compounds. Maintenance of spray patterns is helped by detergents.

This research established cetane improvers because of ignition quality are the most important properties in diesel fuels.

## 2.6 Vegetable oils

Triglycerides were interested to produce a cetane improver. Due to (1) relatively low cost and (2) chemical functional groups that allow nitration at a carbon:nitrogen ratio >6. In addition, triglycerides have carbon-carbon  $\pi$  bonds and ester bonds, both of which can be chemically modified leading to high nitration yields [11].

Most vegetable oils have a common molecular structure, which is represented by Figure 2.8.



**Figure 2.8** Structure of a triglyceride.

### 2.6.1 Palm oil

The oil palm, *Elaeis guineensis*, fruit is unusual in that it yields two distinct oils: palm kernel oil is obtained from the kernel and palm from the bulb (about 50% oil).

Palm oil is colored deep orange-red by the large amount of carotene (0.05-0.20%). The color is not much affected by alkali refining, but palm oil is bleached to a yellow color similar to that of other vegetable oils by hydrogenation. Palm oil has a pleasant, characteristic odor, is very stable to oxidation, and has no drying properties.

At ordinary temperatures at 20-25 °C, it is semisolid. Its consistency and melting point depend on its content of fatty acids because the free acids has melting point higher than the triglycerides. The commercial palm oil with a relatively low free fatty acid content are known as soft oil, whereas those with high acidity are termed hard oils.

The triglyceride composition of palm oil evidently does not adhere to the random or even theories of distribution. Typically, palm oil has 32-47% palmitic acid and 40-52% oleic acid in its triglyceride, and is thus more unsaturated. Fatty acid content of palm oil is shown in table 2.5.

**Table 2.5** Fatty acid composition of palm oil [12].

Component acids	Amount of fatty acid composition (wt%)
<b>Saturated acids</b>	
Lauric acid	0.1-1.0
Myristic acid	0.9-1.4
Palmitic acid	37.9-41.7
Stearic acid	3.0-5.0
<b>Unsaturated acids</b>	
Oleic acid	40.7-44.0
Linoleic acid	10.4-14.0
Linolenic acid	0.1-0.6

### 2.6.2 Soybean oil

Soybean is of the family *Leguminosae*, subfamily *Papilionaceae*, and the genus *Glycine max*. The soybean is a typical legume seed differing in color, size, and shape, depending upon variety. The common field varieties grown in the United States are nearly spherical and are yellow in color.

Soybean oil is the most important vegetable oil produced in the world because of its high quality and low cost. Favorable agronomic characteristics, reasonable returns to the farmer and processor, high-quality protein and edible oil products, and plentiful, dependable supply of soybeans available at a competitive price will enable soybean oil to maintain its dominance in both domestic and world markets.

**Table 2.6** Fatty acid composition of soybean oil [12].

Component acids	Amount of fatty acid composition (wt%)
<b>Saturated acids</b>	
Palmitic acid	7-12
Stearic acid	2-6
<b>Unsaturated acids</b>	
Oleic acid	15-33
Linoleic acid	35-60
Linolenic acid	2-13

### 2.7 Literature Reviews

Suppes, G.J. *et al.*[3], synthesized fatty acid glycol nitrate as cetane improvers by acid catalyzed esterification of organic acid ranging from C<sub>6</sub> to C<sub>18</sub> with ethylene glycol followed by nitration of the terminal alcohol group to form fatty acid glycol

nitrates. All the nitrates compounds provided good cetane improving capabilities, fatty acid glycol nitrates with carbon numbers between 8 and 14 exhibited the best performance. All organic acid glycol nitrates evaluated cetane improver capabilities that were up to 60% of the efficacy of 2-ethylhexyl nitrate (EHN).

Suppes, G.J. *et al.*[11], synthesized nitrate compounds from oleic acid as cetane improvers in diesel fuel by epoxidation, hydrolysis and nitration reaction, respectively. The results were obtained that the nitrate compound provided cetane improving capabilities near 2-ethylhexyl nitrate and they also provided significant lubricity enhancement to the fuels at the same concentrations used to provided the cetane enhancement.

Purcell, R.F. *et al.* [13], examined the addition of nitrate ester cetane improvers in base diesel fuel. The nitrate esters were 3-methyl-3-nitro-2-butyl nitrate, 2-methyl-2-nitro-3-pentyl nitrate, and 5-methyl-5-nitro-3-oxo-1-hexanol. The diesel oils containing nitroalkyl nitrate, nitroalkoxy nitrate or octyl nitrate was tested for cetane number under standard test procedure ASTM D613. They had found that 3-methyl-3-nitro-2-butyl nitrate and 2-methyl-2-nitro-3-pentyl nitrate increased higher cetane number than octyl nitrate. The many studies supporting are followed.

Liotta, F.T. [14], had reported that improved cetane rating were achieved with a base diesel fuel having a cetane number of 43 by addition of a small amount of methyl benzyl alcohol nitrate (MBAN). In addition to the blends containing MBAN, blends were prepared using the same concentrations of the commercial cetane number improver, 2-ethylhexyl nitrate. The results were obtained that MBAN was slightly less effective than the commercial material but it had a cost advantage over the commercial material. In fact, cetane improvers containing ring benzene tend to decrease cetane number but MBAN are comprised of nitrate groups which induce the

higher cetane number. It could be depicted that cetane improvement additive in the presence of nitrogen and oxygen in the molecular structure was used to increase cetane number.

Mason, M.H. *et al.* [15], synthesized nitrate compounds from fatty acid of methyl oleate and soybean oil as cetane improvers by epoxidation, hydrolysis and nitration reaction, respectively. The results were obtained that nitrate of methyl oleate was slightly less ignition delay time than dinitrate of soybean oil. Due to soybean has an average 4.5-5 double bonds per mole of triglycerides; the unreacted  $\pi$  bonds may quench the radical cascade caused by thermal decomposition of these molecules during combustion. This would also lower the cetane improving capability of dinitrate of soybean oil.

Moreover, several studies by Siraprapakit, S. [6], Vasaruchtragul, J. [9] and Suttipitakwong, C. [16] revealed that a diesel fuel containing dinitrate compounds such as triethylene glycol nitrate, 1,10-decane dinitrate and tripropylene glycol dinitrate increased cetane number. The results were directly compared to the response obtained with a commercial cetane improver, 2-ethylhexyl nitrate. It was found that these dinitrate compounds gave higher cetane number than commercial cetane improver.

As the above reports showed, the cetane improver containing nitro, nitrate and oxy- group was an outstanding cetane improver, especially at very low concentrations and had many times as effective as the commercial additive. Hence, the available cetane number. From what has been mentioned, the need for further research of these compounds is urgent.