CHAPTER II

THEORETICAL CONSIDERATION

Diesel Engines [6]

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 lead 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 dictates 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.

In general, two combustion chamber forms are principally used in automotive diesel engine applications. These are the direct injection system as illustrated in Figure 2.1 and the pre-chamber, indirect injection system shown in Figure 2.2.
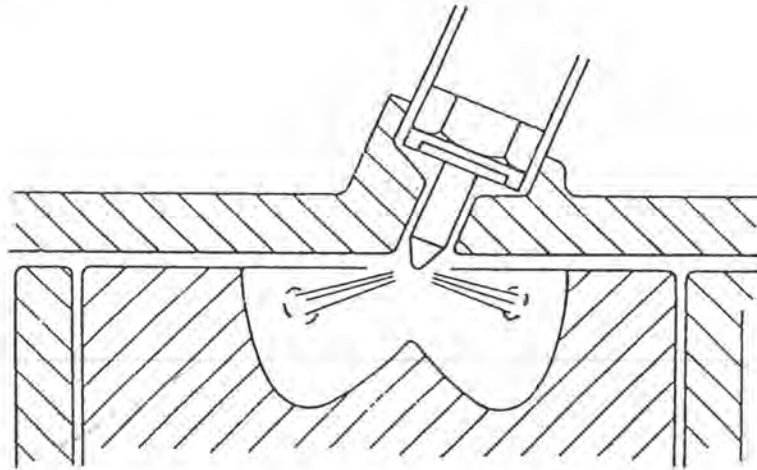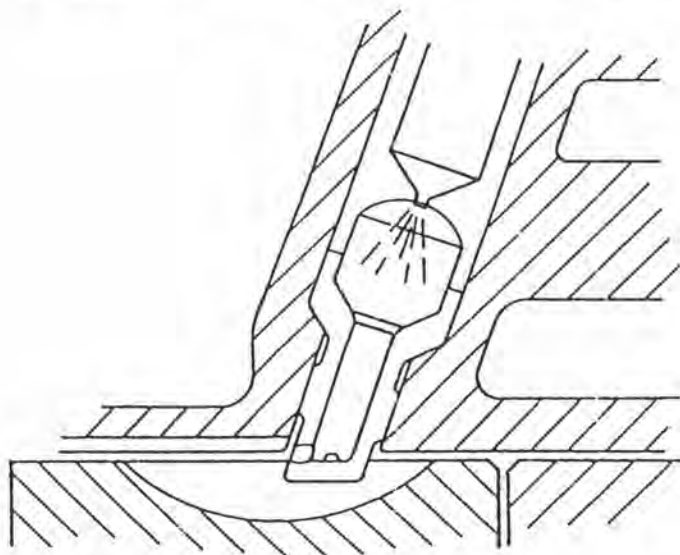
Figure 2.1 Direct injection combustion system

Figure 2.2 Indirect injection combustion system

With the deep bowl direct injection system the required fuel-air mixing is achieved by direct injection of fuel into an open cylinder into which air has been introduced with a high degree of rotational movement. The air movement is initiated during the induction stroke by correctly sited and shaped inlet ports which causes the air to swirl in the cylinder. The swirl continues as the piston rises during compression.

In contrast, in the pre-chamber indirect injection system air is forced into a pre-chamber during the compression stroke. Fuel is injected into the turbulent air and because the chamber is not particularly sensitive to atomization pintle- type nozzles are often used. After ignition the pressure in the chamber force the burning mixture through a narrow passage or passages into the cylinder, where it mixes with air to complete combustion.

The different characteristics of indirect and direct injection engines result from the following: the split of the combustion chamber gives rise to a delay in the combustion process and thus fulfills comfort requirements (lower combustion noise; less vibrations) in particular.

If the ignition delay is too high, large quantities of fuel reach the combustion chamber unburned. The length of ignition delay depends on both the design and construction of the engine and the ignition quality of the diesel fuel.

The Diesel Combustion Process [4,7,8]

When used in a diesel engine, a fuel passes through the following processes: storage, pumping and handling, filtering, heating (if necessary), atomization and mixing with air, combustion, power extraction, heat exchange and exhaust.

The fuel properties control performance in these processes and particularly influence combustion and resultant energy extraction.

In any combustion process, there are at least three basic requirements:

1. formation of a mixture of fuel and air;

2. ignition of the fuel/air mixture;

3. completion of combustion of the fuel/air mixture.

In the diesel engine, these requirements are met as indicated diagrammatically in the Figure 2.3. Figure 2.4 shows a typical pressure vs crank angle diagram for a diesel engine combustion chamber.

Prior to the injection of the fuel, air alone is compressed and raised to a high temperature during the compression stroke. The final compression pressure and resultant air temperature will very with such factors as compression ratio, speed, and engine design; but a pressure of 450 psi (31.6 kg/sq.cm) and a temperature of 1000 °F (538 °C) are representative values. Shortly before the end of compression, at a point controlled by the fuel injection timing system, one or more jets of fuel are introduced into the combustion chamber.
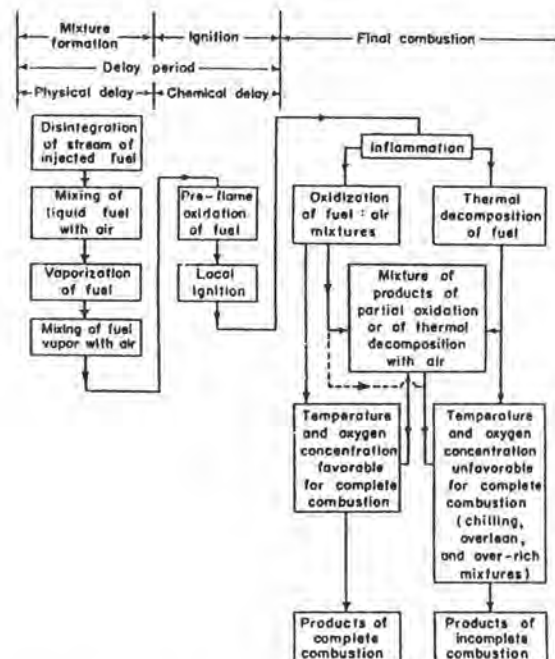
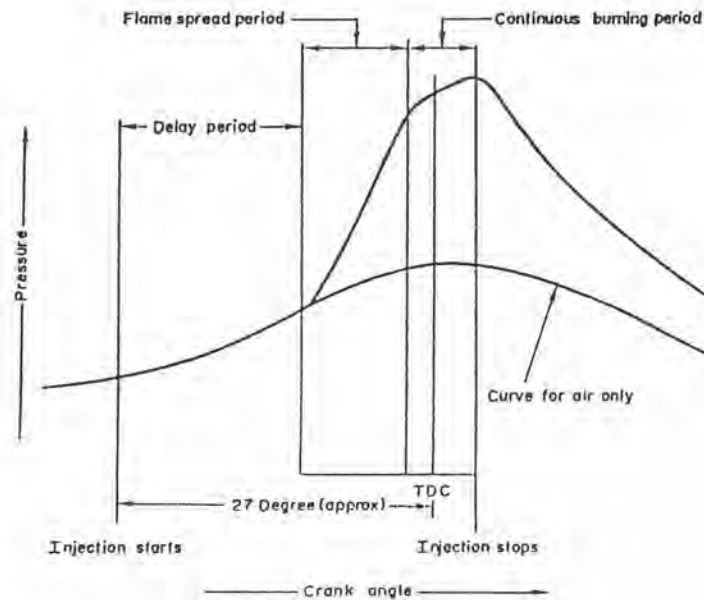Figure 2.3 Outline of the combustion process in the diesel engine

Figure 2.4 Pressure variations in a diesel engine cylinder during
combustion

Ignition does not occur immediately on injection. The fuel droplets
absorb heat from the compressed air. This is necessary for vaporization and for
increased efficiency. The duration of the delay period between injection and
ignition is controlled by engine design, fuel and air inlet temperatures, degree
of atomization of the fuel, and fuel composition. This delay period is
commonly known as "ignition delay."

The fuel/air mixture finally reaches a temperature at which self-
ignition occurs and the flame begins to spread. Injection of fuel continues
during this time. Therefore, the ignition delay period must be short in order to
avoid "diesel knock" which is caused by very rapid burning or detonation of
relatively large amounts of fuel gathered in the cylinder before combustion on
begins. Once the flame has been initiated completely, the only fuel in the
cylinder is that being injected into the burning mixture. This fuel burns almost

instantaneously. The final part of the combustion cycle is the completion of burning after injection has ceased.

The quantity of fuel, the rate at which it is injected into the engine, and the timing and duration of the injection period are all accurately controlled by a cam-driven injection pump. The pump delivers the fuel to the injectors at a pressure at the time of injection varying from 1800 to 30,000 psi (130 to 2100 kg/sq. cm), depending upon the design of the injection equipment.

Variation in the fuel quantity to conform to different speed and/or load conditions usually is by means of a governor, which admits fuel to the combustion chamber at a preset maximum rate until the new conditions are attained. The governor is set to avoid the onset of black smoke caused by an excessive amount of fuel.

The air that can be delivered to an engine is determined by design considerations. The amount of this air is sufficiently utilized determines the optimum injection rate of fuel and hence the maximum power output of the engine. Below this maximum, the output of the engine is controlled solely by the amount of fuel supplied.

Pressure charging frequently is used as a means of increasing the amount of air delivered to an engine without increasing its size. A compressor, either directly coupled to the crankshaft (a supercharger) or driven by a turbine using the heat energy in the exhaust gases (a turbocharger), is used to increase the amount of combustion air available. Consequently, the engine is able to burn a greater quantity of fuel and power increases in the order of 50 percent are possible without exceeding the normal level of exhaust smoke. The amount of fuel ultimately is limited by the thermal and mechanical stresses that can be tolerated by engine components.

Cetane Number Improvers

1. Cetane Number [4,6,9-11]

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 rise

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. Ignition delay can be reduced by the use of high fuel injection pressures and high fuel/air turbulence to promote rapid fuel jet break-up and thorough fuel distribution.

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. It thus becomes desirable to have a numerical basis for evaluating the fuel ignition delay and for measuring and predicting this property.

The cetane number of a diesel fuel is the numerical result of an engine test designed to evaluate fuel ignition delay. To establish the cetane number scale, two reference fuels were selected. One, normal cetane, has excellent ignition qualities and, consequently, a very short ignition delay. A cetane number 100 was arbitrarily assigned to this fuel. The second fuel, alphamethylnaphthalene, has poor ignition qualities and was assigned a cetane number of 0. In 1962, alphamethylnaphthalene was replaced as a primary reference fuel by heptamethylnonane, which has a cetane number of 15 as determined by use of the two original primary reference fuels.

To determine the cetane number of any fuel, its ignition delay is compared in a standard test engine (single cylinder test engine with a variable compression ratio) with a blend of reference fuels, which gives a standard 13° crank angle ignition delay at the same compression ratio as test fuel. This engine and the prescribed test method are described in ASTM D613 or IP41.

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:

$$\text{Cetane No.} = \% \text{ n-cetane} + 0.15 \, (\% \text{ heptamethylnonane}) \qquad (1)$$

When fuel is injected into the combustion chamber of a diesel engine, ignition does not occur immediately. The interval between the beinning

of the fuel injection and its self-ignition is known as the ignition delay period. This delay period depend on the fuel, the engine and its design, and on the operating conditions. The shorter the ignition delay period the higher the cetane number of the fuel and the smaller the amount of fuel in the combustion chamber when the fuel ignites. Consequently, high cetane number fuels generally cause lower rates of pressure rise and lower peak pressures, both of which tend to lessen combustion noise and to permit improved control of combustion, resulting in increased engine efficiency and power output. In addition to the above, higher cetane number fuels tend to result in easier starting, particularly in cold weather, and faster warm-up. The higher cetane number fuels also usually form softer and hence more readily purged combustion chamber deposits and result in reduced exhaust smoke and odor. 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 depends 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. For satisfactory performance in these respects the fuel required by individual engines will very and cannot be defined sharply because of difference in engine design and operating conditions.

The hydrocarbon composition of diesel fuel is belived 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 fuel and gasoline

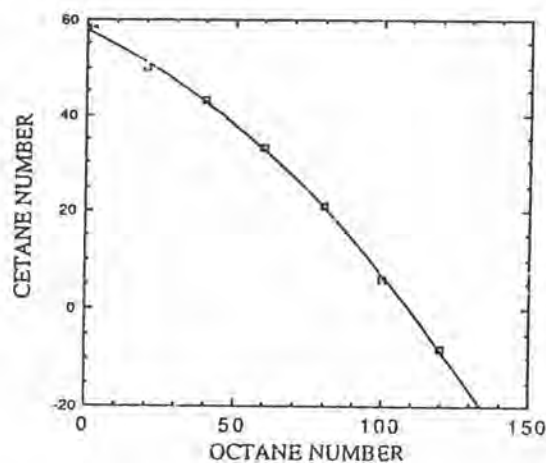suggests an inverse relationship between cetane and octane numbers, as illustrated in Figure 2.5. [2,3]

Figure 2.5 The inverse relationship between cetane and octane numbers

The most universally acepted measure of the ignition quality of diesel fuels is cetane number . As Shown in Figure 2.6, the self-ignition characteristics of hydrocarbons vary markedly with both boiling point and chemical structure.

The cetane numbers of a variety of compounds are shown in table 2.1. 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.

The long chain normal parrafins have a high pour point and a low volatility. The melting point of cetane is 65 °F ; hence, low pour point, high cetane number fuels are not easily obtainable. Straight-run fuels from paraffin base crudes high cetane numbers. Crudes rich in aromatics and cracked distillates give lower cetane number fuels. The cetane number can be improved by solvent refining cracked distillates to reduce the aromatic content. Solvent refining simultaneously reduces the sulfur content.
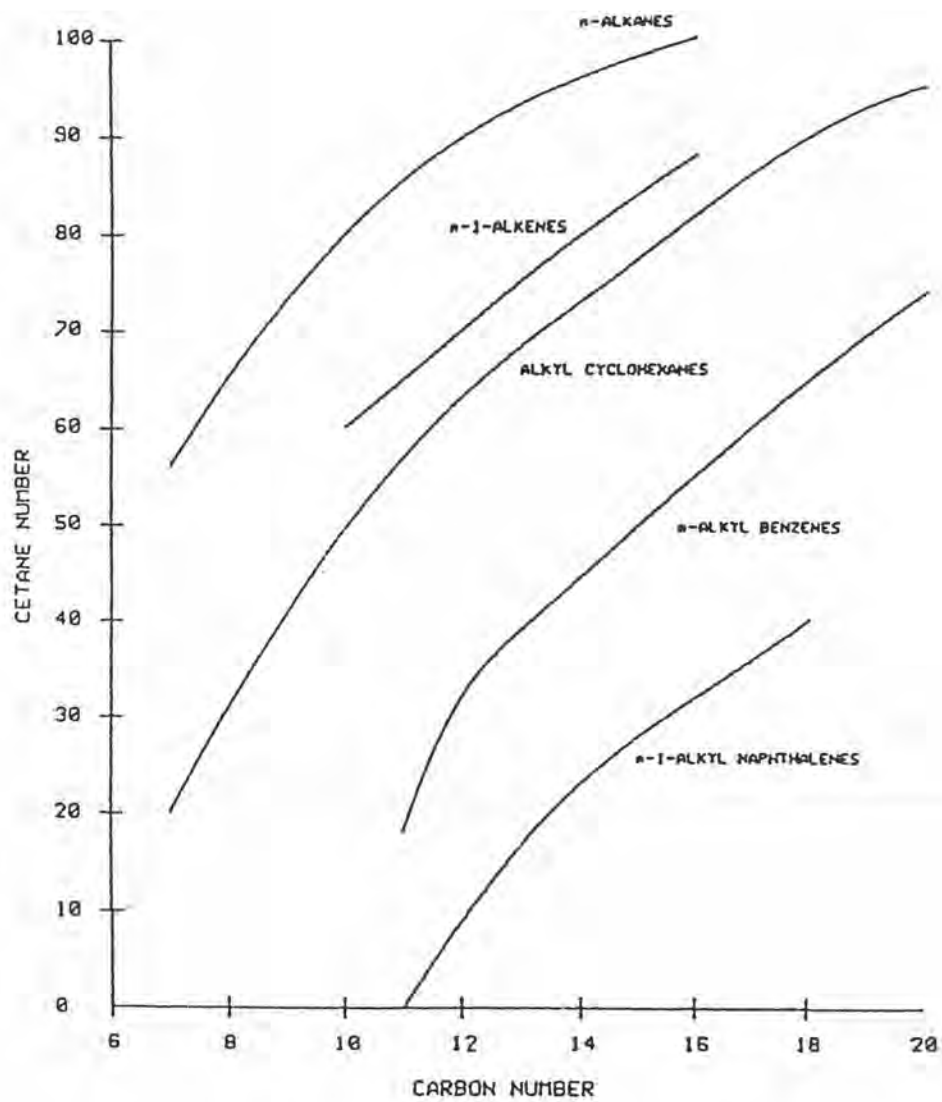
Figure 2.6 Cetane number of pure hydrocarbons

Table 2.1 Cetane number for pure organic compounds

Normal Paraffins		Olefins	
Heptane	56.3	1-Octene	40.5
Octane	63.8	1-Decene	60.2
Decane	76.9	1-Dodecene	71.3
Dodecane	87.6	1-Tetradecene	82.7
Tetradecane	96.1	1-Hexadecene	84.2
Hexadecane	100.0	1-Octadecene	90.0
Naphthenes		Aromatics	
Methylcyclohexane	20.0	n-Amylbenzene	8
Dicyclohexyl	47.4	n-Hexylbenzene	26
Decalin	42.1	n-Nonylbenzene	50
		n-Diisopropylbenzene	-12

2. Cetane Index [4,12-13]

Since the determination of cetane number by engine by 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 are 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. This formula represents a method for estimating the cetane number of distillate fuels from API gravity and mid-boiling point. The

index value as computed from the formula is designated as a Calculated Cetane Index (ASTM D976 or IP 218). Since the formula is complicated in its manipulation, a nomograph based on the equation has been developed for its solution.

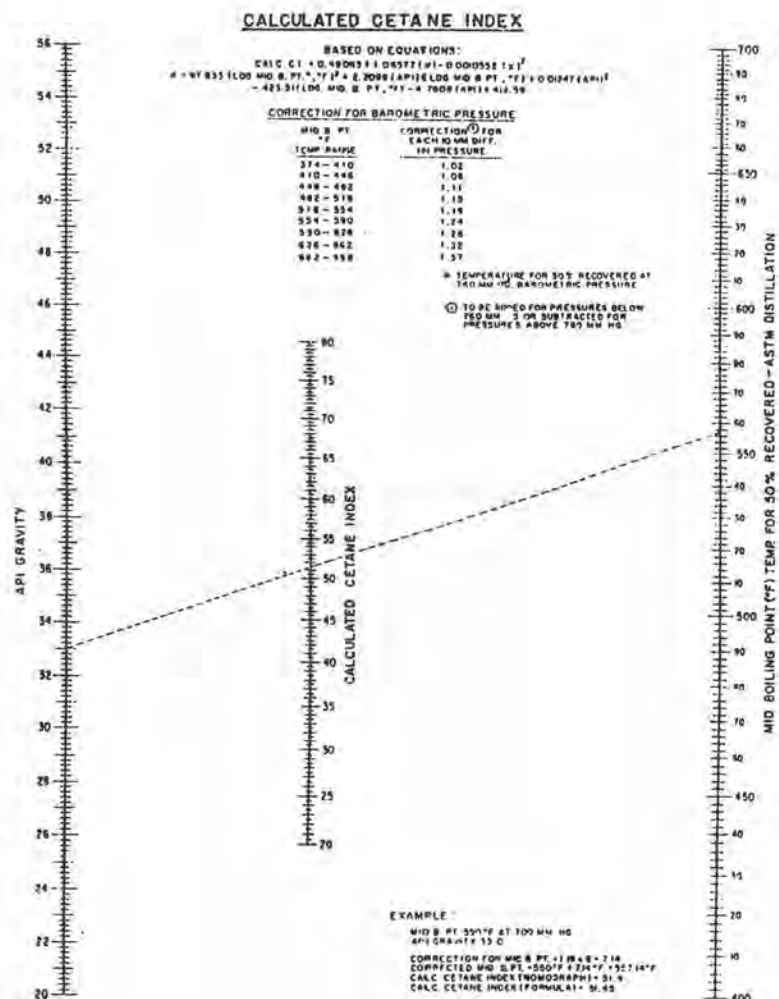This nomograph, together with the equation, are shown in figure 2.7.

Figure 2.7 Nomograph for calculated cetane index (ASTM D976-IP 218)

An example illustrating the use of the chart is also presented. It must be recognized that the calculation of Cetane Index is not an optional method for expressing cetane number. Rather, it is a supplementary tool for

predicting cetane number with considerable accuracy when used with due regard for its limitations. Among the limitations of Calculated Cetane Index are following:

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 and products. Correlation is fair for a given type of fuel but breaks down if fuels of widely. Different compositions are compared. Appreciable inaccuracy in correlation may occur when used for crude oils. Residuals, or products having end points below 500 °F (260 °C).

The Calculated Cetane Index is determined from the following equation:

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

$$\text{Calculated cetane index (CCI)} = -420.34 + 0.016G^2 + 0.192G \log M + 65.01 (\log M)^2 - 0.0001809 M^2 \qquad (2)$$

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 [12]

$$\text{Improver value} = 0.1742(0.1G)^{1.4444} (0.1M)^{1.0052} \{\ln(1+17.5534D)\} \qquad (3)$$

where

G = API gravity, determined by Test Method D287 or D 1298,

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

D = percent weight of cetane improver, % wt.

$$\text{CCI improver} = \text{CCI} + \text{Improver value} \qquad (4)$$

3. The cetane quality of diesel fuels and diesel fuel components [6]

Cetane number or cetane index requirements are present in most diesel fuel specifications but, as illustrated in Table 2.2, signification variation in the quoted values is evident. Within Europe the cetane quality of diesel fuel has traditionally been high, and importance is attached to the performance benefits this offers in terms of:

1. Improved cold
2. Reduced smoke emission during warm-up
3. Reduced noise
4. Reduced fuel consumption and exhaust emissions
5. Improved engine durability

The scope of refiners to produce diesel fuel of high cetane quality varies significantly with the types of crude oil processed and the process units available within the refinery. In general, throughout the world the conversion refinery utilizing catalytic cracking predominates, and the diesel fuel blending components typically available are shown in Table 2.2 and 2.3, the effect of crude source on light gas oil quality being illustrated by the data in Table 2.2 and the effect of components type by the data in Table 2.3.

Trends in the production and use of petroleum products are dictating that increased quantities of the lower cetane quality components are used in diesel fuel blending. Projections are that, without the use of additives, marked falls in the cetane quality of diesel fuels could occur. In this situation cetane improvers are invaluable, as they provide refiners and blenders with a simple and effective means of achieving operational flexibility on a day-to-day basis.

Table 2.2 Effect of crude source on diesel fuel blending component quality

Property	Crude source		
	Light gas oil ex Kuwait crude	Light gas oil ex Forties crude	Light gas oil ex Nigerian crude
Density (kg/l at 15 °C)	0.8517	0.8558	0.8785
Viscosity (cSt at 40 °C)	4.5	4.6	4.5
Cloud point (°C)	4	6	- 8
Cold filter plugging point (°C)	- 4	1	- 11
ASTM distillation			
50% distilled at °C	304	294	283
sulfur (%wt)	1.40	0.19	0.13
Cetane number (ASTM D613)	54.1	52.2	40.9

Table 2.3 Effect of component type on diesel fuel blending component quality

Property	Component type			
	Kerosene ex North Sea crude	Light gas oil ex North Sea crude	Light cracked gas oil ex North Sea crude	
			Non-hydrotreated	Hydrotreated
Density (kg/l at 15 °C)	0.8011	0.8558	0.9613	0.9294
Viscosity (cSt at 40 °C)	1.2	4.6	3.1	3.0
Cloud point (°C)	- 58	6	- 11	- 11
Cold filter plugging point (°C)	- 58	1	- 9	- 9
ASTM distillation				
50% distilled at °C	190	294	276	273
sulfur (%wt)	0.03	0.19	1.35	0.24
Cetane number (ASTM D613)	41.3	52.2	21.0	24.1

Current experience would suggest that cetane number improvers are being increasingly used to:

1. Upgrade diesel fuels quality to meet specification requirements in conversion refineries where there is a requirement to use increasing quantities of cracked components in diesel fuel production.

2. Provide the flexibility required to process significant quantities of low cetane naphthenic crude oils when geographic or economic conditions dictate this.

3. Upgrade diesel fuel quality to give the premium grade products now being marketed by many oil companies in certain markets throughout the world.

Additives for Diesel Fuels [5,14]

Apart from a few exceptions treatment of diesel fuel with additives has only recently (from ca. 1987 onward) 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 because apparent at the same time and made the use of additives very attractive. Additives for diesel fuel have many type, such as cetane improvers, detergent additives, corrosion inhibitors, stability improvers, etc. This thesis estabilished cetane improvers.

Ignition or Cetane Improvers [5,15]

The cetane number is a measure of the ignition quality of a diesel fuels. Because a range of aspects essential to the operation of diesel engines are

also connected with the cetane number (cold-start properties, white and black smoke emission, noise emission, fuel consumption, engine durability), the increase in cetane number by additives is a valuable means of improving diesel fuel quality.

The effect that can be achieved by the addition of an ignition improver depends on the base diesel fuel. Unfortunately, base fuels with high natural cetane numbers react better to additive treatment than those with lower cetane numbers, for which an increase in the cetane number is more essential (figure 2.8).
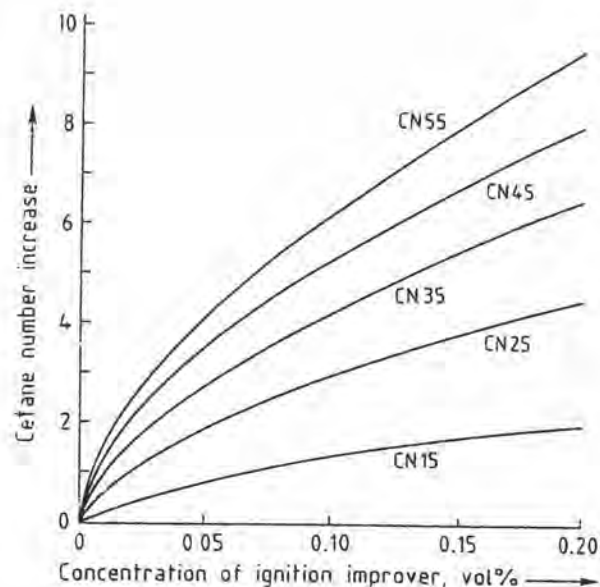

Figure 2.8 Response of different base fuel types to
addition of ignition improvers

In view of constantly increasing efforts to reduce exhaust gas emissions, the fact that even small qualities of ignition improvers can improve the exhaust gas quality of the diesel engine is important (Figure 2.9)
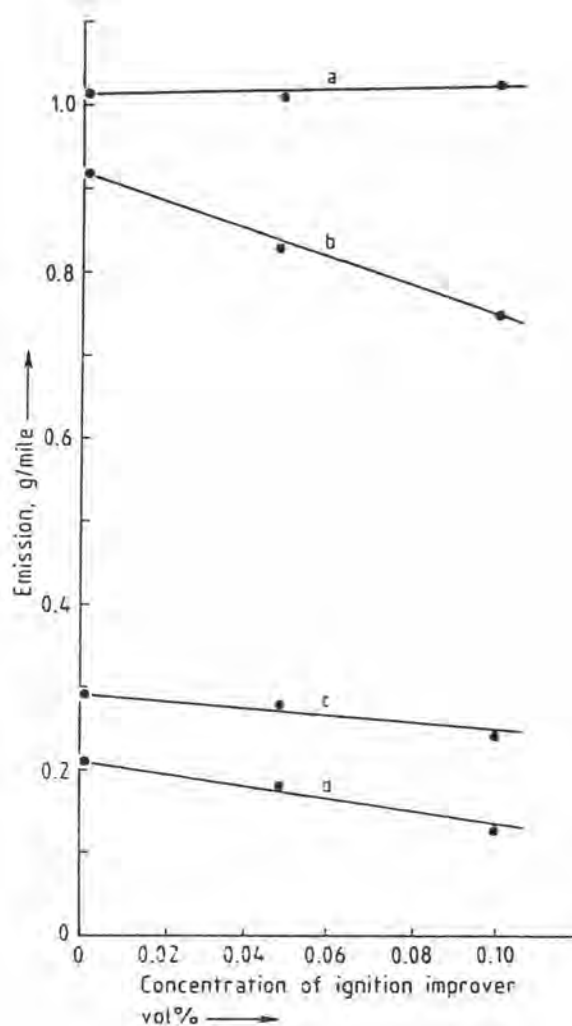
Figure 2.9 Improvement of exhaust gas emission by ignition improvers

a) Oxides of nitrogen; b) Carbon monoxide; c) particulates;

d) hydrocarbons

The effect of ignition improvers is based on their rapid decomposition, with the formation of free radicals that accelerate the chain reaction of diesel fuel combustion. Suitable compounds are alkyl nitrates, ether nitrates, alkyldiglycol nitrates and organic peroxides, for example. From a commercial viewpoint, only alkyl nitrates such as isopropyl nitrate, isoamyl nitrate, isohexyl nitrate, cyclohexyl nitrate, or isooctyl nitrate have been

successful. With these compounds, the ready cleavage of the RO-NO$_2$ bond leads to radical formation.

At present there is no widespread use of ignition quality improvers because: (a) most commercial high-speed diesel fuels are adequate as far as ignition quality is concerned, and (b) the additive dosage required (and therefore cost) is high; (c) many of the materials are very volatile and cause a significant reduction in the flash point of the fuel.

Literature Review

Somboon Nontaganok [8] studied on the synthesis of tetrazole derivatives by direct synthesis from either trialkyltin azide and nitrile compound or sodium azide and nitrile compound. However the synthesis of tatrazole derivatives especially alkyltatrazole by using nitrile containing an electron releasing substituent reacted more readily with trialkyltin azide than with sodium azide. Subsequent tetrazole products were obtained by treatment with hydrochloric acid.

Tetrazole derivatives are effective in increasing cetane number only when used in a concentration of 0.05 % by weight. The antiknock property was determined by cetane number and cetane index. They are easy to blend with diesel fuel by organic solvent helping refiners to upgrade diesel fuel qualitatively and economically.

Martella, D.J. and Plainsboro, N.J. [1] examined the use of 5-propyltetrazole as a cetane improver in base diesel fuel and compares its against commercial cetane improver such as 2-ethylhexylnitrate. Four base fuel samples were each treated with 500 ppm of the 5-propyltetrazole and four other base fuel samples were each treated with 500 ppm of 2-ethylhexylnitrate. The test samples were paired and rated in accordance with the ASTM D613 test

procedure. 5-Propyltetrazole gave cetane number more than 2-ethylhexyl nitrate. This difference was statistically significant at 95 % confidence level.

It can be seen that tetrazole derivatives, particularly 5-alkyl tetrazoles gave cetane number at satisfactory level. There was not many tetrazole derivatives in the literature which could be use as cetane improver. For this thesis, it will be some search of various tetrazole derivatives to be use as cetane improver.

Synthesis of Tetrazole Derivatives

There are many approaches for the tetrazole derivatives. Tetrazole derivatives can be synthesized by direct synthesis from sodium azide and nitrile compound or hydrazoic acid and nitrile compound. The synthesis of tetrazole derivatives shown as follows.

1. Synthesis of tetrazole derivatives from the reaction of nitriles with hydrazoic acid [16]

The reaction of hydrazoic acid to the cyanide group with the formation of 5-substituted tetrazole derivatives was first observed by Hantzsch and Vagt, who prepared 5-aminotetrazole by the interaction of hydrazoic acid and cyanamide. The same product could be prepared from the more readily accessible dicyandiamide and hydrazoic acid. Presumably the dicyandiamide dissociated under the conditions of the reaction so that the process was essentially the same as that described by Hantzsch and Vagt. The synthesis of the parent heterocycle was the interaction of hydrazoic acid and hydrocyanic acid in alcoholic solution. These authors suggested that tetrazole formation took place through the formation of an imide azide which immediately cyclized to tetrazole as indicated in the following general reaction.
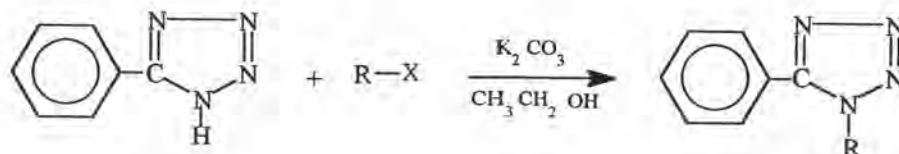
R= Alkyl, Aryl, Nitroalkyl and Nitroaryl
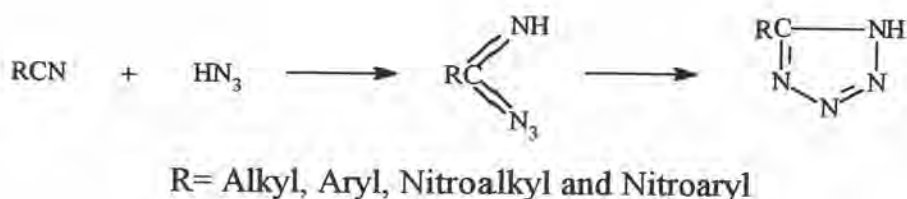
Scheme 2.1

When alkyl or aryl nitriles were heated with benzene solution of hydrazoic acid at temperature of 120-150 °C for periods of 96-120 hours,excellent yield of the 5-alkyl- or 5-aryl-tetrazoles were obtained.

2. Preparation nitroaryltetrazole by nitroarylation of the 5-substituted tetrazole derivatives [12]

In an attempt to obtain characteristic derivatives 5-phenyltetrazole was treated with nitroaryl halide in alkaline, aqueous alcoholic solution. Easily crystallizable, neutral products that gave correct nitrogen analyses for the nitroaryl-5-pheyltetrazole was formed. In order to determine whether the aryl group occupied the 1 or the 2 position on the ring, the same reaction was carried out with nitroaryl halide and 5-phenyltetrazole as indicated in the following general reaction.

R = nitroalkyl, nitroaryl

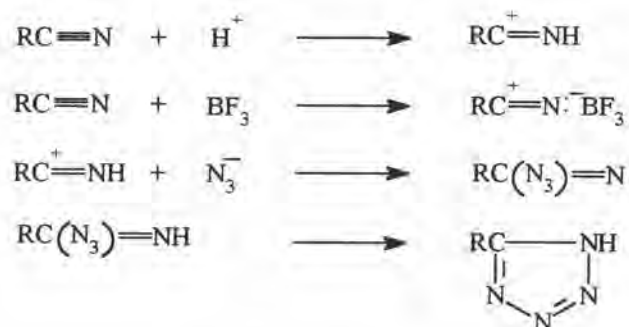X = Halide group: F⁻, Cl⁻, Br⁻, I⁻

Scheme 2.2

3. Synthesis of tetrazole derivatives from sodium azide and alkyl or arylnitrile derivatives [17,18]

The previously described synthesis of 5-alkyl and 5-aryltetrazole derivatives, although generally capable of giving good yields, are not all adaptable to larger scale. In several instances they suffer the disadvantage of requiring the independent preparation of non-aqueous solutions of hydrazoic acid. Multi-step reaction sequences proceeding via imino ether, hydrazides and azides, result in only modest yields. Reactions using solutions of hydrazoic acid in benzene, toluene or xylene, or sodium azide and acetic acid in butanol either in glass or pressure equipment at high temperatures require extended reaction times of four to seven days The recently described synthesis of 5-substituted tetrazoles by the reaction of aluminum azide with aliphatic nitriles in tetrahydrofuran overcomes many of these difficulties, but an examination of the experimental evidence indicates that only one-third of the available azide groups is utilized.
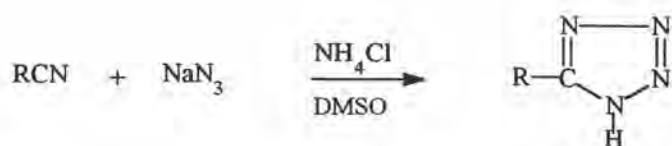
In an attempt to simplify and improve the synthesis of 5-substituted tetrazoles the reaction of certain azide salts such as ammonium, substituted ammonium, sodium and lithium azides, with nitriles in organic solvents, such as dimethylformamide, was investigated carefully. With the ammonium and substituted ammonium azides, the action has been found to be general and can be made to give excellent of 5-substituted tetrazoles after very reasonable times. For example, with aliphatic and electropositively substituted arylnitriles, conversions of 90 % or better can be achieved in 18 to 24 hours at temperatures of 125 °C. With electronegatively substituted nitriles even lower reaction temperatures and shorter reaction times can be used.

The general mechanism for the reaction appears to be a nucleophilic attack of azide ion on the carbon of the nitrile group, followed by ring closure of the imino azide to form the tetrazole ring. Apparently, a $+\delta$ charge on the

nitrile carbon is necessary for the azide ion attack since conditions which enhance or favor such a charge increase the rate of reaction. The reaction has been found to be subject to general acid catalysis. Hydrazoic acid, amine hydroazides and Lewis, such as BF_3, more than double the yield of 5-phenyltetrazole from benzonitrile when added in amounts from 4 to 10 mole% of the sodium azide in a 7 hours reaction at 123-127 °C. Coordination of a Lewis acid or proton with the nitrile nitrogen would generate a $+\delta$ charge on the nitrile carbon and facilitate the approach of the azide ion.

$$RC{\equiv}N \; + \; \overset{+}{H} \quad \longrightarrow \quad RC\overset{+}{=}NH$$

$$RC{\equiv}N \; + \; BF_3 \quad \longrightarrow \quad RC\overset{+}{=}N{:}^-BF_3$$

$$RC\overset{+}{=}NH \; + \; N_3^- \quad \longrightarrow \quad RC(N_3){=}N$$

$$RC(N_3){=}NH \quad \longrightarrow \quad \underset{\underset{N}{\diagdown}}{\overset{RC{-\!\!-\!\!-}NH}{\underset{N}{\parallel\!\!\diagup}}}$$

Scheme 2.3

$$RCN \; + \; NaN_3 \quad \xrightarrow[\text{DMSO}]{NH_4Cl} \quad R{-}C\underset{\underset{H}{\diagdown N\diagup}}{\overset{N{-\!\!-\!\!-}N}{\diagup\diagdown}}N$$

R = alkyl, aryl, nitroalkyl, nitroaryl group

Scheme 2.4

The solubility of the azide salt also influences the rate of reaction: lithium and tetramethylammonium azides are very soluble in dimethylformamide and their rates of reaction with benzonitrile are greater than that of the moderately soluble sodium azide but less than the rates obtained with the equally soluble amine hydroazides.