

## CHAPTER II

### THEORETICAL CONSIDERATIONS

#### 2.1 Diesel fuel [9, 10]

Distilling crude oil, which is a mixture of heavy and light hydrocarbons requires different degrees of heat to produce different products. Lighter hydrocarbons have lower boiling points and can be separated using relatively little heat. For instance, gasoline components are lighter than those of diesel. The boiling range of gasoline currently in use is between 30°C and 210°C, while that of kerosene is between 150°C and 300°C. Diesel fuel is a distillate boiling between 150°C and 300°C, but this is not a unique description: other fractions boiling within this range, but meeting different secondary specifications comprise naphtha, jet fuel, kerosene, and so on. An approximate classification is shown in Table 2.1

**Table 2.1** Classification of distillate fuels.

Classification	Approximate boiling range
Gas	< 30°C
Straight run gasoline	30 - 200°C
Light naphtha	30 - 110°C
Heavy naphtha	80 - 200°C
Middle distillate fuels	135 - 360°C
Kerosene and jet fuel	145 - 280°C
Diesel fuel	160 - 330°C
Light fuel oil	215 - 360°C
Heavy fuel oil	290 - 400°C

The higher boiling range of diesel fuel comparing to gasoline indicates that larger molecules will be present in the diesel fuel. The diesel fuel may contain alkanes in the  $C_{15}$ - $C_{17}$  range and aromatics as large as alkylated naphthalenes. It should therefore also expect that diesel fuel will be higher density and higher viscosity comparing to gasoline. For example, octane has an API gravity of  $70^\circ$  and a viscosity of 0.54 mPa-s at room temperature, whereas hexadecane has a gravity of  $51^\circ$  and viscosity of 3.34 mPa-s. Many diesel fuels have API gravities in the range  $33$ - $44^\circ$ , even lower than would be anticipated from the values for the alkane compounds in the diesel fuel boiling range. The lower value of the API gravity comparing to the alkanes reflects the presence of substantial quantities of aromatics. As a matter of fact, alkanes have much higher API gravities than aromatics having the same number of carbon atoms, as summarized in Table 2.2

**Table 2.2** Comparative API gravities of alkane and aromatic compounds.

Carbon atom	Alkane	API gravity	Aromatic	API gravity
10	Decane	$62^\circ$	Naphthalene	$-8^\circ$
11	Undecane	$59^\circ$	1-Methylnaphthalene	$7^\circ$
12	Dodecane	$57^\circ$	2-Ethylnaphthalene	$9^\circ$

Today, with the various refinery cracking processes, diesel fuels also may contain varying amounts of selected cracked distillates to increase the volume available for meeting the growing demand, while still maintaining cost at a minimum. Within certain limits, the relative amounts of gasoline, diesel and/or jet fuel, and of heavier oils, that can be obtained by simple fractional distillation, are fixed, and if there is a mismatch between this and what the market demands, then either shortages will ensue, or the legislated standards

will not be met. To compensate for this, refinery processes have been developed whereby heavier gas oil fractions are subjected to catalytic cracking and hydrogenation to give more gasoline and distillate, but these cracked materials tend to be aromatic in nature; consequently, they make good gasolines, but poor diesel fuels. Mass spectrometric analysis show that they are much richer in alkylbenzenes, as well as in 2- and 3-ring aromatic compounds; it requires much more severe hydrogenation conditions to saturate the aromatic rings. At the same time, some countries have undertaken massive projects to extract oils from shale and tar-sands deposits: typically, bitumen is separated from the rock or sand, and cracked at high temperature to form lighter materials; hydrogenation is then used to reduce both the nitrogen and sulfur content, and to help to stabilize the cracked products. Again, these materials possess much more aromatic character than does diesel oil from conventional source: typical assays are shown in Table 2.3

**Table 2.3** Comparison of composition (in wt %) of conventional diesel fuel with those of synthetic materials

Compositions	Conventional Diesel fuel	Cracked Gas oil	Synthetic Diesel Fuel
Paraffins	39	19	17
Naphthenes	34	16	37
Alkylbenzenes	18	34	36
2-Ring Aromatics	8	28	8
3-Ring Aromatics	1	3	2

Furthermore  $^1\text{H}$  and  $^{13}\text{C}$ -NMR studies on the alkylbenzenes show that the same molecular weight, those found in conventional fuel have relatively few (1-3) longer aliphatic side-chains, whereas those from synthetic sources

have many (4-6) shorter side-chains, several of them perhaps being methyl groups. Thus, it is this preponderance of short side-chains, rather than the increase in the aromatic content itself, that is the principal cause of the lower cetane numbers for synthetic diesel fuels; also, the high content of naphthalenic compounds in the cracked oil fractions makes them unsuitable for augmenting the diesel fuel and jet fuel supply.

A temporary palliative to the diesel fuel quality problem is the addition of ignition promoters, either organic nitrates or organic peroxides, but if the cetane numbers of the available fuels were to continue to decline in the future, the cost of the addition would become significant: for example, to raise the cetane number of diesel fuel from 35 to 40 by addition of iso-octyl nitrate would add about 10% to the untaxed cost at present-day prices, and release many unwanted tones per annum of  $\text{NO}_2$  into the atmosphere in major urban areas. Thus, a better understanding of how these additives work is becoming essential.

The physical characteristics of a diesel fuel are vitally important with respect to the production of a fuel suitable for commercial use. Ignition quality is of prime importance when considering combustion, but other properties such as volatility, viscosity, hydrocarbon composition and stability can not be overlooked if optimum engine performance is to be achieved.

## **2.2 Specifications for Diesel Fuel [11,12]**

The specifications for diesel fuel are broad as the engines. Because of the complex nature of diesel fuels and the various modern-day refining methods, plus the number of cruds used in the refineries, the specifications seem to be decreased, and the price of the fuels tended to be increased.

Most of the fuels, whether used to produce heat under a boiler, or power a diesel engine, have the same tests and specifications. They are listed here, with a brief statement of each.

The gravity is indirectly related to engine operation. A lower gravity fuel increases power output and reduces fuel consumption.

The cloud point should be below the lowest operating temperature at which the engine will operate so that the filter will not become plugged and clogged with wax crystals.

The pour point of distillate diesel fuels bears the same relationship to that of combustion or heating fuel. This specification should be at least 10 °F below the lowest operating temperature of the engine.

The flash point is important only to safe-handling of the fuel, having little bearing upon engine operation, except if it is extremely low, which is not common.

The viscosity of the diesel fuel, whether a distillate or residual type, is of extreme importance. This specification must be correctly controlled for satisfactory fuel pumping, fuel atomization, injector operation, fuel-spray penetration and lubrication of the fuel pump and injector nozzle.

Distillate diesel fuel of low initial boiling point can cause smoking while fuels of high distillate range or volatility can produce engine deposits and high fuel consumption vaporization and clean combustion, resulting in low residual deposits.

Ash is responsible for engine deposits and excessive wear, necessitating the diesel fuel of an ash content as low as possible.

Sulfur can be related to engine corrosion particularly at low temperature and with intermittent operation. Engine manufactures generally recommend low sulfur fuel to combat this problem, usually specifying a 0.75% maximum content.



Carbon residue is related to the quantity of deposits formed inside the engine. The higher the carbon residue content of the diesel fuel, the greater will be the amount of carbonaceous engine deposits.

## **2.3 Diesel ignition improvers**

### **2.3.1 Cetane number [13,14]**

The ignition quality of a diesel fuel is measured by “ delay ”, the time lapse between the beginning of ignition and the onset of a significant pressure rise in the cylinder. The shorter the delay, the better the ignition quality. A good ignition quality is essentially the opposite of good knock resistance. The ignition quality is often expressed in term of the “ cetane number “, which is determined by comparing the combustion performance of a test fuel to that of a mixture of hexadecane (cetane) and heptamethylnonane.

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 rate 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 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.

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;

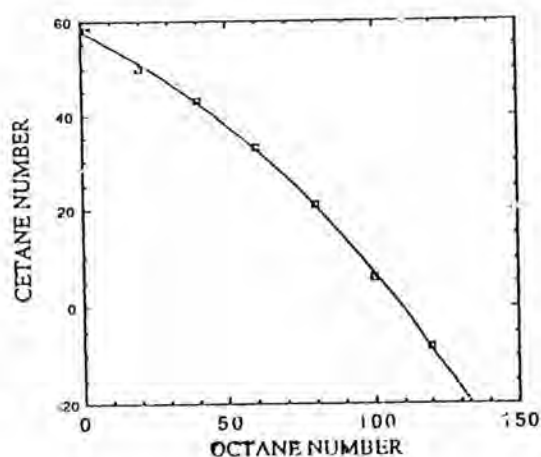
1. Ignition delay.
2. Rapid pressure rise.
3. Constant pressure or controlled pressure rise.
4. Burning on the expansion stroke.

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 presents uncontrolled and inefficient combustion resulting from the burning of fuel accumulated during the ignition delay period, it is desirable to limit ignition delay to a minimum. This limitation can be accomplished mechanically by the development and selection of a spray pattern configuration property tailored to the combustion chamber. Ignition delay can be reduced by the use of high fuel injection pressure 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.

Some hydrocarbons ignite more readily than others and are desirable because of this short ignition delay. The desired molecular structures for a good fuel for a CI engine are essentially the opposite of those desired for a SI engine fuel. The fuel for the CI engine should have abundant straight chain alkanes, whereas these are undesirable in the SI fuel. We have also seen that aromatics in gasoline have very high octane numbers. This reversal of desirable fuel properties when comparing diesel fuels and gasoline suggests an inverse relationship between cetane and octane numbers, as illustrated in Figure 2.1.



**Figure 2.1** The inverse relationship between cetane and octane numbers.

The cetane numbers of compounds are in Table 2.4. 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. For example, compare dodecane, 7-dodecene, dicyclohexane, and 1-phenylhexane. Among the alkanes, cetane number drops with decreasing chain length; compare octadecane, tetradecane, and decane, for example.



**Table 2.4** Cetane numbers for pure organic compounds.

Compounds	Cetane number
Octadecane	103
Hexadecane	100
Tetradecane	96
1-Octadecene	90
Dodecane	88
1-Hexadecene	84
1-Tetradecene	83
Decane	77
7-Dodecene	71
Octane	64
1-Decene	60
Heptane	56
1-Phenylnonane	50
Dicyclohexyl	47
Decalin	42
1-Octene	40
1-Phenylhexan	26
Methylcyclohexane	20
1-Phenylpentane	8
Di-isopropylbenzene	-12

### 2.3.2 Cetane Index [15,16]

Since the determination of cetane number by engine testing requires special equipment, time consuming, and costly, alternative methods have been developed for calculating estimates of cetane number. The calculations 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 formation 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 formular is designated as Calculated Cetane Index. Since the formular is complicated in its manipulation, a monograph based on the equation has been developed for its solution.

The Calculated Cetane Index is determined from the following equation:

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

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

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 .

$$\text{Improver value} = 0.1742(0.1G)^{1.4444}(0.01M)^{1.0052} \{ \ln (1+17.5534D) \} \quad (3)$$

Note: 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;

$$\text{CCI improved} = \text{CCI} + \text{Improver value} \quad (4)$$

## 2.4 Fuel Properties Affecting Ignition Delay [17-19]

### 2.4.1 Fuel rating.

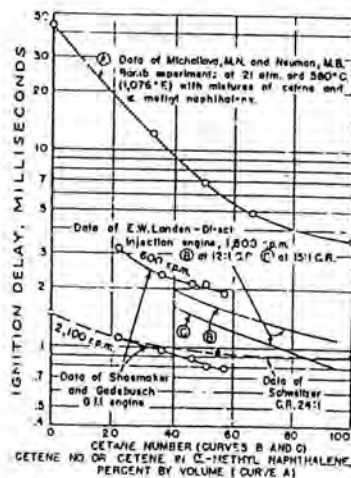
A discussion of the effect properties on ignition delay must be prefaced by a discussion of methods for evaluating fuels to determine these effects. In the case of diesel fuels, this is done in the familiar CFR engines by matching, under standard test conditions, the ignition delay of the unknown fuel with the ignition delay of a reference fuel.

Since high cetane fuels ignite in the CFR engine at low temperatures and pressure than low cetane fuel, it is apparent that the cetane number permits us to put the fuels in the proper order with respect to the ease with which they may be ignited by compression. It is, therefore, useful in rating fuels and as a basis for correlating data on certain fuel performance factors in engines.

It should be emphasized that the cetane number has no quantitative significance, since it tells us only that Fuel A is better than Fuel B, but not how much better.

To attach quantitative significance to the cetane number, it is necessary to study the performance of the fuel under the particular environment in which we are interested. This point is illustrated in Figure 2.2, which shows the relation between cetane number and ignition delay in tests in three different engines and between cetane number and ignition delay in the bomb tests. This figure emphasizes the importance of the environment in attaching quantitative significance to the cetane number. This is indicated by the effect of speed on the ignition delay of a given cetane number fuel in one engine, by the effect of compression ratio in another engine, and by the comparison between bomb and engine experiments.

Closer study on Figure 2.2 shows that, in the low range of cetane numbers, a given increase in cetane number corresponds to a greater decrease in ignition delay than in the high range.



**Figure 2.2** Relation between ignition delay and cetane number in tests in engines and bombs.

### 2.4.2 Effect of chemical structure.

A determination of the effect of molecular structure on the ignitability or on the cetane number of a fuel is important not only from the standpoint of producing suitable fuels for diesel engines but also because the information obtained can be applied at least qualitatively to extending our knowledge of combustion of hydrocarbons. Unfortunately, very little information of this type for hydrocarbons in diesel fuel range has been published, and no analysis of the available data similar to that made by Lovell-Campbell for hydrocarbons in the gasoline range has been made.

The effect on cetane number of adding one side chain to a normal paraffin hydrocarbon is shown in Figure 2.3. The data were obtained by Petrov in a bomb which had been calibrated against a CFR engine.

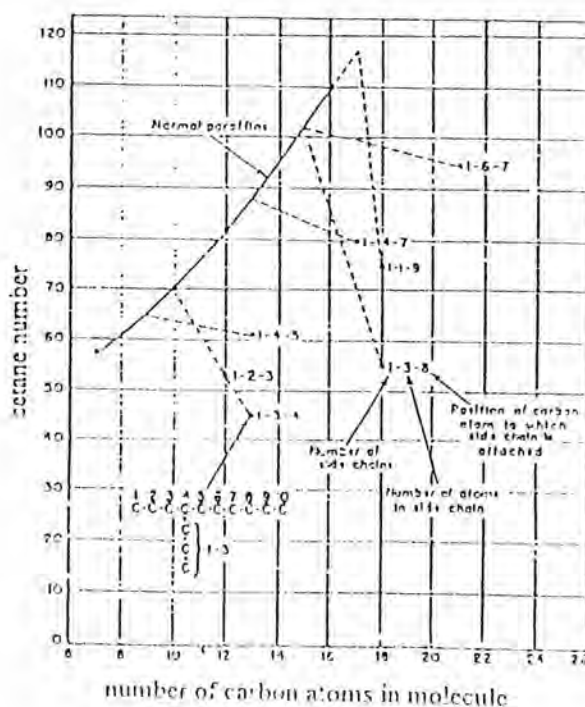


Figure 2.3 Cetane number of normal alkyl paraffin hydrocarbons.



Figure 2.3 shows qualitatively that, in every instance, the addition of one side chain to a normal paraffin hydrocarbon reduces the cetane number. In general, the side chain was added near the middle carbon atom of the normal paraffin and this should be recognized in any conclusions drawn. Data were obtained on side chains containing one to seven carbon atoms; but in Figure 2.3 it is very difficult to separate the effect of length of side chain on cetane number, because in no instance was the length of the main chain held constant nor did the length of the side chain increase systematically.

The cetane number of n-alkyl benzenes has been determined by Ju and Wood and is shown in Figure 2.4 as a function of the number of carbon atoms in the molecule. Here again, the data leave a great deal to be desired, but there is a definite indication of a minimum cetane number for an alkylbenzene containing two, three, or four carbon atoms in the side chain.

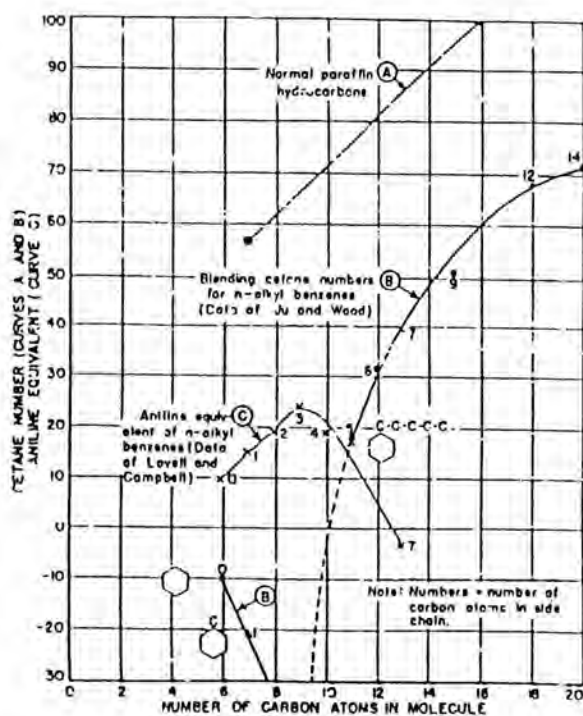


Figure 2.4 Cetane number and aniline equivalent of n-alkyl benzenes.

To examine the results of Lovell and Campbell, who obtained data on the knocking tendency in a gasoline engine of n-alkylbenzene having side chain containing from one to seven carbon atoms. The measure of knocking tendency was the aniline equivalent; the lower the value of the aniline equivalent, the greater the tendency to knock, or, in other words, the shorter the ignition delay. From this, it is evident that the aniline equivalent is inversely proportionally the cetane number. Figure 2.4 shows also the results of the tests of Lovell and Campbell, and it is evident that the aniline equivalent is a maximum for propylbenzene. Here again, we have further evidence of the specificity of a single three carbon straight side chain resulting in a molecular configuration having maximum stability toward oxidation. Lovell and Campbell call attention to this possibility; but at the time their results were published, the data on the effect of side chains on the cetane number of normal paraffins had not been obtained.

Although the evidence is admittedly meager, it is difficult to believe that the indicated effect of a single three carbon n-alkyl side chain is fortuitous. In any case, this is a point that should be checked in a systematic investigation; if it is found to be as indicated in the foregoing, we will have an important lead to follow in fundamental studies of the mechanism of oxidation of hydrocarbons.

The foregoing discussion has considered only the effect on the cetane number of adding one side chain to a normal paraffin or to benzene. Limited data are available on the effect of adding two or more side chains. Although the data are too meager to warrant a detailed discussion, the indications are that the addition of two side chains cause a significantly greater reduction in the cetane number of a normal paraffin than the addition of one side chain.

Data on the cetane number of other pure hydrocarbons also too incomplete to warrant detailed discussion. The limited information available on decalin and naphthalene is presented in Figure 2.5. It will be observed that the decalins and naphthalenes have cetane numbers considerably less than that of a

normal paraffin with the same number of carbon atoms. In the case of the decalins, the addition of a side chain further decreases the cetane number. In this connection, it is interesting to note that the cetane number of octyl decalin is less than that of either octane or decalin.

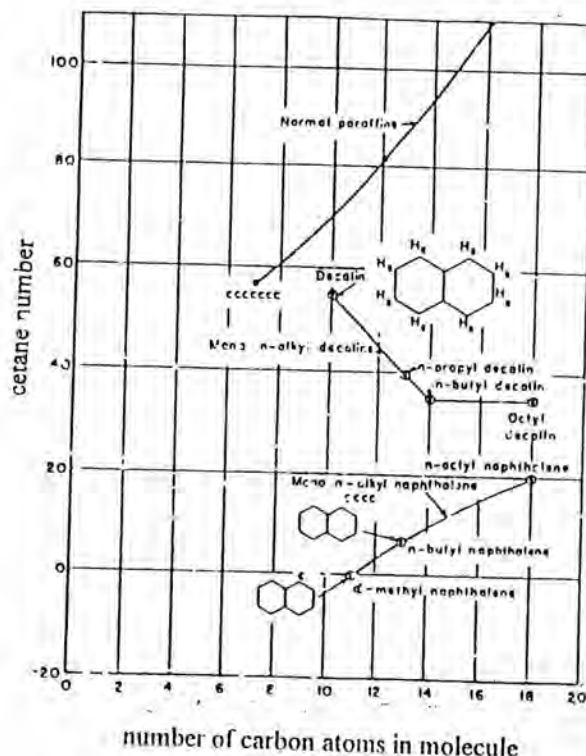
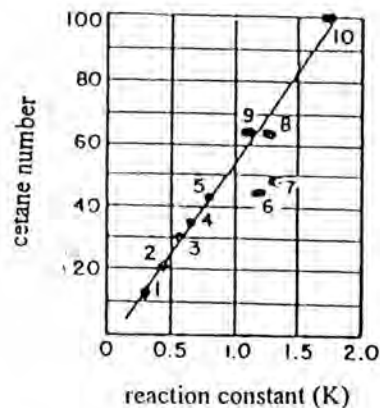


Figure 2.5 Cetane number of n-alkyl decalins and naphthalenes

### 2.4.3 Effect of thermal stability.

The effect of the thermal stability of a fuel on its ignitability was studied by Boerlage and van Dyck. In their tests, the thermal stability of the fuel was measured by the rate at which the fuel cracked or decomposed into lower molecular weight hydrocarbons. The results of these tests are shown in Figure 2.6, which indicates good correlation between rate of cracking and cetane number in eight out of ten fuels. These results clearly show that low

thermal stability of a fuel is associated with high oxidation rate. The reason for this association probably is related to the high reactivity of hydrocarbon free radicals produced in the thermal decomposition process.



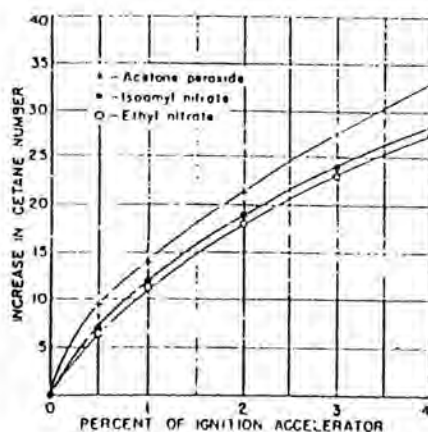
**Figure 2.6** Reaction constant K in relation to cetane number.(cranking temperature 635 °C)

#### 2.4.4 Ignition accelerators.

The rate of the chemical reactions proceeding the auto-ignition of a fuel may be increased by the addition of ignition accelerators. Numerous compounds have been proposed as ignition accelerators, but probably the most effective, reasonably stable accelerator is acetone peroxide, and the most effective semicommercially available accelerator is amyl nitrate. The average increase in cetane number obtained in tests of nine different fuels is shown in Figure 2.7, in relation to the concentration of ignition accelerator. It will be observed that significant improvement is obtained with comparatively small additions of accelerator.

The question of what is the probably mechanism of ignition acceleration and why comparatively small additions of accelerator produced a remarkable effect has been answered by Broeze and Hinze, who show on the reduction in

ignition delay by accelerators are explained on the basis of chain reaction theory. Therefore, the accelerators or their thermal decomposition products enter into chain branching reactions. In connection with the effect of alkyl nitrate, it is noted that  $\text{NO}_2$  in certain concentrations accelerates the reaction between hydrogen and oxygen and between carbon monoxide and oxygen.



**Figure 2.7** Average increase in cetane number of a test fuel in relation to concentration of ignition accelerator.

## 2.5 Additives for Diesel Fuels [2,10,13]

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 additives very attractive. Additives for diesel fuel have many type which was shown in Table 2.5.



**Table 2.5** Additives for diesel fuels.

Additives	Function
1. Cetane Improvement	-Increased cetane number
	-Enhanced Ignitability
2. Oxidation Inhibitors	-Reduced sediment and gum occurring
	from reacting with oxygen during
	storage.
3. Corrosion & Rust Inhibitors	-Reduced corrosion and rust in fuel
	lines throughout the storage.
4. Pour Point Depressant	-Low temperature flowability.
5. Detergent/Dispersants	-Keep clean the fuel lines.
6. Demulsifiers	-Rapid separation between water and
	fuel.
7. Lubricating Agent	-Lubricate pump system and fuel
	nozzle.

## 2.6 Literature Reviews

Liotta, F.T. Jr. [20] 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. The many studies supporting are followed.

As Filbey, A.H.[4] had found that cetane number of diesel fuel, both hydrocarbon and alcohol, was increased by adding a small amount of a tetrahydrofuranol nitrate. The cetane increase caused by the present additives was measured in comparison with that caused by a commercial cetane improver, isooctyl nitrate, using a base diesel fuel having cetane number of 46. Likewise the prior reports, Hinkamp, J.B.[21] concluded that an aliphatic hydrocarbyl nitro nitrate additive such as 2-methyl-2-nitro-1-propanol nitrate (ester) increased cetane number higher than isooctyl nitrate, using 38 cetane number base diesel fuel.

Moreover, several studies by Martella, D.J.[6], Nontaganok, S. [7], and Ratttanatawonkiti, W. [8] had revealed that a diesel fuel containing a tetrazole derivatives such as 5-propyltetrazole ,and 5-(4'-nitrophenyl) tetrazole slightly increased cetane number, except the tetrazole derivatives containing so many benzene rings.

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