

CHAPTER II

THEORETICAL CONSIDERATION

2.1 Diesel Engine

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.

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 [4].

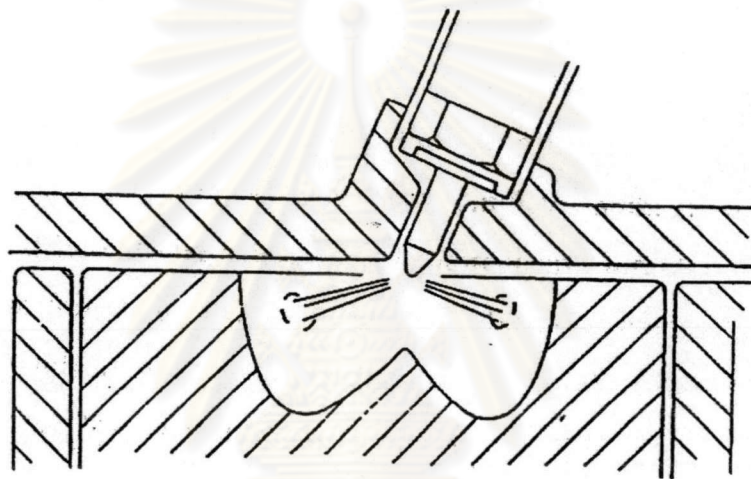


Figure 2.1 Direct injection combustion system.

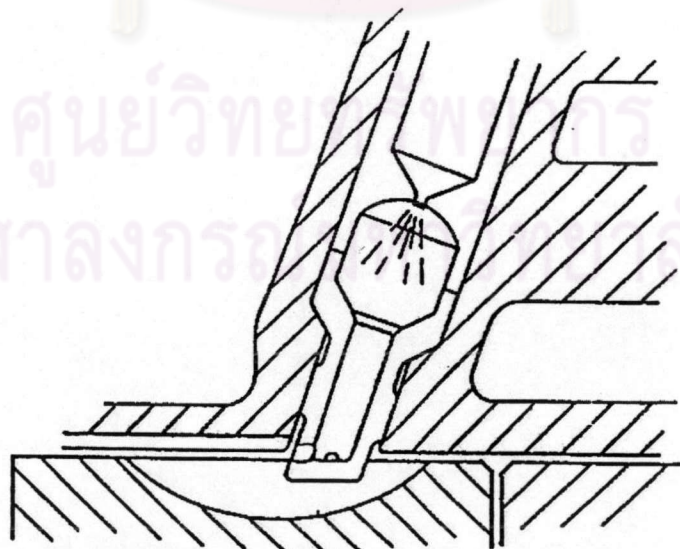


Figure 2.2 Indirect injection combustion system.

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 forces the burning mixture through a narrow passage or passages into the cylinder, where it mixes with air to complete combustion [10].

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.

2.1.1 The Diesel Combustion Process

Combustion fuel in a liquid state is injected in the cylinder at a precise rate ensures that the combustion pressure is forced on the piston too early nor too late. The fuel enters the cylinder where the heated compressed air is present.

Fuel will burn only when it is in a vaporized state (attained through addition of heat) and intimately mixed with a supply of oxygen. All these conditions are present in the cylinder. When the first minute droplet of fuel enters the combustion chamber,

it is quickly surrounded by its own vapor because the compression temperature at this point is about 343 °C (650°F). Heat is withdrawn from the air surrounding the droplet causing it to vaporize. It takes time for the heat to build up again and cause the vapor to ignite since the core of the droplet is still liquid and relatively cold. Once ignition has started and a flame is present, the heat required for continuous vaporizing is supplied from that released by combustion and the higher compression temperature. The liquid droplet surrounded by its own vapor, burns as fast as fresh oxygen is supplied. This process continues unchanged until the fuel oil is burned or the oxygen is used up [3, 11].

2.1.2 Combustion of Diesel Fuel Oils

Both physical and chemical processes are involved to any combustion process. In the diesel engine, the physical processes include transportation of the fuel and air into the combustion chamber, mixing of fuel and air, and provision of environmental conditions favorable to chemical reaction. The chemical processes involve self-ignition or auto-ignition of the fuel and finally extensive chemical reaction that liberates the potential energy in the fuel.

2.1.3 General Outline of Combustion in the Diesel Engine

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 Fig. 2.3

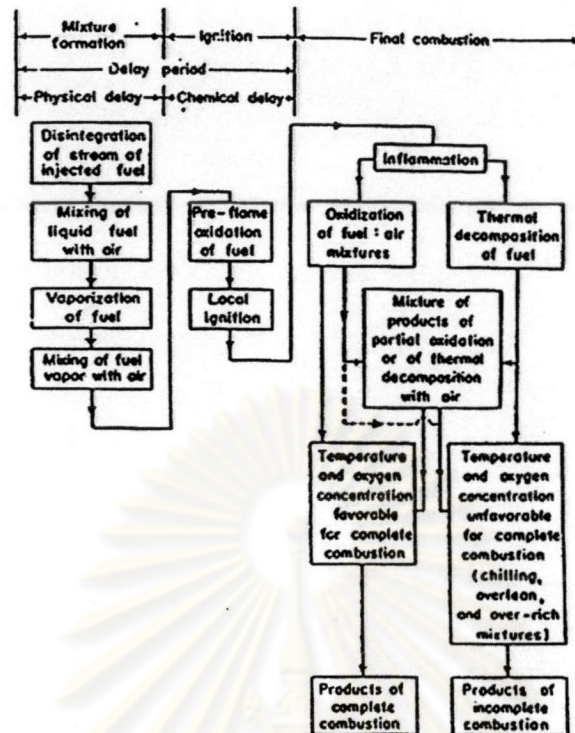


Figure 2.3 Outline of combustion process in the diesel engine.

Ignition in the diesel engine occurs as the result of auto-ignition of the fuel. This is accomplished by the direct oxidation of the fuel, the rate of which is comparatively slow at first and accelerates rapidly until ignition occurs. After ignition, the mixture inflames and combustion may proceed as indicated in Fig. 2.3, either by rapid oxidation of mixtures of fuel and air or by rapid oxidation of products of thermal decomposition of the fuel. If mixing is complete under conditions favorable for combustion, then combustion is complete. If mixing is inadequate or if combustion reactions or thermal decomposition reactions are chilled, products of incomplete combustion will result.

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.

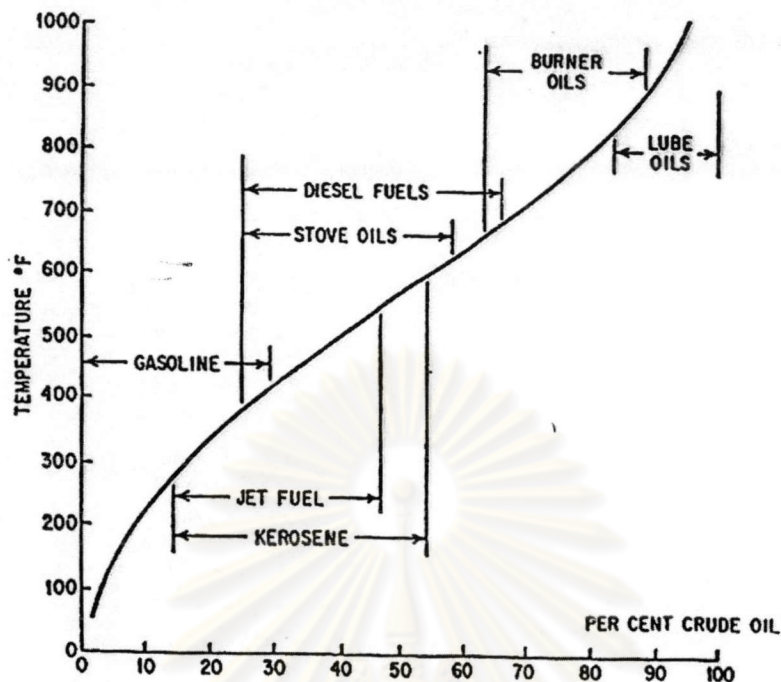


Figure 2.4 Proportion of diesel fuel and other petroleum products processed from crude petroleum.

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.

With reference to Fig. 2.4 [12], 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 [11];

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 most simple 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 fractins 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 [13].

<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	°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) °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.

2.3 Diesel Ignition Improvers

2.3.1 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 [10]:

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

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 [12]:

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 engines 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. 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 through 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 [14]. 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 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 2.5.

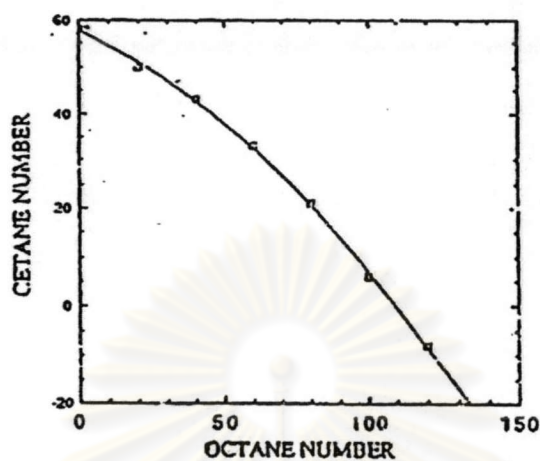


Figure 2.5 The inverse relationship between cetane and octane numbers.

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 [15].

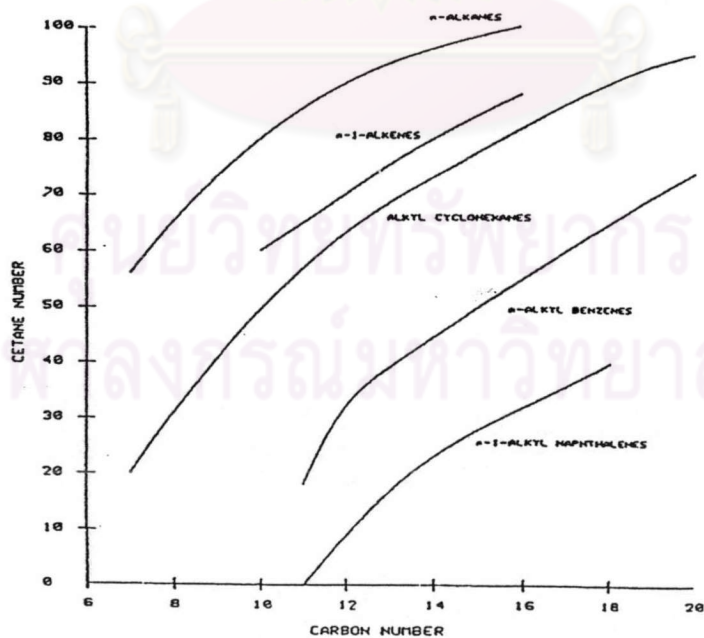


Figure 2.6 Cetane number of pure hydrocarbons.

Table 2.1 Cetane number for pure organic compounds.

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
Naphthenes	Dicyclohexyl	47.4
	Decalin	42.1
	Methylcyclohexane	20.0
Aromatics	n-Nonylbenzene	50
	n-Hexylbenzene	26
	n-Amylbenzene	8
	n-Diisopropylbenzene	-12

2.3.2 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 [16]. 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 [17]:

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;

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

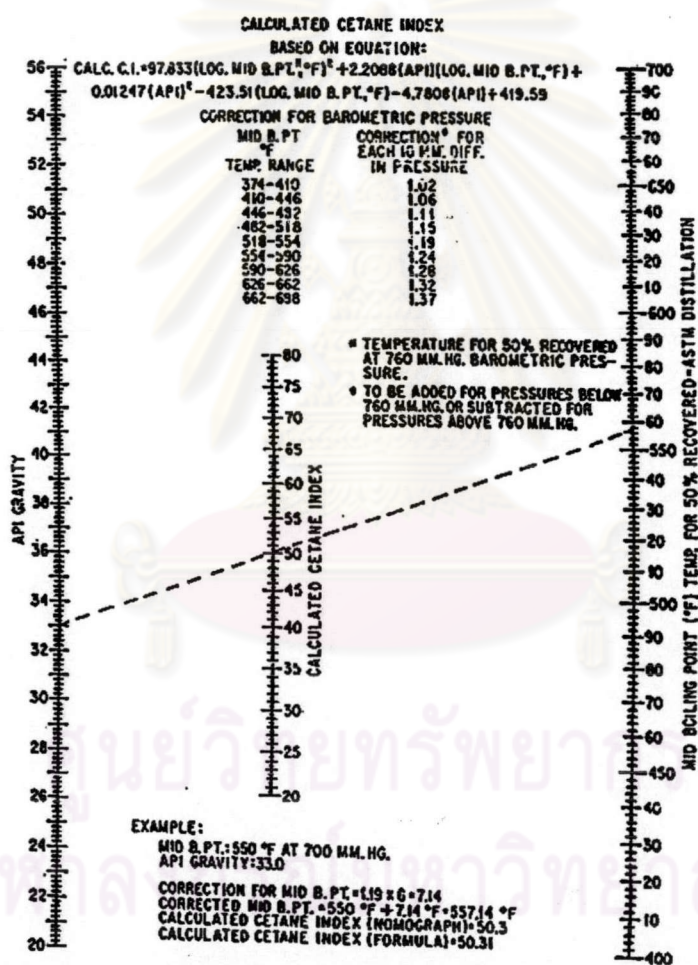


Figure 2.7 Nomograph for calculated cetane index.

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 ± 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.

2.3.3 The Cetane Quality of Diesel Fuels and Diesel Fuel Component.

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 starting
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

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 component type by the data in Table 2.3.

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	304	294	283
50% distilled at °C			
Sulfur (%wt)	1.40	0.19	0.13
Cetane number (ASTM D613)	54.1	52.2	40.9

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

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
Sulphur (%wt)	0.03	0.19	1.35	0.24
Cetane number (ASTM D613)	41.3	52.2	21.0	24.1

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.

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

1. Upgrade diesel fuel 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 [10].

2.3.4 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 [7]. 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 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 [9].

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 RO-NO_2 bond in isooctyl nitrate provides the available source of the free radicals required to enhance diesel combustion [10].

2.4 Fuel Properties Affecting Ignition Delay

2.4.1 Fuel Rating

A discussion of the effect of fuel 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 engine 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 lower temperatures and pressures than low cetane fuels, it is apparent that the cetane number permits us to put 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 2.8, which shows the relation between cetane number and ignition delay in tests in three different engines, and between cetane number and ignition delay in 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.

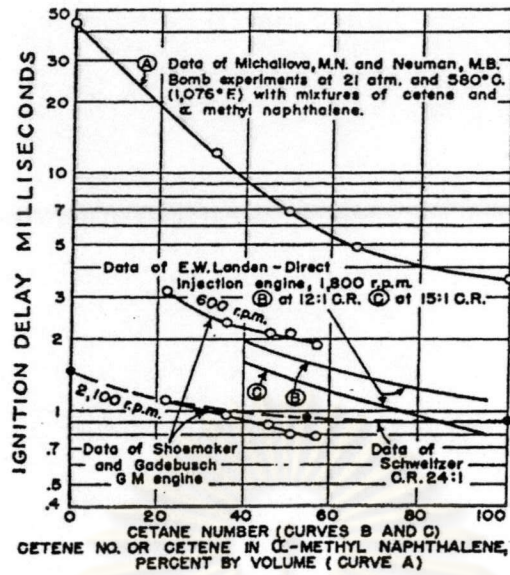


Figure 2.8 Relation between ignition delay and cetane number in tests in engines and bombs.

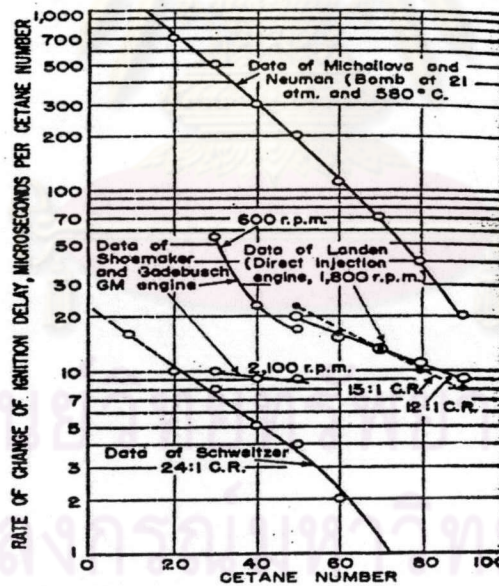


Figure 2.9 Variation of rate of change of ignition delay with cetane number.

Closer study of Figure 2.8 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. This may be seen more clearly in Figure 2.9, which shows the relation between cetane number and decrease in ignition delay in microseconds per unit increase in cetane number. From the standpoint of ignition delay, it is evident that, in most instances, the cetane number is a larger unit at low cetane than at high cetane numbers. However, this does not seem to be true in the case of one engine at 1800 r.p.m., and therefore, this further emphasizes the importance of environment in attaching quantitative significance to the cetane number. These results also emphasize the limitations of cetane number as a means of rating fuels quantitatively [11].

2.4.2 Effect of Chemical Structure

The effect on cetane number of adding one side chain to a normal paraffin hydrocarbon is shown in Figure 2.10. The data were obtained by Petrov in a bomb which had been calibrated against a CFR engine. Figure 2.10 shows quantitatively 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 2.10 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.

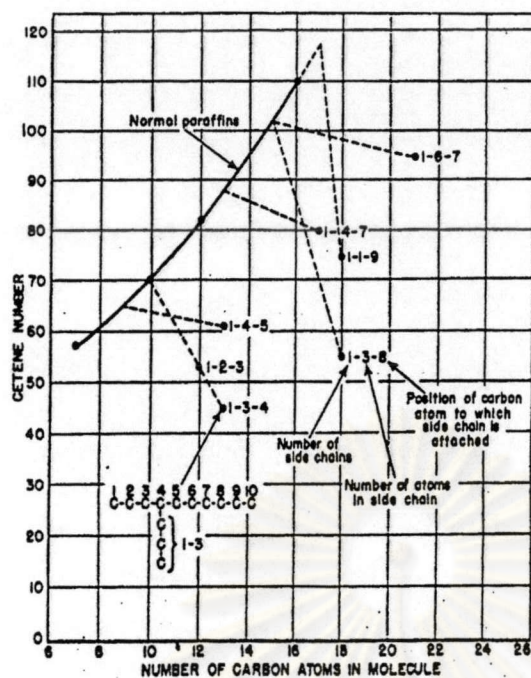


Figure 2.10 Cetane number of n-alkyl paraffin hydrocarbons (Data of Petrov).

In order to overcome this difficulty, the results have been plotted as shown in Figure 2.11. The ordinate is the ratio of the cetane number of the hydrocarbon with one side chain to the cetane number of the normal paraffin hydrocarbon to which the side chain is added. By plotting this ratio against the number of carbon atoms in the molecule, the indications are that we have essentially a linear relation in the case of three and four carbon side chains. Even though we have only two experimental points, it seems reasonable to expect that if, as an example, the line for a three carbon side chain is extrapolated to a molecule containing only three carbon atoms, there will obviously be no side chain and therefore the ratio should be unity. The limited data seem to support this reasoning. Even if this reasoning is not valid, we can still use Figure 2.10 for interpolation and slight extrapolation.

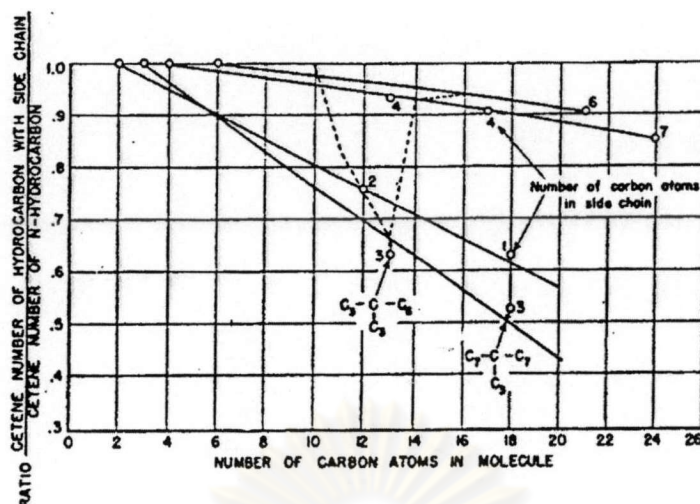


Figure 2.11 Effect of adding n-alkyl side chains on cetane number of paraffin hydrocarbons (derived from data of Petrov).

By interpolation, using Figures 2.10 and 2.11, it can now estimate the effect of adding different length side chains to a given normal paraffin hydrocarbon, say, for example, decane. Thus it can estimate the cetane number of methyldecane, ethyldecane, propyldecane, butyldecane, etc. Such an estimate is shown graphically in Figure 2.12 for n-alkyldecanes and n-alkylpentadecanes. It will be observed that, in both instances, a progressive and significant reduction in cetane number is indicated, as one, two, and three carbon atoms are added in the side chain. However, the addition of a side chain containing four or more carbon atoms gives a hydrocarbon having a cetane number only slightly less than that of the normal paraffin to which the side chain has been added. These results strongly indicate that an unbranched side chain containing three carbon atoms or, in other words, a propyl side chain, results in a chemical structure that is more resistant to oxidation than any other structure in the homologous series of n-paraffins having one n-alkyl side chain (mono n-alkyl n-paraffins). Admittedly, this statement is based on very meager evidence, if there are

other instances where a three-carbon side chain results in maximum stability toward oxidation [11].

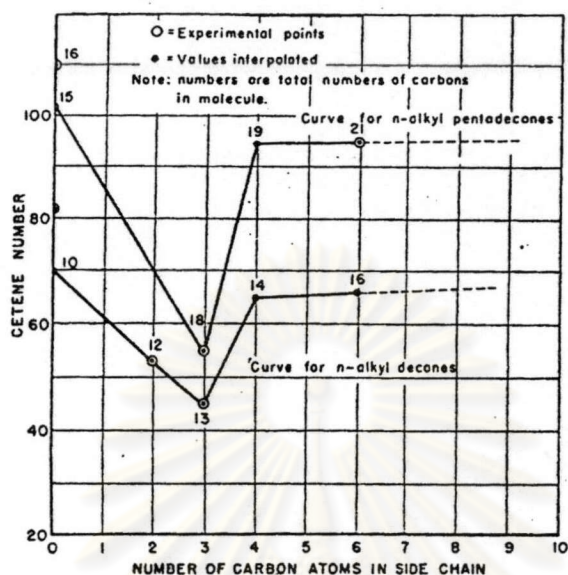


Figure 2.12 Relation between cetane number and number of carbon atoms in a single side chain in n-alkyl paraffin hydrocarbons (Derived from Data of Petrov).

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 2.13, 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.

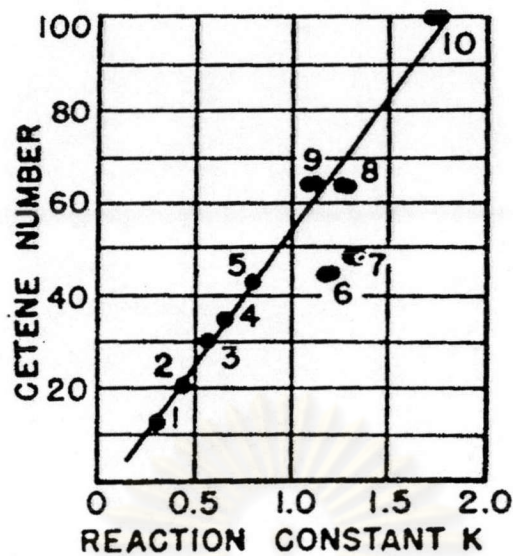


Figure 2.13 Reaction constant K in relation to cetane number. (cracking temperature 635°C). (Data of Boerlage and Van Dyck.)

2.4.4 Ignition Accelerators

The rate of the chemical reactions preceding 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 semi-commercially available accelerator is amyl nitrate. The average increase in cetane number obtained in tests of nine different fuels is shown in Figure 2.14, in relation to the concentration of ignition accelerator. It will be observed that significant improvement is obtained with comparatively small additions of accelerator.

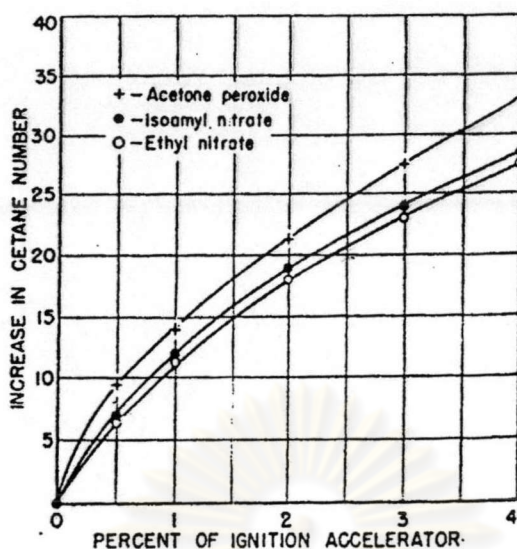


Figure 2.14 Average increase in cetane number of 9 test fuels in relation to concentration of ignition accelerator (data of Bogen and Wilson).

Let us now see what is the probable mechanism of ignition acceleration and why comparatively small additions of accelerator produced such a marked effect. This question has been considered by Broeze and Hinze, who show that their results on the reduction in ignition delay by accelerators can be explained on the basis of chain-reaction theory. It is probable, therefore, that the accelerators or their thermal decomposition products enter into chain-branching reactions. In connection with the effect of alkyl nitrates, it is significant to note that NO_2 in certain concentrations accelerates the reaction between hydrogen and oxygen and between carbon monoxide and oxygen.

2.4.5 Effect of Physical Properties of Fuel

The interrelation between the physical properties of a fuel and cetane number is shown in Figure 2.15, which was developed by Blackwood and Cloud. It is evident

from this chart that boiling point, viscosity, and gravity are so interrelated with cetane number that in correlating data on combustion performance with cetane number, considerable care must be exercised to make sure that the effects observed are not due to changes in one of the physical properties of the fuel. This is particularly true of volatility which, as we have already seen, is related to the air required for combustion and therefore affects mixture distribution.

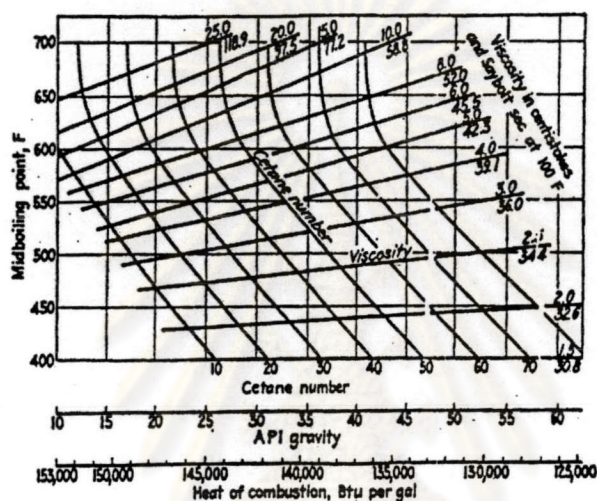


Figure 2.15 Interrelated properties of diesel fuels (According to Blackwood and Cloud).

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 [24].

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 [18].

Table 2.4 Commercial diesel fuel additives-function and type.

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
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

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

Class or Function	Common Additive Type
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 Literature Reviews

Purcell, R.F. et al. [6], 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. Jr. [19], 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.

Von Schickh, O. [8], in U.S. Patent No. 3,301,891, disclosed method of producing cycloaliphatic nitrates from cycloaliphatic alcohols. The cycloaliphatic nitrate obtained were valuable fuel additives especially by reason of improving the ignition quality of diesel fuels.

Filbey, A.H. [9], in U.S. Patent No. 4,406,665, reported that cetane number of diesel fuel, both hydrocarbon and alcohol, was increased by adding a small amount of a tetrahydrofuranol nitrate. The results of cetane increment which caused by the present additives was measured in comparison with that caused by a commercial cetane improver, 2-ethylhexyl nitrate, indicated that tetrahydrofuranol nitrate was more effective at very low concentration and it gave a cetane number increase that was almost linear with concentrations.

Moreover, several studies by Siraprapakit, S. [20], Suttipitakwong, C. [21] and Vasaruchtragul, J. [22] had 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 these dinitrate compounds gave higher increased 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.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย