

CHAPTER II

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

The Diesel Engine Combustion Process (6-8)

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 2.1. Figure 2.2 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 vary 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.

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

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.

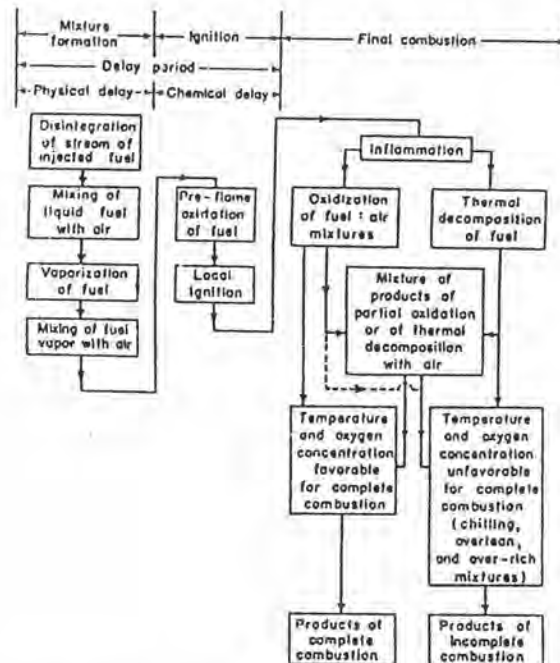


Figure 2.1 Outline of the combustion process in the diesel engine.

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.

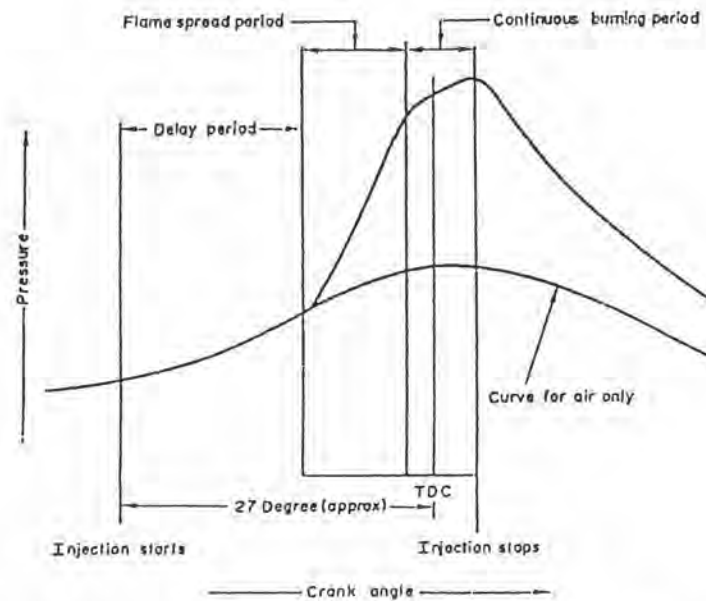


Figure 2.2 Pressure variations in a diesel engine cylinder during combustion.

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 engines 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.

General Characteristics of Diesel Fuel

Diesel fuels originally were straight-run products obtained from the distillation of crude oil. Today, with the various refinery cracking processes, diesel fuels also may contain varying amounts of selected cracked distills to increase the volume available for meeting the growing demand, while still maintaining cost at a minimum. Care is taken to select the cracked stocks in such a manner that specifications are met as simply as possible. The boiling range of distillate fuels is approximately 150 °C to 370 °C (300-700 °F) (6), 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 (9).

Table 2.1 Classification of distillate fuels

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

Within certain narrow limits, the relative amounts of gasoline, diesel and/or jet fuel and of heavier (heating) oils, that can be obtained by 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 gasoline, but poor diesel fuels. Mass-spectrometer analysis shows 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 sources; typical assays are shown in Table 2.2.

Table 2.2 Comparison of composition (in %wt.) of conventional diesel fuel with those of synthetic materials

Fraction	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

Under the broad definition of diesel fuel, there exist many possible combinations of various characteristics such as volatility, ignition quality, viscosity, gravity, stability, and other properties. To characterize diesel fuels and thereby establish a framework of definition and reference, various classifications are used in different countries.

The entire range of diesel engines can be divided into the three broad classification groups, indicated in Table 2.3.

Table 2.3 Classification diesel fuel

Classification	Speed range	Conditions	Typing applications
Low speed	Below 300 rpm	Sustained heavy load, constant speed	Marine main propulsion; electric power generation
Medium speed	300 to 1000 rpm	Fairly high load and relatively constant speed	Marine auxiliaries; stationary power generators; pumping units
High speed	1000 rpm or above	Frequent and wide variation in load and speed	Road transport vehicles; diesel locomotives

Cetane number (6,10-13)

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 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 a 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 furring 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, alpha-methylnaphthalene, has poor ignition qualities and was assigned a cetane number of 0. In 1962, alpha-methylnaphthalene 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 with a blend of reference fuels. This engine and the prescribed test method are described in ASTM D613 or IP 41.

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:

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

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 pressure, 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, hence, result in more readily purged combustion chamber deposits and in reduced exhaust smoke and odor.

High speed diesel engines normally are supplied with fuels in the range of 45 to 55 cetane number. Table 2.4 summarizes the typical inspections of various diesel fuels characterized primarily on the basis of use. As can be seen, the cetane number ranges from 50 for kerosene to 38 for marine distillate fuel.

Table 2.4 Typical inspections of diesel fuels

Fuel property	Fuel type			
	Kerosene	Premium diesel	Railroad diesel	Marine distillate diesel
Cetane number	50	47	40	38
Boiling range °C	163-288	360-675	176-357	176-250(90%)
Viscosity,SSU at 100 °C(38°C)	33	35	36	47
Gravity, API	42	37	34	26
Sulphur, %wt	0.12	0.30	0.50	1.2
Uses	High speed -city buses	High speed -Buses -Trucks -Tractors -Light marine engines	Medium speed -R.R. engines -Marine engines -Stationary engines	Low speed -Heavy marine engines -Large stationary engines

The hydrocarbon composition of diesel fuel is believed to influence ignition quality and combustion characteristics, 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 number (14,15).

Table 2.5 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

The cetane numbers of a variety of compounds are shown in Table 2.5. 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 paraffins 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 have 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.

Additives for Diesel Fuels (9,14)

With 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 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 are of many types, such as cetane improvers, detergent additives, corrosion inhibitors, stability improvers, etc.

Cetane Improvers (9,15)

The cetane number is a measure of the ignition quality of a diesel fuel. 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 important (Figure 2.3).

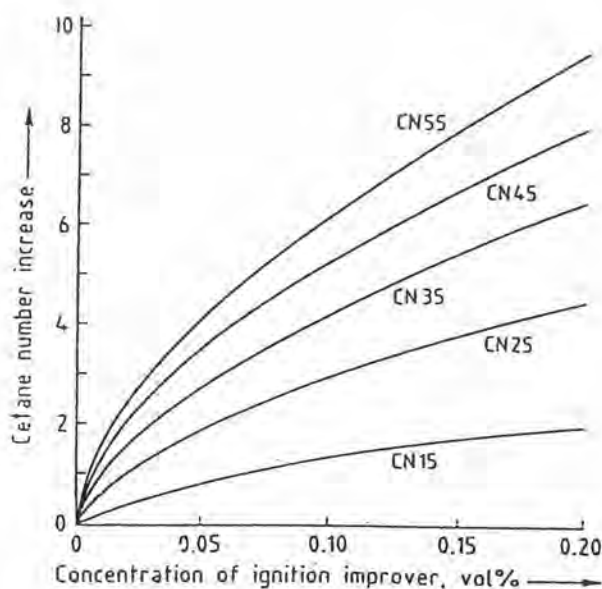


Figure 2.3 Response of different base fuel types to addition of ignition improvers.

In view of constantly increasing efforts to reduce exhaust gas emissions, the fact that even small quantities of ignition improvers can improve the exhaust gas quality of the diesel engine is important (Figure 2.4).

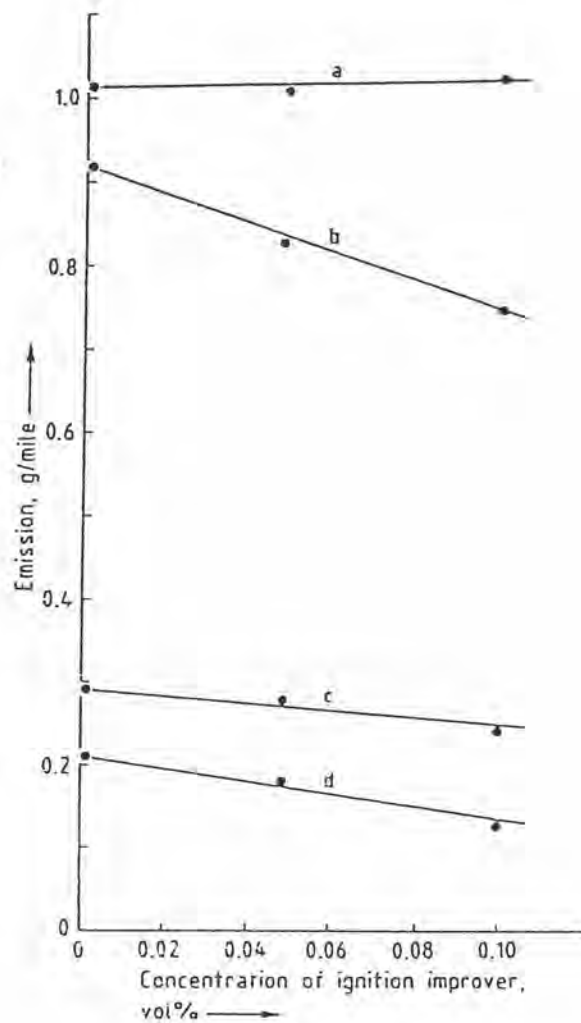


Figure 2.4 Improvement of exhaust gas emission by ignition improvers
 a) Oxide of nitrogen; b) Carbon monoxide; c) Particulates;
 d) hydrocarbon.

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-NO₂ 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.

Distillation (6)

Distillation (or volatility) characteristics of diesel fuel exert a great influence on its performance, particularly in medium and high speed engines. Distillation characteristics are measured using a procedure (ASTM D86-IP 123) in which a sample of the fuel is distilled and the vapour temperatures are recorded for the percentages of evaporation or distillation throughout the range.

The average volatility requirements of diesel fuels vary with engine speed, size and design. However, fuels having too low volatility tend to reduce power output and fuel economy through poor atomization, while those having too high volatility may reduce power output and fuel economy through vapor lock in the fuel system or inadequate droplet penetration from the nozzle. In general the distillation range should be as low as possible without adversely affecting the flash point, burning quality, heat content, or viscosity of the fuel. If the 10% point is too high, poor starting may result. An excessive boiling range from 10% to 50% evaporated may increase warm-up time. A low 50% point is desired in preventing smoke and odor. Low 90% and end points tend to ensure low carbon residuals and minimum crankcase dilution.

The temperature for 50% evaporated, known as the mid-boiling point, usually is taken as an overall indication of the fuel distillation characteristics where a single numerical value is used alone. For example, in high speed

engines, a 50% point above 575°F (302°C) probably would cause smoke formation, give rise to objectionable odor, cause lubricating oil contamination, and promote engine deposits. At the other extreme, a fuel with excessively low 50% point would have too low a viscosity and too low a heat content per unit volume. Thus, a 50% point in the range of 450-535°F (232-280°C) is most desirable for the majority of automotive type diesel engines. This average range usually is raised to a higher temperature spread for large, slower speed engines.

Pollutants from Diesel Engine (13)

Concentrations of pollutants in diesel exhausts vary enormously depending upon engine type, speed, and load. Viewed broadly, the values for diesel emissions bracket values for automotive emissions averaged over a traffic cycle. The general pattern is that concentrations of pollutants in diesel exhaust decrease with load while the absolute values are dependent upon both speed and load in a manner not yet reliably defined.

The available experimental data are inadequate to permit satisfactory generalizations concerning influences of fuel and engine parameters upon diesel emissions. Experience in the Bartlesville Petroleum Research Center suggests a surprising lack of any correlation between fuel quality or its predominant hydrocarbon character, and concentration levels of any of the objectionable emissions.

The hydrocarbon portion of diesel exhaust includes both fuel components and light, i.e., low molecular weight, cracked products. Fuel components predominate in the mixture of fuel and cracked products except in exhausts produced at or near full load in engines that are inherently low emitters (Table 2.6). Portions of the combustion products (the unsaturated hydrocarbons) are photochemically reactive, and some or all of the unfractured fuel components may also be reactive. Experiment with automotive fuel

components has shown that both heavy paraffins and most aromatics (i.e., those in motor fuels) are photochemically reactive. Therefore, lacking more definitive information on hydrocarbons in the diesel boiling range, it can only be assumed that the heavy hydrocarbons in diesel exhausts also are reactive as atmospheric pollutants.

Table 2.6 Hydrocarbon Distribution in Diesel Emissions ^a
(Steady-state, engine dynamometer tests)

	Rated speed			
	Full load	Half load	No load	Idle
Four-cycle engine				
C ₁ -C ₅	22	10.3	18.3	19
C ₆ -C ₈	4.7	2.2	6.6	3.3
C ₉ -C ₁₂	2.0	21	20.0	39
C ₁₃ -C ₁₅	-	19	17	29
C ₁₆ -C ₁₈	-	12	8	10
C ₁₉ ⁺	-	4	3	4
Total	29	68	73	104

^a Emissions by gas-liquid chromatography, ppmC.

Literature Review

Increasingly stringent emissions requirements for heavy-duty diesel engines stresses the importance of both engine design and diesel fuel quality. Several diesel fuel properties have been identified as having significant effects on diesel engines.

Ullman (1989) and co-workers studied the effects of fuel composition on heavy-duty diesel engine emissions. This VE-1 study was supported by the

CRC (Coordinating Research Council) to yield quantitative emission data and emission models to relate diesel fuel properties to emissions from modern heavy duty diesel engines. Variation of aromatics content (10-40%), volatility ($T_{90}=282-338^{\circ}\text{C}$), and sulfur content (0.05-0.30%) of the fuels were used in three types of heavy-duty engines to examine regulated (CO , NO_x , HC, TPM) and non-regulated emissions (SOF, Sulfate, SOOT).

The results of the analyses showed that aromatic content and volatility were significant for emissions of HC, CO, and NO_x . Aromatics and sulfur contents were significant for TPM. Overall, decreasing fuel aromatics content, sulfur, and volatility (increasing T_{90}) were generally associated with reductions in regulated emissions (16).

From VE-1 study, aromatic levels and cetane numbers were generally correlated so variation in emissions due to aromatics could not clearly be assigned to variation in aromatic levels alone.

In the VE-1 Phase II project (1990), to separate the effects of aromatics and cetane number, a fuel set with controlled variation in aromatics and cetane number was developed, including the use of ignition improver to increase the cetane number of selected fuels. This project was conducted using a 1991 prototype heavy-duty diesel engine and eight fuel compositions of varying aromaticity and natural cetane numbers. The cetane numbers of four selected fuels were increased to approach a target cetane number using an ignition improver. Gaseous and particulate emissions were measured over EPA transient cycle operation.

Emissions from the engine on the various fuels were analyzed and indicated that cetane number was the key fuel property affecting transient HC and CO emissions. In addition, cetane number was the principle fuel property affecting composite particulate emissions, but aromatic effects were also significant. For emission of NO_x both cetane number and aromatics were significant for transient emissions (3).

In the same year, Cunningham and co-workers studied the effects of diesel ignition improvers in low-sulfur fuels on heavy-duty diesel emissions. Four commercially available low-sulfur diesel fuels were supplemented with chemically different cetane improvers. Both neat and supplemented fuels were evaluated in a 1991 prototype heavy-duty diesel engine using the EPA Hot Start Transient Cycle. CO, HC, NO_x, and particulate emissions were determined for each of the 18 fuel formulations tested.

Results showed that cetane improvers lower HC and CO emissions and, in some cases, NO_x and particulate emissions. CO and HC emissions decreased as cetane number increased. The use of cetane improvers should help refiners design diesel fuel formulations which meet California requirements and assist original equipment manufacturers (OEM's) in meeting their emission targets (17).

McCarthy et.al. (1992) determined the effect of fuel cetane number and aromatic content on emissions from a heavy-duty diesel engine meeting 1994 emissions standards. The fuel set was selected to separate the cetane effects from the aromatics effects, since otherwise these effects can be easily confused. Other fuel property effects, such as density, were also considered in the selection of the fuel set.

The study found that increasing cetane number reduces all regulated diesel emissions species. Reducing aromatic content reduces NO_x and particulate emissions and the aromatics effect was less and the cetane effect was greater. When compared to the CRC VE-1 Phase II study, aromatic effects were almost identical and cetane effects were similar on all emissions (18).

Shell Research (1994) has aimed at identifying fuel properties that actually influence emissions and quantifying the effects. They did this by testing several different heavy-duty engines and a fleet of different cars on fuels having a wide range of properties, such as sulfur content, density, cetane number, volatility, and aromatics content.

Results have shown that a reduction in fuel sulfur to 0.05% mass will assist heavy-duty engine designers to meet the most stringent future emissions standards. The cetane number influences both gaseous and particulate emissions for heavy-duty engine, higher cetane numbers giving lower emissions, but an increase in cetane number does not lead to a reduction in light-duty engine particulate emissions. While fuel volatility could have an impact on particulate emissions, its effects on gaseous emissions were of secondary importance compared with the cetane number. In addition, Fuel density has a direct effect on light-duty IDI vehicle emissions, increasing density giving increasing particulate emissions (19).

In 1994, Nandi studied the effectiveness of additive improvers in diesel fuels in reducing the regulated and unregulated engine emissions in a variety of diesel fuels. A prototype 1991 Detroit Diesel Series 60 heavy-duty diesel engine was used for the study. A standard hot-start FTP protocol was followed for the testing. The low sulfur base fuels used varied in aromatic content from 20 vol% to 38 vol%., treated with di-t-butyl peroxide and 2-ethylhexyl nitrate treated at the same cetane level, were evaluated.

Most of the regulated and unregulated emissions from the cetane improved fuels showed a significant reduction compared to those from the untreated base fuels. Higher reductions in the NO_x emissions, although not statistically different, was observed for the peroxide treated fuels when compared to that of the nitrate treated fuels. The hydrocarbon emissions from all the fuels were speciated. The total amount of "toxics" were also significantly reduced by the cetane improvers (20).

In a recent report, Ladommatos studied the effect of fuel cetane improver on diesel pollutant emissions. A base fuel having a cetane number of 40.2 was split into nine batches. To eight of these batches, varying quantities of ignition improver were used in a co-operative fuel research (CFR) diesel engine, and the exhaust emissions of NO_x unburnt hydrocarbons (UHC) and

smoke were measured, to ascertain the effect of varying cetane number on emissions when the basic chemical structure and physical properties of the fuel were almost unaltered.

The results showed that the exhaust NO_x progressively decreased with increasing cetane number. Similarly, the UHC decreased. However, the smoke increased due to the reduction in the amount of relatively smoke-free premixed fuel burnt (20).

Griffiths, et.al. (1991) studied the effectiveness of additives for reducing the ignition delay period of diesel fuels. Engine tests have been conducted to establish the ignition delay period of two representative diesel fuels of cetane ratings 40 and 50, and of the lower rated fuel blended with additives. The latter included six organic peroxides, two nitrates and mixtures of additives.

All the additives were effective in reducing the ignition delay period of the cetane 40 fuel to that shown by the cetane 50. In terms of volumetric concentrations the two nitrates tested were more effective than the peroxides (21).

The effect of diesel fuel properties on emissions have been studied extensively in many countries. However, the result of these tests are some differences because of engine technology, standard test method, fuel compositions, and environment differences. For this reasons, this research has aimed at studying the effect of diesel fuel properties on emissions in Thailand. It is hoped that the study will help reduce significantly diesel emissions.