CHAPTER I

INTRODUCTION

Diesel engine is a high compression and self-ignition engine and no spark plug is used. The diesel cycle consists of charging the combustion chamber with air; compressing the air, injecting the fuel, which ignites spontaneously, expanding the burned gases and expelling the products of combustion.

Diesel engines are operated by compression ignition. They have compression ratios in range of 14:1 to 17:1 or higher and for that reason obtain more useful work from a given amount of fuel, compared to an Otto cycle engine. Historically, diesel engines have been operated on a petroleum-derived liquid hydrocarbon fuel boiling in the range of about 150 °C to 370 °C (300 °F to 700 °F). Recently, because of dwindling petroleum reserves, alcohol-hydrocarbon blends have been studied for use as diesel fuel. [1-3]

The ignition quality of diesel fuel is expressed in term of cetane number, which number has been developed on a basis very similar to that adopted for measuring the ignition quality of gasoline in term of octane number.

Cetane number is related to ignition delay after the fuel is injected into the combustion chamber. If ignition delays are too long, the amount of fuel in the chamber is increased and upon ignition results in a rough running engine and results of smoke. A short ignition delay results in smooth engine operation and less smoke. Commercial petroleum diesel fuel generally have a cetane number of about 40-55. Alcohols have a much lower cetane number value and require the additive of a cetane improver for successful engine operation.

The amount of cetane improver added depends on the type of fuel being used, the initial cetane value, and the amount of cetane number increase desired. Alcohol fuels such as methanol, ethanol, isopropanol, isobutanol, hexanol, and the like, have very low cetane values and large amounts of cetane improvers are required.

Blends of alcohol and petroleum-derived diesel fuel have higher cetane values and require less cetane improver. A useful range is about 0.5-10 weight percent. Petroleum-derived distillate fuels in the diesel boiling range require only small amounts of cetane improver to achieve a significant increase in cetane number. Such fuels without any cetane improver generally have cetane number in the range of about 25-60. Cetane number in the range of 25-35 are considered low and those in the range of 50-60 are considered top grade diesel fuels. Diesel fuels in the mid-range (35-50) are most common. An object of the invention is to upgrade the low cetane number fuels at least into the mid-range and to increase the cetane value of the mid-range fuels into the upper portion of the mid-range (e.g. 45-50) or even into the premium range above 50. It has been found that highly beneficial results can be achieved using as little as 0.05 weight percent of the present additive. Accordingly, a useful concentration range in petroleum derived diesel fuels is about 0.01-5.0 weight percent and more preferably about 0.05-0.5 weight percent.

Through the years, many types of additives have been used to rise the cetane number of diesel fuel. These include peroxides, nitrites, nitrates, nitrosocarbamates and the like. Alkyl nitrates such as amyl nitrate, hexyl nitrate and mixed nitrates have been used commercially with good results. Suitable azole from which the salt are prepared include aromatic and/or aliphatic hydrocarbon substituted or unsubstituted cyclopenta diazole, triazole, and tetrazoles.

General Characteristics of Diesel Fuel [4]

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 distillates 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 fuel is approximately 150 °C to 370 °C (300 °F to 700 °F) [4], but this is not unique description: other fractions boiling within this range, but meeting different secondary specifications comprise naphtha, jet fuel, kerosene, and so on; an apporximate classification is shown in table 1.1. [5]

The relative merits of the diesel fuel types to be considered will depend upon the refining practices employed, the nature of the crude oils from which they are produced, and the additive package (if any) used.

Table 1.1 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 under taken 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 from ligher materials; hydrogenation is then used to reduce both the nitrogen and sulfur content and to help to stabilize the cracked products. Again, these materials process much more aromatic character than does diesel fuel from conventional sources; typical assays are shown in table 1.2.

Table 1.2 Comparation 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

Furthermore, ^{1}H and ^{13}C NMR studies on the alkylbenzenes show that, for 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 are methyl groups. Thus, it is this preponderance of short side-chains, rather than the increase in 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.

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

The entire range of diesel engines can be divided into the three broad classification groups indicated in the following Table 1.3.

Table 1.3 Classification groups of 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

Specifications for Diesel Fuel [5]

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 curdes used in the refineries, the specifications seem to be decreased, and the price of the fuels are trend to increasd.

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.

Ash is reponsible 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.

Distilllate 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.

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-spary penetration and lubrication of the fuel pump and injector nozzle.

Diesel Fuel Components [6]

The ignition performance of the diesel fuel represents an important criterion, similar to the octane quality of gasoline. The ignition performance of the diesel fuel described by the cetane number and determined by its composition and behaves opposite to octane quality. Hydrocarbons with a high octane number have a low cetane number and vice versa. Further criteria determined by the composition of the diesel fuel are its cold flow properties, volumetric calorific value, density, and smoking tendency. None of the classes of substances present in diesel fuel fulfills all the criteria equally well: for example, n-paraffins, which have a very good ignition performance and low smoking tendency, show poor low-temperature behavior and have a low calorific value (Table 1.4).

Table 1.4 Properties of various hydrocarbon groups with regard to their suitability as diesel fuels

Hydrocarbon groups	Ignition Quality	Cold flow properties	Volumetric calorific value	Density	Smoking tendency
n-Paraffins	good	poor	low	low	low
Isoparaffins	low	good	low	low	low
Olefins	low	good	low	low	moderate
Naphthenes	moderate	good	moderate	moderate	moderate
Aromatics	poor	moderate	high	high	high

The properties of hydrocarbons in diesel fuel as follow :

Paraffinic hydrocarbons are lower in specific gravity, or higher in API gravity than aromatic hydrocarbons at the same boiling point, while the naphthenic and olefinic compounds are intermediate in gravity or density. Their stability to oxidation or chemical change is very good. These hydrocarbons are completely burned. The spontaneous ignition point of paraffinic hydrocarbons are very poor.This is the useful properties in gas oil and fuel oil when used in diesel engines.

Aromatic hydrocarbons possess a much higher specific gravity, or lower API gravity than the other three classes. They are very stable under heat and chemically active to a moderate degree. The aromatic compounds contain a higher proportion of carbon than the other hydrocarbons. Due to this verson they have a tendency to smoke which limits their desirability in kerosine, as well as limiting their use in diesel engines. This type of hydrocarbon is present in cracked oils in a large amount compare straight-run oils.[5]

Naphthenic hydrocarbons are extremely stable compounds and in many cases have stability greater than the paraffins. These hydrocarbons are not found in large volume in light oils, but they have good burning quality in illuminating oils and are usually found in heavy portions of fuel oils.

Olefinic hydrocarbons are usually distinguished by a characteristic odor. These compounds are more chemically active than the other three classes of hydrocarbons. They are subject to oxidation or polymerization, to form the gums. Olefins are not present in large amounts in straight-run distillate, kerosine, gas oil or fuel oils, but these are found in large quanlities in cracked oils.

The diesel fuel engine can also theoretically be run on low-boiling hydrocarbons. Its particular value lies, however, in its ability to utilize economically, the middle distillates in the distillation range 150-370 °C. Accordingly, the diesel fuel components produced in refineries must correspond to the aforementioned requirements as far as possible.

1. Straight-Run Middle Distillate

Straight-run middle distillate (distillate gas oil) represents a valuable diesel fuel component because of its usually high cetane number (see figure 1.1)

The quality of straight-run middle distillate never-theless depend on the quality of crude petroleum used. In many cases, distillate gas oil has a relatively high paraffin and low aromatic content. Although middle distillates can be used for the diesel engine without further processing (apart from desulfurization), other diesel fuel components are also employed. The following reasons are decisive:

1) the natural middle distillate fraction in crude petroleum is generally not sufficient to meet the demand for middle distillate.

2) unwanted heavy components in crude oil are present in excess and therefore, converted into lighter products.

3) the refinery structures also provide a certain "compulsory fraction" of the middle distillates from conversion processes.

4) particular quality requirements can also make the production of special diesel fuel components necessary.

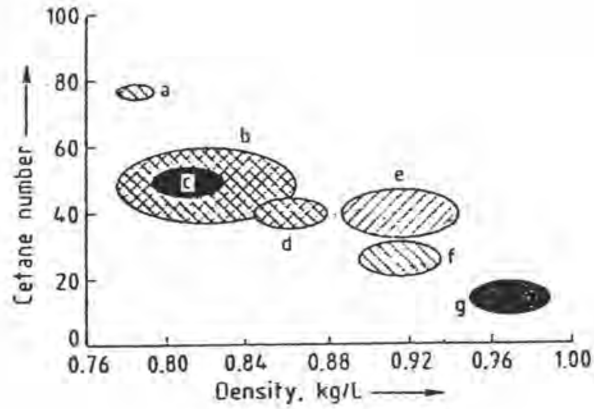

Figure 1.1 Typical properties of gas-oil components

a) Synthetic middle distillate; b)straight-run gas oil;

c) Hydrocracked gas oil; d) Thermally cracked gas oil;

e) Syncrude gas oil; f) Coker gas oil;

g) Light catalytically cracked cycle oil

2. Thermally Cracked Gas Oil

Thermally cracked gas oil originates from etheir the visbreaking or the coking process and tends to have a lower cetane number and higher density than distillate gas oil (Table 1.5). Thermally cracked gas oil usually goes through a subsequent hydrogenation step because of the formation of unstable olefinic components during the cracking process. After hydrogenation, it represents a useable diesel fuel component.

3. Catalytically Cracked Gas Oil

Catalytically cracked gas oil is generally characterized by a very low cetane number and high density. Because of its instability, catalytially cracked gas oil must be hydrogenated. However, because of the poor ignition performance resulting from the high aromatic content and the high smoking tendency, it can be added to diesel fuel in the limitation of quantities.

Table 1.5 Properties of diesel fuel components

Process	Component	Component	
		Before treatment	After treatment
Distillation	distillate gas oil (straight-run)		content of aromatics: medium; olefins: very low, paraffins: high
Thermal cracking	thermocracked gas oil	content of aromatics: low; olefins: medium; paraffins: high	content of aromatics: low; olefins: none; paraffins: high
Catalytic cracking	catalytically cracked gas oil	content of aromatics: high; olefins: low; paraffins: low	content of aromatics: high; olefins: none; paraffins: low
Hydro cracking	hydrocracked gas oil		content of aromatics: very low; olefins: none; paraffins: very high
SMDS synthesis	synthesis gas oil		content of aromatics: none; olefins: none; paraffins: very high
Distillation or hydro cracking	kerosene		content of aromatics: low; olefins: none; paraffins: very high

4. Hydrocracked Gas Oil

Hydrocracked gas oil is a very valuable diesel fuel component. Because of its very high isoparaffins content, the ignition performance is good and the smoking tendency is low.

5. Kerosene

The low-temperature stability of diesel fuel can be achieved by addition of kerosene. Because kerosene is normally used as jet fuel and, therefore, it is not suitable for being used as diesel fuel component due to it is expensive and its addition is limited to particular climatic conditions. In most cases, the density, calorific value, and viscosity of kerosene, however, much lower than those of other diesel fuel components, which can lead to problems. The low density and low calorific value lead to decreased engine power and increased fuel consumption, and the low viscosity can lead to wear in the injection pump because of poor lubricity.

6. Synthetic Diesel Fuel

Diesel fuel can also be obtained from fossil energy sources other than crude petroleum. During World War II diesel fuel was produced from coal by the Fischer-Tropsch process in Germany. This synthetic fuel (kogasin) had a range of outstanding properties: cetane number ca. 100, almost sulfur-free composition, low density, and high gravimetric calorific value. This synthetic diesel fuel component was used principally for enhancing low-value coal tar oil. In the near future, (1992) synthetic diesel fuel will be produced by the Shell Middle Distillate Synthesis (SMDS) process in Malaysia from the natural gas present there in large quantities. The process includes the following steps:

1) steam reforming of natural gas (conversion to synthesis gas).
2) buildup of long-chain n-paraffins (Fischer-Tropsch synthesis).
3) isomerization to isoparaffins.
4) distillative separation into kerosene and diesel fuel.

The product will be used mainly for improvement of the poor quality of the straight-run middle distillate otherwise available in Malaysia. The middle distillate produced by the SMDS process results in lower exhaust emission in diesel engines because it has a high cetane number (>60).

Objective and Scope of the Research

1. Objective

The principle objective of this study was to synthesize of tetrazole derivatives and study their properties as cetane improver.

2. Scope of the Research

1. To synthesize tetrazole derivatives.
2. The tetrazole derivatives synthesized will be purified and characterized using chromatographic and spectroscopic methods.
3. Determining cetane index and cetane number of blending of tetrazole derivatives in base diesel fuel.