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Relationship between Fuel Properties and Cetane Response of Cetane Improver for Non-Aromatic and Aromatic Fuels Used In A Single Cylinder Heavy Duty Diesel Engine

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Abstract

Ignition improver additives are used to improve the ignition quality, or reduce the ignition delay; i.e. the time between when fuel is injected and time when combustion start is different this difference in time is minimize by additive is called cetane improver (CN). The Cetane Number (CN) is the most widely accepted measure of ignition quality to get desired value of centane number some additive are used hence ignition improvers are usually characterized by the fact that at what extent they can increase CN. By increasing cetane number we have two benefits that it helps smoother combustion and lower emissions. Fuel properties are always considered as one of the main factors to diesel engines concerning performance of cetane improver. There are still challenges for researchers to identify the most correlating and non-correlating fuel properties and their effects on cetane improver .In this study to derive the most un-correlating and correlating properties. In parallel, sensitivity analysis was performed for the fuel properties as well as to effect on performance of cetane improver.

Introduction

Cetane number (CN) is a measure of the ignition quality of the diesel fuel and is determined by a standard engine test as specified by ASTM (ASTM D613).1The ignition quality is quantified by measuring the ignition delay, which is the period between the time of injection and the start of combustion (ignition) of the fuel. A fuel with a high CN has a short ignition delay period and starts to combust shortly after it is injected into an engine. The ignition quality of the diesel fuel depends on its molecular composition. Some of the Simpler molecular components such as the n-paraffin's can ignite in a diesel engine with relative ease, but others like aromatics have more stable ring structures that require higher temperature and pressure to ignite. We would be using different chemicals or additives to improve the cetane number. Therefore, they are termed as Cetane improvers.

Importance of Cetane Number

There is no benefit to using a higher cetane number fuel than is specified by the engine's manufacturer. The ASTM Standard Specification for Diesel Fuel Oils (D-975) states. "The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions. Increase in cetane number over values actually required does not materially improve engine performance. Accordingly, the cetane number specified should be as low as possible to insure maximum fuel availability." This quote underscores the importance of matching engine cetane requirements with fuel cetane number. Diesel fuels with cetane number lower than minimum engine requirements can cause rough engine operation. They are more difficult to start, especially in cold weather or at high altitudes. They accelerate lube oil sludge formation. Many low cetane fuels increase engine deposits resulting in more smoke, increased exhaust emissions and greater engine wear. Using fuels which meet engine operating requirements will improve cold starting, reduce smoke during start-up. Improves fuel economy, reduce exhaust emissions, improve engine durability and reduce noise and vibration. These engine fuel requirements are published in the operating manual for each specific engine or vehicle

The role of 'additives' for diesel and diesel blended (cetane improvers) fuels

Chemical cetane improvers are those compounds that readily decompose to form free radicals, which in-turn promotes the rate of initiation. This increased rate of chain initiation leads to improved ignition characteristics of diesel fuel. Chemicals selected from alkyl nitrates, certain peroxides, tetraazoles, and thioaldehydes can serve as cetane improvers. Due to their low costs, alkyl nitrates have played the most significant role in commercial use. 2-Ethylhexyl nitrate (EHN) has been used as a commercial cetane improver for a number of years and today is the predominant cetane improving additive in the marketplace. Di-tertiary-butyl peroxide (DTBP) was first recognized as an effective cetane improver. Due to its higher cost, DTBP has not achieved the same wide spread usage as

EHN. New technology has been developed that will substantially reduce the cost of DTBP to a level comparable to that of EHN. Moreover, DTBP has a potential advantage over alkyl nitrates in reducing NOx emissions since it does not contain nitrogen. DTBP is currently used in limited amounts.2-Ethyl hexyl nitrate (2EHN or iso-octyl nitrate) has become the most common ignition improver due to its low production costs and good response in a wide range of fuels.EHN is used at dose levels typically varying from 0.05% to 0.4% (m/m), to yield about 3 to 13 cetane number improvement. Another category of cetane number improvers are peroxide based compounds, for example di-tertiary butyl peroxide (DTBP). Their effect is also strongly dependent on fuel composition these have been shown to be less effective than 2EHN and are generally more expensive. It is widely accepted that increasing the cetane number represents one option for production of cleaner burning diesel fuels. Numerous studies, including the Coordinating Research Council VE-1 and VE-10 programs, have demonstrated that increasing the cetane number of the fuel significantly reduces all the regulated emissions.1 increasing the cetane number of diesel fuel can be achieved by lowering aromatic content of the fuel through hydro treating and or by addition of chemical cetane improvers. It is generally recognized that chemical cetane improvement additives represent a low cost alternative to obtaining higher cetane number achieved through aromatic reduction. Moreover, deep hydro treating to reduce aromatics tend to adversely affect some fuel properties, e.g., waxing and cold flow. Chemical cetane improvers are those compounds that readily decompose to form free radicals, which in-turn promotes the rate of initiation. This increased rate of chain initiation leads to improved ignition characteristics of diesel fuel. Chemicals selected from alkyl nitrates, certain peroxides, tetraazoles, and thioaldehydes can serve as cetane improvers. Due to their low costs, alkyl nitrates have played the most significant role in commercial use. 2-Ethylhexyl nitrate (EHN) has been used as a commercial cetane improver for a number of years and today is the predominant cetane improving additive in the market place low aromatic fuels will respond well to the additive. The relationship between the cetane responses of the additives for the different fuels and the mid-range distillation temperature of the fuel is less clearly understood. In general, it was observed that the lighter fuels respond better to cetane improvers compared to the heavier fuels especially at low additive levels. More work is needed to understand this effect. It must be emphasized that although the cetane response equation, described here, use the base diesel fuels' properties to compute the expected change in its cetane number, the relationship between these changes and the fuel properties are by no means causal. Rather, the fuel properties are merely manifestations of some other more fundamental attributes of the fuel.

Mechanism for Acceleration of Diesel-Fuel Ignition by EHN

$RO\text{-}NO_2 \rightarrow RO + NO_2$

$NO_2 + RH \rightarrow HONO + R$

$HONO \rightarrow NO + OH$

$OH + RH \rightarrow H_2O + R$

$R + O_2 \rightarrow RO_2$ .... Etc.,

$RO + O_2 \rightarrow RO_3$ .... Etc.,

$2NO + O_2 \rightarrow 2NO_2$

The Reason Why EHN is one of the Most Effective Organic Nitrates is Because When it Decomposes, it Creates a Lot of Formaldehyde(Ch_2o)

$RO = CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}O\text{-}NO_2$

CH_2CH_3

$\rightarrow$ 2-heptene + $CH_2O + NO_2$

Followed by

$NO_2 + CH_2O \rightarrow HONO + CHO$

$NO_2 + CHO \rightarrow HONO + CO$

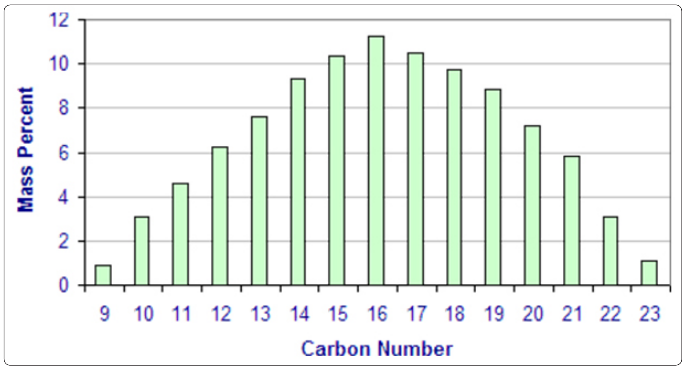
Which are much faster reactions than

$NO_2 + RH \rightarrow HONO + R$

This was confirmed by artificially adding extra formaldehyde to the system, which increases the efficiency of the nitrate Also, it can be proved that the nitrate works in the gas phase because introducing NO_2 via the air intake causes the same acceleration as does the equivalent amount of nitrate present in the fuel

Experimental Measurement

Diesel fuel is a mixture of thousands of hydrocarbon compounds, most of which have carbon numbers between 10 and 22. A typical carbon number distribution in diesel fuel is shown in Figure [Chevron 1998]. Most of the compounds in diesel fuel are hydrocarbons of the paraffinic, naphthenic, or aromatic class. Diesel fuel also contains small quantities of organic compounds of sulfur (e.g., dibenzothiophene), nitrogen (e.g., carbazole) and oxygen.



The properties of a given diesel fuel depend on its exact formulation. An important factor which makes one fuel different from another is the relative proportion of paraffinic, naphthenic, and aromatic hydrocarbons. For instance, high content of paraffinic hydrocarbons yields well Ignition quality of fuel, but it may pose problems in meeting low-temperature specifications, especially with high wax content crude oils. Lower wax content occurs in blend components from cracking processes, but oils from catalytic and thermal cracking have also lower ignition quality. The final blend has to be a careful choice of particular components to meet the fuel specifications.

Cetane Number

A measure of the ignition quality of fuel-or selected hydrocarbon components of diesel fuel are listed in Table. The cetane number depends on the hydrocarbon class, as follows:

Normal paraffin's have high cetane numbers, which increase with carbon number.

Cetane numbers of isoparaffins can range from about 10 to 80. Molecules with many short side chains have low cetane numbers, while compounds with one side chain of four or more carbons have high cetane numbers.

Naphthenes tend to have cetane numbers from 40 to 70. Higher molecular weight molecules with one long side chain have high cetane numbers, while lower molecular weight compounds with short side chains have low cetane numbers.

Aromatics have cetane numbers from 0 to 60. Molecules with a single aromatic ring with a long side chain are in the upper part of the range. Molecules with a single ring with several short side chains are in the lower part of the range. Molecules with two or three aromatic rings fused together have low cetane numbers of below 20.

Cetane Number of Representative Diesel Fuel Hydrocarbons			
Compound	**Hydrocarbon Class**	**Formula**	**Cetane Number**
n-Decane	n-Paraffin	$C_{10}H_{22}$	76
n-Pentadecane	n-Paraffin	$C_{15}H_{32}$	95
n-Hexadecane*	n-Paraffin	$C_{16}H_{34}$	100
3-Ethyldecane	Isoparaffin	$C_{12}H_{26}$	48
4,5-Diethyloctane	Isoparaffin	$C_{12}H_{26}$	20
Heptamethylnonane*	Isoparaffin	$C_{16}H_{34}$	15
3-Cyclohexylhexane	Naphthene	$C_{12}H_{24}$	36
2-Methyl-3-cyclohexylnonane	Naphthene	$C_{16}H_{32}$	70
2-Cyclohexyltetradecane	Naphthene	$C_{20}H_{40}$	57
1-Methylnaphthalene*	Aromatic	$C_{11}H_{10}$	0
n-Pentylbenzene	Aromatic	$C_{11}H_{16}$	8
Biphenyl	Aromatic	$C_{12}H_{10}$	21
* Primary reference material for cetane number scale			

Considering above theoretical data we have prepared diesel by taking two different stream of refinery in a way that it's aromatic content changes from 20 to 35 volume percentage and measured its cetane number without adding cetane improver EHN. During each blending measured cetane number reveals that as the aromatic content of fuel increase its cetane number decreases. Obtained experimental data is as shown in below table.

Property	**Fuel**											
	A1	**A2**	**A3**	**A4**	**C1**	**C2**	**C3**	**C4**	**B1**	**B2**	**B3**	**B4**
Cetane Number (D 613)	35.64	33.28	32.00	30.17	49.84	49.04	48.86	48.00	46.69	45.77	45.00	42.05
Aromatic Vol% (D1319)	30	33	34	35	25	28	29	30	20	22	23	25
Sulfur Wt%	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Density (D4052) kg/M3	835.7	837.8	839.7	840.5	825.8	827.2	830.4	834.8	836.5	835.8	839.6	842.5
Distilation Range (D86)												
IBP C°	172	175	178	180	174	168	165	162	175	176	179	178
50% point (T50) C°	243	246	245	248	250	248	249	252	259	242	240	230
FBP C°	343	343	341	344	341	343	345	346	341	343	345	348

In above prepared blended diesel EHN is added from 0.05% to 2.0% by volume to study change in cetane number. It was observed that after addition of cetane improver EHN there is no much more change in distillation data and density value but measurable changes found in cetane value further change in cetane number of diesel fuel after addition of EHN was not same in all diesel sample as shown in bellowing table.

Diesel ID	Increment in Cetane No. Of diesel with additive 2-EHN							
	100C	500C	900C	Base diesel Cetane No.	0.05%(m/m) EHN added Cetane No.	0.10%(m/m) EHN added Cetane No.	0.15%(m/m) EHN added Cetane No.	0.20%(m/m) EHN added Cetane No.
A1	170	243	345	35.64	38.64	40.12	40.24	40.28
A2	169	246	347	33.28	36.52	37.62	37.68	37.70
A3	172	245	349	32.00	36.00	37.44	37.81	37.90
A4	170	248	354	30.17	26.17	36.44	36.65	36.70
B1	185	259	335	46.69	56.75	65.89	71.78	75.82
B2	187	242	338	45.77	55.29	64.74	70.24	73.99
B3	192	240	336	45.00	55.22	65.25	70.28	74.58
B4	184	230	340	42.05	51.98	61.21	67.18	71.65
C1	165	250	336	49.84	54.92	57.78	59.92	61.90
C2	168	248	338	49.04	54.42	57.21	59.23	61.25
C3	166	249	338	48.86	53.42	56.10	58.80	60.15
C4	167	252	337	48.00	53.10	56.92	58.94	60.94

It was observed that as the aromatic percentage of diesel changes its cetane number changes accordingly. We got cetane number value from 30 to 49.86 effect of EHN increases as the cetane number increases e.g. for diesel having cetane number 48 to 50 is added by 0.05% EHN shows increase in cetane number of approximately 5 number but this increment is not linear because on addition of 1.0% EHN same diesel shows increment of approximately 8 number and on addition of 1.5%EHN increment of cetane number is 10 number and on addition of 2.0% EHN further increment was of 12number. It indicates that relative change of cetane number of fuel is not linear with increase in additive percentage. Same experiment done with some other diesel having some different value of cetane number but none of them shows and direct relation between percentage addition of EHN and increment of cetane number of diesel. But one pattern observed in this experiment was that diesel having higher cetane number having better performance of EHN rather than diesel having lower value of cetane number. It indicate that fuel having lower value of aromatic having better effect of cetane improver than diesel having higher value of cetane number this is dare to reason that EHN work with paraffinic species of diesel only it has no any reaction with aromatic content of diesel as shown in its reaction mechanism. Not only that but at certain level EHN performance is increased in case of paraffinic content and then it became constant. Means After certain increment in cetane value in case of paraffinic content diesel further addition of EHN has no effect on cetane number.

Conclusion

The increase in cetane number is greater for a fuel whose natural cetane number is already high. The incremental increase becomes smaller as more 2EHN is added. The fuels with the highest natural cetane number (high alkenes, low aromatics) show the best response to 2EHN. Correlations to calculate the cetane number increase as a function of 2EHN concentration can be found. Effect of EHN addition on cetane number increase for fuels with different aromatic/alkane proportions. Fuels with high aromatic content or highly aromatic blend stocks like light cycle oil (LCO) or light cycle gas oil (LCGO) will respond very poorly to cetane improvers. Indeed, a highly aromatic (87%) LCGO blend stock did not respond at all to either of the cetane improvers. Assuming the cetane improvers react through formation of free radicals to accelerate combustion, this low response for the aromatics may be attributed to the higher activation energy required for the nitrate or peroxide free radicals to react with an aromatic fragment compared to an aliphatic hydrocarbon fragment of the fuel. This, in fact, follows a similar trend for natural cetane for different fuel fragments, where aromatics have poor natural cetane numbers while straight chain aliphatic hydrocarbons have the highest natural cetane numbers.

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