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Performance of Ultra Low Sulphur Diesel Fuel Additives and its Side Effects

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Abstract- Demand of ultra low Sulphur diesel fuel and cost of additives have created interest in fuel additives. Cetane improver (CI) and lubricity additive (LA) are being regularly added in the ultra low Sulphur diesel (ULSD) fuel to meet the requirements of the specification. The additives are always costlier than diesel fuel and the price depends on the performance of additives. Sometimes, additives may have side effects on other properties of fuel. Hence additive's performance as well as its adverse effect on other properties of fuel are paramount while using additives.

Nayara Energy Research and Development team has conducted laboratory scale experimental study to evaluate performance and side effects of different additives used for ULSD fuel viz. cetane improvers and acid & ester based lubricity additives.
Following are the aspects studied using ULSD fuel:

1) Alternate cetane improvers.
2) Performance of cetane improvers.
3) Effect of cetane improver on lubricity of ULSD fuel.
4) Performance of lubricity additives in presence of cetane improvers.
5) Effect of cetane improver on twenty other Diesel fuel properties.
6) Two months stability study for key Diesel fuel properties.

The observations derived from experimental study are quite interesting and valuable. The study results clearly indicate that, cetane improver can deteriorate the lubricity of fuel and also affect the performance of lubricity additives. 2EHN is increasing total nitrogen content of the fuel which will produce more NOx while combustion. Ester based lubricity additives perform well as compared to acid based lubricity additives. Hence globally, the study work will be highly useful for petroleum refineries to select the best additives and combination of additives to produce ULSD fuel. It will be equally important for additive manufacturers to develop and produce best additives for ULSD fuel. This experimental study work will also be helpful to research and analytical scientists for evaluation of additives performance and its side effects. It will provide information of alternate additives / improvers to various users.

Study report includes the observations and test results of various laboratory experiments, the performance evaluation data of cetane improvers, the side effect of cetane improvers, the performance of lubricity additives (acid based and ester based) in presence of cetane improvers. Study report also includes two months stability study results and literature study information.

Index Terms—*Cetane Improver, Diesel,* Di-Tertiary Butyl Peroxide (DTBP), 2-ethylhexyl nitrate (2-EHN), *Lubricity Additive, Ultra Low Sulphur Diesel (ULSD)*

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Introduction

Diesel fuel is being used globally for many applications mainly for transportation, farm & construction equipment, heating etc. Diesel fuel used for automobile engine is having stringent specifications to provide better performance of engine as well as to control exhaust emission level. Looking to the ULSD fuel demand and economics of refinery product margin, most of the refineries target to upgrade maximum diesel components into diesel product. Additives are being used to produce diesel fuel meeting the specification requirements. The cetane number and lubricity of diesel fuel are key properties which can be controlled by addition of improvers / additives.

Cetane Number is a performance parameter of diesel fuel and it is measured by using standard engine method ASTM D 613. The cetane number depends on chemical composition of fuel, which are either from crude oil or generated through refinery processes. Diesel blending components produced from refinery have cetene number in the range of 25 to 70 and required specification is mostly 51 minimum. There are two primary ways to improve cetane number of diesel fuel (a) refinery processes viz hydro treating and hydro cracking and (b) addition of cetane improver (CI). Most of refineries use hydro treating / hydro cracking technique to reduce sulphur level as well as to improve cetane number. These technique can enhance cetane number up to certain level and after that, if required, refineries use cetane improver to meet the required specification.

Lubricity of ULSD fuel is primarily required to minimize wear & tear of engine components and it is measured by using standard method ISO 12156 (Lubricity by High Frequency Reciprocating Rig). As per BIS IS-1460 Diesel fuel standard, the specification is 460 microns max, while as per IQCM (Industrial Quality Control Manual of India) requirement is 420 microns max for coastal transfer, hence refineries needs to produce fuel meeting the above requirements. Lubricity of fuel is also depend~~s~~ on chemical composition and treatment employed during production of fuel. Since ULSD fuel specification demands for lower total Sulphur (10 ppm Max) to reduce environmental impact, the fuel has to pass through severe hydro treatments. The hydro treatment also decompose chemical molecules which are having natural lubricity behaviour. The straight run diesel is having lubricity approx. 500 micron and it became 600+ after hydro treatment, which can be then corrected by addition of lubricity additives (LA).

The additives are always costlier than fuel and the consumption of additives are increased drastically after implementation of ULSD fuel specification. The price of additives are mostly controlled by the performance data of additives for specific application, considering there is no harm on other properties of fuel, but literature / study data is not available for the same in public domain. Currently, only 2EHN is being used as cetane improver and alternate cetane improvers are not well known. For lubricity improvers, acid based and ester based are being widely used.

Hence, the need arises to identify alternate cetane improvers as well as conduct comprehensive study on performance of ULSD fuel additives and its side effects to effectively manage and optimize the fuel additives.

Nayara Energy Research and Development team has conducted literature study as well as laboratory experiments to conclude comprehensive study for ULSD fuel additives.

Following aspects are studied,

1) Alternate cetane improvers
2) Performance of cetane improvers.
3) Effect of cetane improvers on lubricity of ULSD fuel.
4) Performance of lubricity additives in presence of cetane improver.
5) Effect of cetane improver on twenty other diesel properties.
6) Two months stability study for key diesel properties.

Laboratory Experiments and Test Results

Stepwise experimental study has been conducted and all the tests are performed in NABL accredited laboratory using standard test methods mentioned in the diesel fuel specification.

1) Alternate Cetane Improvers:

Since a long period of time, 2-EHN is being used as cetane improver globally because of its cost effectiveness and dosage level in the range of up to 5000 wt. ppm. Through literature study, we come to know, that some of alkyl nitrates, peroxides components are having capability to improve cetane number of Diesel fuels. As per California diesel regulation (CARB) 13 CCR 2293, di-tertiary butyl peroxide (DTBP) chemical is permitted as cetane improver up to 10000 wt. ppm. Hence DTBP chemical is considered as alternate cetane improver for laboratory scale experimental work.

2) Performance of Cetane Improver (CI) :

Generally, cetane improver performance is defined by increase of the cetane number of the diesel fuel against the added concentration of cetane improver and it is a key factor for commercial acceptance.

ULSD fuel having 43.2 cetane number was used for the study of cetane number response of 2-EHN and DTBP at various concentration in the range of 0 to 4000 wt.ppm. Tests are performed as per ASTM D 613 test method and test results are tabulated in table-1/ Fig-1.

Table 1

Sample Details	2-EHN	DTBP
LSD + Zero CI	43.2	43.2
ULSD + 1000 ppm CI	46.4	45.8
ULSD + 2000 ppm CI	48.7	47.6
ULSD + 3000 ppm CI	50.6	49.5
ULSD + 4000 ppm CI	52.4	51.0

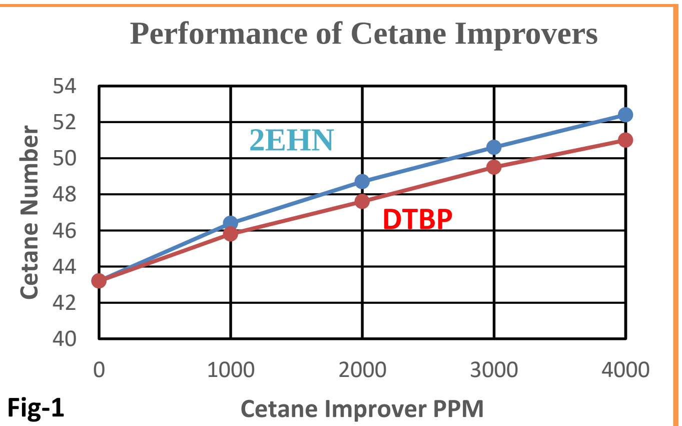

Fig-1

Observations: Experimental study data indicate that, both, 2-EHN and DTBP are increasing cetane number of ULSD fuel and response delta found to be lower at higher dosage level. The relative performance of DTBP as cetane improver is found lower than 2EHN.

3) Effect of Cetane Improvers on Lubricity of Diesel Fuel.

Study has been conducted to identify the effect of cetane improvers (2EHN and DTBP) at various concentration on lubricity of ULSD fuel, which is having lubricity of 600 microns. Tests are performed as per standard test method ISO 12156 (Lubricity by High Frequency Reciprocating Rig). All the test results of lubricity are in microns WSD and tabulated in table-2 / Fig-2.

Table 2

Sample Details	2-EHN	DTBP
ULSD + No CI	600	600
ULSD + 1000 ppm CI	740	590
ULSD + 2000 ppm CI	770	600
ULSD + 3000 ppm CI	780	610
ULSD + 4000 ppm CI	790	590
ULSD +10000 ppm CI	830	610

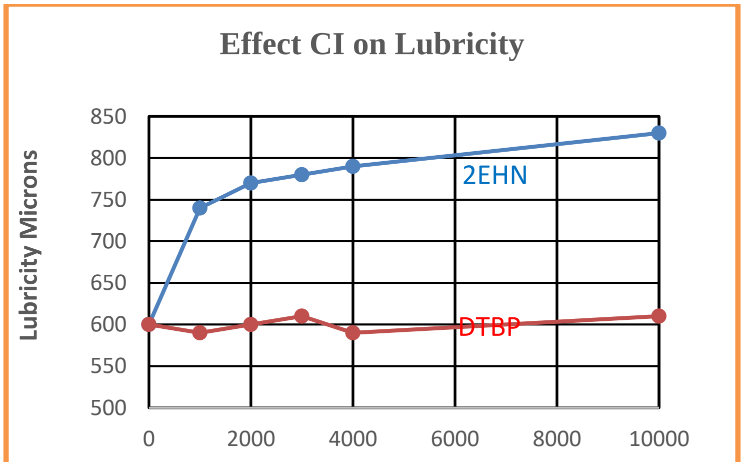

Fig-2

Observations:

Table-2 test results indicates that, there is no adverse effect of DTBP on ULSD fuel even at higher concentration. 2-EHN has increased wear scare diameter (indication of lubricity deterioration) of fuel from 600 to 830 microns and it is proportional to the dosage. Hence, more quantity of lubricity additives will be required to correct the same.

4) Performance of Lubricity Additives in Presence of Cetane Improver

As per BIS IS-1460 Diesel fuel standard, specification is 460 microns max, while as per IQCM (Industrial Quality Control Manual of India) requirement is 420 microns max for coastal transfer, hence refinery needs to produce fuel meeting the above requirements.

A) Performance of Acid Based Lubricity Additive

In this experiment, ULSD sample is collected, which does not have any additives and three sets of samples were prepared as mentioned below to see the performance of acid based lubricity additive with and without cetane improvers.

Set-1, ULSD fuel with acid based lubricity additive at different concentration

Set-2, ULSD fuel + 1900 ppm 2EHN + acid based lubricity additive at different concentration

Set-3 ULSD fuel + 1900 ppm DTBP + acid based lubricity additive at different concentration

All three sets of sample were tested for lubricity test and are presented in tabular and graphically form below.

Table 3

Acid Based LA	ULSD + LA	ULSD + 1900 ppm 2EHN + LA	ULSD + 1900 ppm DTBP + LA
0.0 wt. ppm	600	780	593
180	440	500	420
230	405	460	380
280	387	430	399
330	370	480	401

Graphical Data:

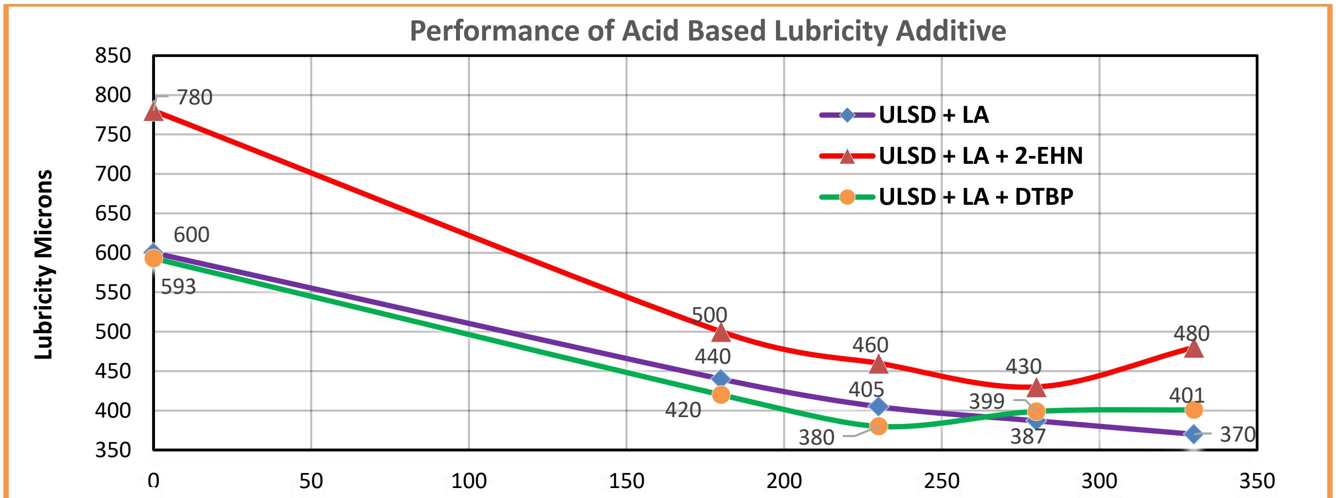

Fig-3

Observations:

a) ULSD + LA: Lubricity WSD reduced linearly when diesel is not having any cetane improver.
b) ULSD + LA + DTBP: Lubricity WSD reduced linearly up to 380 microns and after that there is no effect of additive.
c) ULSD + LA + 2-EHN : 1) Initial lubricity of fuel found increased from 600 to 780 microns 2) Lubricity is reduced only up to 430 microns 3) After 325 ppm LA dosage, lubricity is further increasing, it indicates that 2EHN has adverse effect on performance of acid based LA. 4) This problem can be further worsen when 2-EHN dossing will be at higher level.
d) Study was conducted using different acid based lubricity additives, but found same behavior.

B) Performance of Ester Based Lubricity Additive

In this experiment, ULSD fuel sample having 630 microns lubricity was selected for the study and then high concentration of cetane improver (3000 wt ppm 2EHN or DTBP) was added. Further ester based lubricity additives dosage at 150 & 200 ppm into it and then tested for lubricity. The observed test results are tabulated in table-4 below.

Table 4

Lubricity Additive Details	Ester Based LA			
Lubricity of ULSD (Without CI & LA) microns	630			
Dosage of Cetane Improver, ppm	3000 2EHN		3000 DTBP	
Dosage of Lubricity Additive, ppm	150	200	150	200
Lubricity of ULSD in microns	455	405	350	330

Observations: Ester based lubricity additives are more effective compared to acid based LA.

5 Effect of Cetane Improvers on Diesel Properties

Most of the standard diesel specifications are having 18 to 22 test properties, hence the study was extended for cetane improvers effect on all properties which are mandatory as per product specification. Three samples are prepared viz a) Diesel fuel + LA b) Diesel fuel + LA + 3000 ppm 2EHN and 3) Diesel fuel + LA + 3000 ppm DTBP. All three samples are tested for full specification properties using standard test method and test results are tabulated in separate Annexure-A.

Observations: There is no effect on other properties of fuel except 2EHN has increased Nitrogen content of fuel sample.

6 Two Months Stability Study for key Diesel Properties

To verify the stability of diesel fuel with additives, two months stability study was conducted. All three Diesel samples were prepared and tested at experiment -5 are retested after two months for key properties.

Observations: All key properties of fuel samples are found close to initial test results.

Conclusions:

Based on the various test results and observations of above laboratory experiments, it is concluded that,

Cetane Improvers:

1) Both cetane improvers (2-EHN and DTBP) found to be capable to increase cetane number of diesel fuel.
2) Both cetane improver's (2-EHN and DTBP) response delta found to be lower at higher dosage compared to initial.
3) The relative performance of DTBP as cetane improver is found to be lower than 2EHN.
4) DTBP is not having any adverse effect on any diesel properties even at higher dosage.
5) Based on study observations and information available through literature survey (California regulation), DTBP can be used as cetane improver.
6) 2EHN is deteriorating lubricity of diesel fuel and it is proportional to dosage.
7) 2EHN is also has an adverse effect on performance of acid based lubricity additives and becomes worse at higher dosage. It may be impossible to control lubricity at extreme high level of 2-EHN dossing.

Lubricity Improvers:

8) Performance of acid based as well as ester based lubricity additive in diesel without cetane improver found normal.
9) Performance of ester based lubricity additives is better than acid based at same dosage level.
10) Performance of ester based lubricity additive found to be normal with both cetane improvers.
11) Performance of acid based lubricity additives found to be normal with DTBP but abnormal in presence of 2EHN cetane improver and becomes worse at higher dosage level, hence may be difficult to achieve target specification.
12) User has to develop proper additives evaluation system for ULSD fuel to manage and optimize additives consumption.

Effect on other fuel properties and stability:

13) There is no effect of DTBP on any other properties of Diesel fuel
14) There is no effect of 2EHN on other properties of Diesel fuel except nitrogen content, it is increasing from 13 to 295 ppm.
15) All key properties of Diesel fuel with additives found to be stable up to two months

Benefits:

The observations derived from experimental study work are quite interesting and valuable, hence following benefits envisaged,

- The study work will be highly useful globally for petroleum refinery to select the best additives and combination of additives to produce USLD fuel. It will also help to develop evaluation procedure.
- It will be equally important for the additive manufacturer to develop and produce best additives for ULSD fuel.
- It will be helpful to research and analytical scientists for evaluation of additives performance and its side effects.
- It will provide information of alternate additives / improvers to various users.

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References:

1) Bureau of Indian Standard, IS 1460, Automotive Diesel Fuel-Specification
2) ISO 12156-1, Assessment of lubricity using the high-frequency reciprocating rig (HFRR) — Part 1: Test method
3) ASTM D 613, Standard Test Method for Cetane Number of Diesel Fuel Oil
4) California's Diesel Fuel Program, November 29, 2018, Oil & Gas and GHG Mitigation Branch California Air Resources Board (CARB)
5) Manish K Nandi ARCO Chemical Company, Newtown Square, PA 19073 "The Performance of di-tertiary-butyl peroxide as Cetane improver in diesel fuels." Publication Date: 1996-12-31, Report Number(s): CONF-960807, Journal ID: ACFPAI; ISSN 0569-3772; TRN: 97:000002-0022, Additional Journal Information: Journal Volume: 41; Journal Issue: 3; Conference: 212. national meeting of the American Chemical Society (ACS), Orlando, FL (United States), 25-30 Aug 1996; Other Information: PBD: 1996
6) Nandi, M.; Jacobs, D. C. Kesling, H. S.; Liotta. F. J.; "The Performance of a Peroxide based Cetane improvement Additive in Different Diesels Fuels": SAE 942019, October 1994. SAE Technical Paper, (19941001)

7) Nandi, M. K.; Jacobs, D. C.; "Cetane Response of Different Dl-tertiary-butyl Peroxide in different diesel fuels"; SAE Paper 952368; October 95.

Annexure-A

Sr. No.	Test Parameters / Properties	Method	Unit	Limit	Diesel with LA	Diesel + 3000 ppm 2EHN	Diesel + 3000 ppm DTBP
1	Appearance	Visual	---		Clear	Clear	Clear
2	Acidity, Inorganic	ASTM D 974	mg KOH/g	Nil	Nil	Nil	Nil
3	Acidity, Total	ASTM D 974	mg KOH/g	0.20 Max	0.03	0.03	0.03
4	Ash	ASTM D 482	% mass	0.01 Max	0.004	0.005	0.004
5	Carbon Residue on 10% residue	ASTM D 4530	% mass	0.3 Max	0.10	0.11	0.10
6	Cetan number	ASTM D 613	---	51 Min	**42.7**	**49.9**	**48.3**
7	Cetan Index	ASTM D 4737	---	46 Min	46.5	46.3	46.3
8	Pour point	ASTM D 97	C	Note 2	-6	-6	-6
9	Copper Strip Corrosion	ASTM D 130	---	1 Max	1b	1b	1b
10	Flash point, Able	IP 170	C	35 Min	41	41	40.5
11	KV at 40 C	ASTM D 445	cSt	2.0 to 4.5	1.912	1.915	1.911
12	Total contamination	EN12662	mg/kg	24 Max	4	5	5
13	Density at 15 C	ASTM D 4052	mg/kg3	815-845	829.9	830.4	829.9
14	Total Sulphur	ASTM D 5453	mg/kg	50 Max	37.0	42.8	37.6
15	Water content	ISO12937	mg/kg	200 Max	132	138	136
16	CFPP	ASTM D 6371	C	Note 3	-2	-2	-2
17	Oxidation stability	ASTM D 2274	g/m3	25 Max	2.6	2.3	1.1
18	PAH	IP 391	% mass	8 Max	3.588	3.364	3.597
19	Lubricity WSD at 60 C	ISO 12156-1	microns	460 max	**400**	**486**	**406**
20	Total Nitrogen	ASTM D 4926	ppm		**13**	**295**	**12**
21	2 EHN Concentration	FTIR	ppm		<100	3366	<100
22	Dist. recovery @ 95%	ASTM D 86	C	360 Max	350.0	351.6	350.8
22a	Dist. Perc. Rec. at 360°C	ASTM D 86	Vol%	90 Min	96.7	96.4	96.6
22b	Residue	ASTM D 86	Vol%		1.5	0.9	1.3

Authors Profile,

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