

STUDY OF ETHANOL, BIODIESEL AND DIESEL FUEL BLEND TO COMPARE EFFECTS OF ANTI OXIDANT ADDITIVES – AMINIC AND PHENOLIC

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ABSTRACT

Scientists have well understood that over the last few decades, humans have utilized natural resources inefficiently and in haphazard manner. This has resulted in devastating effects on Nature, especially climate change. Hence, there is an urgent need to protect nature from further damages. To mitigate the effects of rapid usage of fossil fuels, eco-friendly alternative carbon neutral drop in fuels are been encouraged by both governments and regulatory authorities. The transportation sector which constitutes usage of conventional fossil fuels, needs for a major shift from non-renewable to renewable and environment friendly resources. These resources include use of bio-diesel and ethanol blends which are produced from natural resources as fuels.

As part of this work, we have focused on study of biodiesel, ethanol and diesel fuel blends on the basis of oxidation effects along with effects of natural and synthetic antioxidants using RSSOT analyser.

Antioxidants are substances present at low concentrations in fuel and lubricants, which markedly delay or inhibit or control the oxidation of oxidizable substrate. Addition of antioxidants has been found to be most effective in controlling oxidation due to their unique properties arising from a wide range of chemical structures that extend the shelf-life of petroleum products without any adverse effect on their other qualities.

Keywords: Biodiesel, Antioxidant Additive, Renewable, Synthetic, Olefinic.

I. INTRODUCTION

Renewable energy sources such as biofuels mainly biodiesel and bio ethanol are in limelight now a days due to environment friendly nature of these fuels when compared with conventional fossil fuels. With increasing demand in consumption of fuel by Indian population, government is also keen in increasing blending of biofuels with conventional fuels for marketing in the India. Biodiesel is most suitable alternate fuel now days to reduce consumption of conventional diesel fuel. It is manufactured from plant oils (e.g., soybean oil, cottonseed oil, canola oil, corn oil); recycled cooking greases or oils (e.g., yellow grease); or animal fats (beef tallow, pork lard); and various combinations of these feedstocks. Used cooking oils are mostly plant based, but may also contain animal fats. Used cooking oils are both recycled and renewable. [1] In India, Biodiesel availability is not at par with requirement, therefore Govt. of India has provided option of using Biodiesel as Blend in conventional diesel. IS 15607:2016 Specification is released by Bureau of Indian Standards which covers IS Specifications for Biodiesel (B100)- Fatty acid Methyl Esters (FAME). Biofuels — Ethanol and Biodiesel — are being increasingly used in many countries as renewable fuels and is better option from environmental aspects also. [2] Similarly, IS 16531:2016 Specification is released by Bureau of Indian Standards which covers IS Specifications for Biodiesel, Diesel Fuel Blend (B6 – B20).

On studying these two specifications, it was observed that Oxidation Stability specification requirement differs between B100 Biodiesel and B6-B20 biodiesel, diesel fuels blend. It is 8 minute and 20 minute respectively. This is due to reduction in unsaturated hydrocarbon in Blended Biodiesel when compared to B100 Biodiesel. This makes basis of our study to seek clarifications on effects of usage of Antioxidants – Synthetic and Natural, on Biodiesel blends in different proportions. The biodiesel fuel is highly susceptible to oxidation when it comes in contact with air present in the atmosphere.

The oxidation of biodiesel is an auto-oxidation reaction that includes initiation, propagation, and termination reactions. A carbon-based free radical is created during the initiation stage when hydrogen is taken out of the carbon atom close to the double bond. This free radical creates the peroxide-free radical (ROO), which is extremely reactive with diatomic oxygen. Although less reactive than a carbon-free radical, a peroxide-free radical is nonetheless sufficiently reactive to swiftly remove hydrogen from carbon to create another carbon radical and a hydro peroxide (ROOH). The propagation cycle can then be continued by the new carbon-free radical reacting with diatomic oxygen. When two free radicals join to create a stable compound, the chain reaction is stopped. After a period of time, known as the induction period, the ROOH level increases quickly, signalling the beginning of the entire oxidation process. At first, the ROOH concentration is low. In this study, Biodiesel, Ethanol and Diesel fuel blends are used as a test fuel, and α -tocopherol, p-phenylenediamine, butylated hydroxyl toluene, are used as antioxidant additives. We are presenting results of our study which shows effects of different antioxidant additives on Diesel Fuel Blends with Biodiesel (B100) and Ethanol in different proportions.

II. METHODOLOGY

Production of Biodiesel:

50 Liter of refined Palm Oil was sourced from local market at Navi Mumbai, Maharashtra, India. The process utilized for conversion of Palm Oil to Biodiesel is Transesterification which is a catalyzed chemical reaction using Sodium Methoxide and excess of alcohol (Methanol) to yield fatty acid methyl esters (also known as biodiesel) along with glycerol as byproduct. The catalyst sodium methoxide acts as a strong base which increases rate of reaction and overall yield of desirable product. The reaction is reversible in nature, therefore to avoid this, excess of methanol is used during the reaction which shifts the equilibrium of reaction towards desirable product. Methanol is easily available at low costs. Methanol readily reacts with Palm oil which makes it very common solvent for transesterification reaction. As per literature survey, ratio of 1:2.5 for methanol to Palm oil quantity provides highest yield of biodiesel.

Chemical Reaction:

A closed reaction vessel of capacity 1000 Liters was utilized for transesterification process. The alkoxide mixture prepared above was charged in the reaction vessel in presence of excess of methanol (20 Liters) followed by slow addition of Palm oil heated at 60°C. The Palm oil was digested in presence of excess of Methanol for 2 hours. Temperature was not allowed to exceed from 60°C to avoid evaporation of methanol above its boiling point. The mixture was thoroughly mixed using a stirrer at 500 rpm (constant speed). Mild reaction conditions were maintained to avoid formation of soaps which initiate at higher temperatures.

Separation of Biodiesel and Glycerol:

On completion of reaction after 3 hours, biodiesel alongwith byproduct glycerol is formed inside the reaction vessel. The separation procedure is simple settling of glycerol for 2-3 hours by gravity. As the density of Glycerol is higher than biodiesel, it settles at bottom and forms darker lower layer in reaction vessel. The lower layer can be drained out using tap mechanism provided at bottom of reaction vessel. This removes Glycerol layer completely. Further settling time was provided to remove maximum glycerol layer. In our experiment, total quantity of Glycerol was approx. 12 Liter. Remaining product in reaction vessel is Biodiesel layer.

Washing of Fatty acid methyl ester (Biodiesel)

The Biodiesel layer contains traces of sodium methoxide, methanol and glycerol. To eliminate these, water washing is given using 100 liters of water which is enough to remove excess of sodium methoxide and other contaminants. It is very important to carry out this step since methanol and sodium methoxide traces can corrode engine parts which is very damaging for overall parts of vehicle which come in contact with the fuel. The traces of glycerol in biodiesel effects viscosity and reduces fuel lubricity, this can lead to formation of deposits. These contaminants are readily soluble in water and hence can be removed by washing of biodiesel 4-6 times. The water is heated at 40-50 °C.

Drying of Biodiesel

After completion of water wash, the biodiesel was heated at 110°C to evaporate traces of water present. This step enhanced the appearance of biodiesel to Clear and free from any traces of water.

Characterization of Biodiesel

The Biodiesel prepared in house was tested in accordance with IS 15464:2022 (Specification requirements for B100 in India) for below mentioned parameters prior to considering it as candidate test fuel. Biodiesel enhances fuel lubricity and improves anti-wear properties in blends with petro-diesel. [3, 7]

Table 1: Characterization test results (physicochemical properties) - Biodiesel candidate test fuel

S. No.	Test Parameter	Test Method	Specifications	Unit	Observed Value
1.	Appearance	Visual	Bright and Clear	-	Bright and Clear
2.	Colour	Visual	Report	-	Light Yellow
3.	Density at 15°C	ASTM D1298	860 to 900	Kg/m ³	874.8
4.	Kinematic Viscosity at 40°C	ASTM D445	3.5 to 5.0	cSt	4.693
5.	Flash Point (PMCC)	ASTM D92	Min. 101	°C	160.2
6.	Total Sulphur	ASTM D5453	10.0 Max.	mg/kg	2.9
7.	Carbon residue	IS 1448: P 189	0.05 Max.	% by mass	0.017
8.	Sulfated Ash	ASTM D482	0.02 Max.	% by mass	0.002
9.	Water Content	IS 1448: P 182	500 Max.	mg/kg	265
10.	Total Contamination	EN 12662	24 Max.	mg/kg	12.4
11.	Copper Strip Corrosion	ASTM D130	Class 1	Rating	1a
12.	Cetane Number	ASTM D613	51.0 Min.		66.5
13.	Acid Value	ASTM D664	0.5 Max.	mg KOH/g	0.3
14.	Methanol	EN14110	0.2 Max.	% by mass	0.03
15.	Ester content	EN14103	Min. 96.5	% by mass	97.1
16.	Monoglycerides content	EN14105	0.7 Max.	% by mass	0.15
17.	Diglyceride content	EN14105	0.2 Max.	% by mass	0.04
18.	Triglyceride content	EN14105	0.2 Max.	% by mass	0.03
19.	Free Glycerol	EN14105	0.02 Max.	% by mass	0.0
20.	Total Glycerol	EN14105	0.25 Max.	% by mass	0.21
21.	Phosphorus	ASTM D4951	4 Max.	mg/kg	1.0
22.	Sodium + Potassium	EN14538	5 Max.	mg/kg	1.5
23.	Calcium + Magnesium	EN14538	5 Max.	mg/kg	0.4
24.	Iodine value	EN14111	120 Max.	gm iodine/100g	28.3
25.	Oxidation stability at 110°C	EN15751	Min. 8	hour	0.25
26.	Cold filter plugging point (CFPP)	IS 1448: P 110	6 Max.	°C	18
27.	Linolenic acid methyl ester	EN 14103	12 Max.	% mass by mass	0.16

28.	Polyunsaturated (> 4 double bonds) methyl ester	EN 15779	1 Max.	% mass by mass	0.21
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Diesel fuel

Diesel fuel is also known as Automotive Diesel Fuel (ADF) is marketed in India as per IS 1460:2017 specifications. The fuel used in this study has been sourced from Mumbai Refinery of Hindustan Petroleum Corporation Ltd. The Diesel fuel has been characterized by conducting below mentioned tests on the Diesel Fuel.

Table 2: Characterization test results (physicochemical properties) - conventional Diesel Candidate Fuel.

S. No.	Test Parameter	Test Method	Specifications	Unit	Observed Value
1.	Appearance	Visual	Bright and Clear	-	Bright and Clear
2.	Acidity, inorganic	ASTM D974	Nil	mg KOH/g	Nil
3.	Acidity, total	ASTM D664	0.2 Max.	mg KOH/g	0.04
4.	Ash	ASTM D482	0.01 Max.	% by mass	<0.01
5.	Carbon residue (Ramsbottom)	ASTM D524	0.3 Max.	% by mass	<0.01
6.	Cetane number	ASTM D613	Min. 51	-	53.4
7.	Cetane index	ASTM D4737	Min. 46	-	55.5
8.	Pour point	ASTM D97	3 Max.	°C	-12
9.	Copper strip corrosion for 3 h at 50°C	ASTM D130	Not worse than No. 1	Rating	1a
10.	Distillation, 95 percent v/v, recovery	ASTM D86	360 Max.	°C	356.5
11.	Flash Point (ABEL)	ISO 13736	Min. 35	°C	47.0
12.	Kinematic Viscosity at 40°C	ASTM D445	2.0 to 4.5	CSt	2.814
13.	Total contamination	EN12662	24 Max.	mg/kg	14
14.	Density at 15°C	ASTM D1298	810 to 845	Kg/m ³	0.8287
15.	Total Sulphur	ASTM D5453	10.0 Max.	mg/kg	5.3
16.	Water content	ASTM D6304	200 Max.	mg/kg	160
17.	Cold Filter Plugging Point (CFPP)	ASTM D6371	6 Max.	°C	-1
18.	Oxidation stability by Rancidity meter	EN14112	Min. 20	Hour	110.0
19.	Polycyclic Aromatic Hydrocarbon (PAH)	EN12916	8 Max.	% by mass	2.2
20.	Lubricity corrected wear scar diameter (wsd 1.4) at 60°C,	ISO 12156-1	460 Max.	Microns	420
21.	FAME content	ASTM D7371	7 Max.	% v/v	0.0

Anhydrous Ethanol and its characterization

Anhydrous Ethanol is used as used as such or as admixture with petrol and diesel fuel. It is marketed in India as per IS 15464:2022 specifications. The anhydrous ethanol used in this study has been sourced from reputed supplier available in Maharashtra State. Anhydrous ethanol is name applied to Ethyl alcohol after addition of denaturant. Anhydrous ethanol is not fit for consumption by humans due to addition of poisonous denaturant. It is considered as an alternative fuel source that is environment friendly and needed for sustainable future. The anhydrous ethanol has been characterized by conducting below mentioned tests.

Table 3: Characterization test results (physicochemical properties) for ethanol candidate fuel

S. No.	Test Parameter	Test Method	Specifications	Unit	Observed Value
1.	Appearance	Visual	Bright and Clear	-	Bright and Clear
2.	Relative Density @ 15.6°C	Annex A	0.7961 Max.	-	0.7951
3.	Ethanol	Annex B	99.50 Min.	% v/v	99.81
4.	Methanol	ASTM D4815	0.5 Max.	% v/v	0.2
5.	Residue on Evaporation	Annex C	0.005 Max.	% by mass	0.001
6.	Acidity (as CH ₃ COOH)	Annex D	30 Max.	mg/kg	10
7.	Alkalinity	Annex D	Nil	mg/l	Nil
8.	Aldehyde content	Annex E	60 Max.	mg/l	60
9.	Electrical conductivity	Annex F	300 Max.	uS/m	210
10.	Copper	Annex G	0.1 Max.	mg/kg	0.005
11.	Sulfur Content	ASTM D5453	10 Max.	mg/kg	2
12.	Miscibility with water	Annex J	Miscible	-	Miscible

III. MODELING AND ANALYSIS

Preparation of Blends

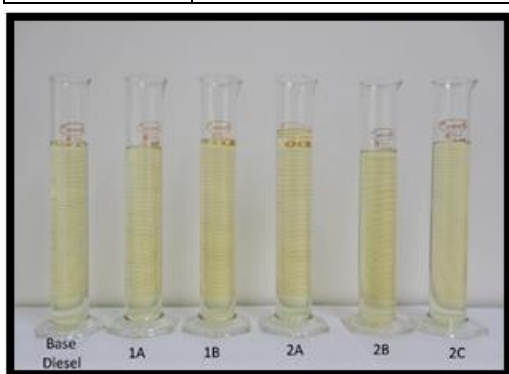
Total 14 Blends were prepared as shown in Table 4 by using Biodiesel, Ethanol and Diesel fuel discussed earlier in chapter. Figure 1 shows actual pictures of blends prepared on the basis of percentage volumes. The basis of blend preparation is variation in percent ratio of Ethanol and Biodiesel with Diesel fuel. Physicochemical properties were tested for all 14 Blends as shown in Table 5.

The blends were studied further for oxidation stability testing using RSSOT Equipment. The details of equipment used for oxidation stability study are provided in experimental section below.

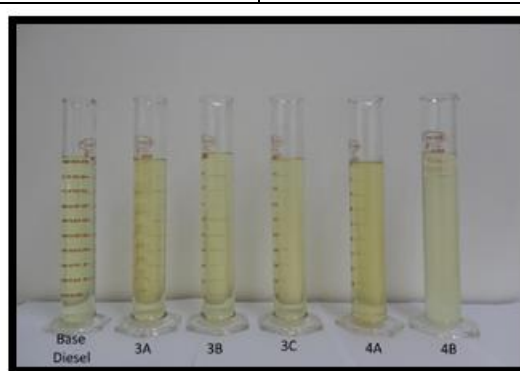
Table 4: Percentage wise composition of Blends using Diesel, Ethanol and Biodiesel.

Blend Code	Diesel (% vol.)	Ethanol (% vol.)	Biodiesel (% vol.)
1A	95	5	0
1B	95	0	5
2A	90	10	0
2B	90	0	10
2C	90	5	5
3A	85	5	10

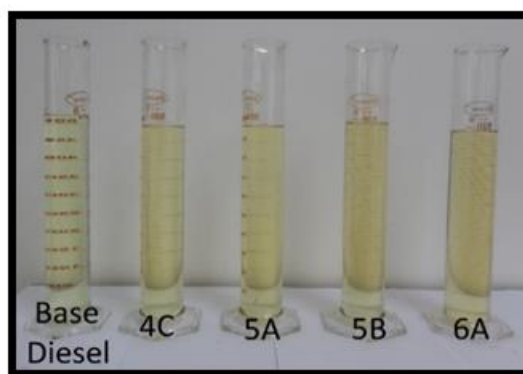
3B	85	10	5
3C	85	7.5	7.5
4A	80	0	20
4B	80	20	0
4C	80	10	10
5A	75	10	15
5B	75	15	10
6A	70	15	15



a.



b.



c.

Figure 1: a) Blends 1A,1B,2A,2B,2C b) Blends 3A,3B,3C,4A,4B, c) Blends 4C,5A,5B,6A

Table 5. Comparison of physicochemical properties

Parameter	100% Diesel	100% Biodiesel	1A	1B	2A	2B	2C	3A	3B
Density @ 15°C (g/cm ³)	0.827	0.874	0.826	0.830	0.824	0.833	0.828	0.830	0.826
Total Sulphur (mg/kg)	5.3	2.9	5.4	6.2	5.0	4.9	5.3	5.4	4.8
Total Nitrogen (mg/kg)	1.4	7.1	1.6	1.4	1.5	1.9	1.7	2.5	1.8

KV @ 40°C	2.814	4.693	2.546	2.889	2.502	2.947	2.579	2.803	2.591
CFPP (°C)	-1	18	0	-5	-2	10	-2	-4	-2
Pour Point (°C)	-12	18	-12	-12	-12	-12	-12	-12	-12
Cloud Point (°C)	-3	18	17	-2	-4	-2	-2	-2	5
Flash Point (°C)	47	160.2	23	49	23	52	23	23	-12.5
Oxidation Stability, D7545 (min)	110	15	116	68	113	55	55	56	89
HFRR (µm)	396	297	403	181	408	188	187	180	187
Total Acid Number	0.141	0.54	0.142	0.145	0.112	0.215	0.193	0.21	0.157

Table 6: Comparison of physicochemical properties (Contd.)

Parameter	100% Diesel	100% Biodiesel	3C	4A	4B	4C	5A	5B	6A
Density @ 15°C (g/cm ³)	0.827	0.874	0.828	0.837	0.822	0.828	0.830	0.826	0.829
Total sulphur (mg/kg)	5.3	2.9	6.4	5.4	2.9	4.6	6.4	4.5	7.2
Total nitrogen (mg/kg)	1.4	7.1	1.9	2.3	NA	1.9	2.2	2	2.4
KV @ 40°C (mm ² /sec)	2.814	4.693	2.679	3.124	2.469	2.727	2.848	2.699	2.714
CFPP (°C)	-1	18	-2	10	-2	7	-2	-2	-2
Pour point (°C)	-12	18	-12	-3	-12	-9	-9	-9	-6
Cloud point (°C)	-3	18	-2	10	21	2	-2	2	3
Flash point (°C)	47	160.2	23	23	23	23	23	23	23
Oxidation stability, D7545 (min)	110	15	69	36	97	58	43	63	56
HFRR (µm)	396	297	194	215	395	173	193	178	177
Total acid number	0.141	0.54	0.185	0.26	0.23	0.25	0.24	0.21	0.245

Experimental Setup

Study of Blends for Oxidation Stability

The experimental studies were conducted at Hindustan Petroleum Corporation Limited, R&D center laboratory situated in Bengaluru, Karnataka, India. The equipment used for Oxidation Stability measurement was Rapid Small Scale Oxidation Test (RSSOT) Anton Paar Make (Styria, Austria). The equipment conforms to requirement of Test Method ASTM D7545. Test Method ASTM D7545 covers a quantitative determination of the stability of middle distillate fuels such as diesel fuels and heating oils, with up to 100 % biodiesel, under accelerated oxidation conditions, by an automatic instrument. This test method is technically matching to requirement of EN 16091. The Test method provides induction period reading under controlled conditions which leads to information about Oxidation and storage stability of diesel fuels. Induction period is the time elapsed between start of heating procedure of the sample vessel and break point. It is measured in minutes. The test method explains use of automatically controlled oxidation tester which determines oxidation stability of Biodiesel/Diesel blends. 5 ml ± 0.1 ml of biodiesel blend sample is introduced in sample cup. Cover the test sample cup with the screw-cap and close the pressure vessel. Oxygen is introduced in pressure vessel until pressure of 700 kPa ± 5 kPa is attained and is stable for 20 seconds. Heater should be started with no delay during oxygen charging and starting of test performance. Timer is automatically started in the equipment. The sample is heated at constant temperature of 140°C ± 0.5°C within 5 minutes from start of the heater.

Now observe the pressure, if during initial 5 minutes, pressure drops steadily, discontinue the test and discard the test specimen. The pressure drop (leakage rate) should be less than 2 kPa/hour. If it is found to be more than this, analyst needs to check O ring for damage or residues of samples, surface of the sample cup for damage; sample cup for sample residues.

The temperature (to the nearest 0.1°C) and pressure (to the nearest 0.1 kPa) of the oxidation vessel is continuously monitored and recorded by apparatus. The test equipment will automatically terminate the test when the pressure readings show a 10% drop from the maximum observed pressure. This is Breakpoint. Induction Point is recorded to nearest 1 min. All determinations were performed in duplicate and mean value is reported for the experimental studies.



Figure 2: RSSOT equipment

Preparation of Blends with Antioxidant

Further these blends were studied for effect of antioxidants on oxidation stability. In the experiment the blends were doped with synthetic antioxidant namely BHT (phenolic) and p-phenylene diamine (aminic). To study effect of variation of dosage two sets of blends were created using 50 ppm and 100 ppm dosage. Details for different types of blends created using these additives are given in Table 6 and Table 7.

Preparation of Blends with Antioxidant

In this study, ethanol, biodiesel and diesel fuel blends are used as a test fuel with phenolic antioxidant as antioxidant additive. We are presenting results of our study which shows effects of natural antioxidant additives on diesel fuel blends with ethanol and biodiesel.

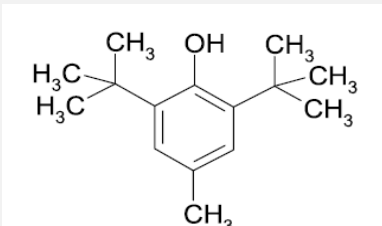
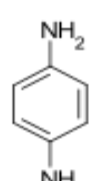
S. No.	Material	Source	Chemical Structure
1.	Butylated Hydroxy Toluene (phenolic)	Sigma Aldrich	
2.	p-phenylene diamine (aminic)	Sigma Aldrich	

Figure 3: Source, Structure and chemical properties of Phenolic and Aminic Antioxidant

Table 7: Anti-oxidant Blends 50 ppm dosage Butylated hydroxy Toluene (phenolic)

Property	Butylated Hydroxy Toluene	p-phenylene diamine
Formula	C ₅ H ₂₄ O	C ₆ H ₈ N ₂
M.W. g/mol	220.35	108.14
Melting Pt./°C	70	145-147
Boiling Pt./°C	265	267
Density/ g/cm ³	1.048	-
Solubility	Alcohol, ether, oils	Water

Table 8: Natural Anti-oxidant Blends 50 ppm dosage p-phenylene diamine (aminic)

Blend Code	Diesel (% vol.)	Ethanol (% vol.)	Biodiesel (% vol.)	Butylated hydroxy Toluene (ppm)
1A	95	5	0	50
1B	95	0	5	50
2A	90	10	0	50
2B	90	0	10	50
2C	90	5	5	50
3A	85	5	10	50
3B	85	10	5	50
3C	85	7.5	7.5	50

4A	80	0	20	50
4B	80	20	0	50
5A	75	10	15	50
5B	75	15	10	50
6A	70	15	15	50

Table 9:

Blend Code	Diesel (% vol.)	Ethanol (% vol.)	Biodiesel (% vol.)	p-phenylene diamine (ppm)
1A	95	5	0	50
1B	95	0	5	50
2A	90	10	0	50
2B	90	0	10	50
2C	90	5	5	50
3A	85	5	10	50
3B	85	10	5	50
3C	85	7.5	7.5	50
4A	80	0	20	50
4B	80	20	0	50
5A	75	10	15	50
5B	75	15	10	50
6A	70	15	15	50

IV. RESULTS AND DISCUSSION

A. Oxidation Stability of Blends

The results obtained from conducting the experiments revealed below mentioned results.

Table 10: Comparison of oxidation stability readings using RSSOT

Blend	1A	1B	2A	2B	2C	3A	3B
Oxidation stability	116	68	113	55	55	56	89
Diesel	95	95	90	90	90	85	85
Ethanol	5	0	10	0	5	5	10
Biodiesel	0	5	0	10	5	10	5
Blend	3C	4A	4B	4C	5A	5B	6A
Oxidation stability	69	36	97	58	43	63	56
Diesel	85	80	80	80	75	75	70
Ethanol	7.5	0	20	10	10	15	15
Biodiesel	7.5	20	0	10	15	10	15

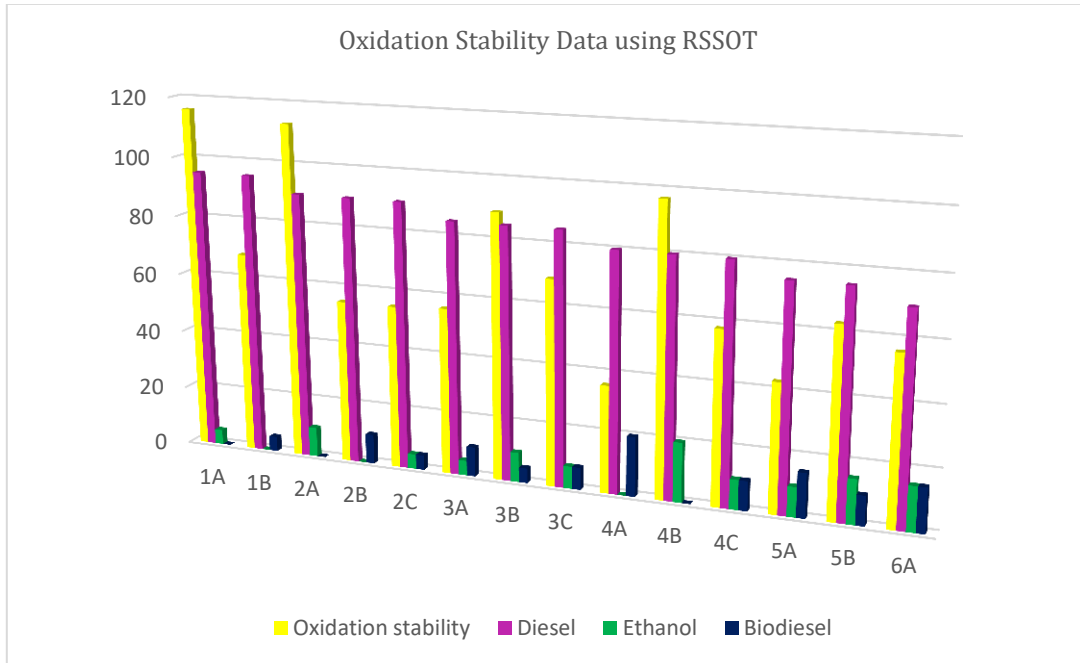


Figure 4: Comparison of Blend contents and oxidation stability – RSSOT

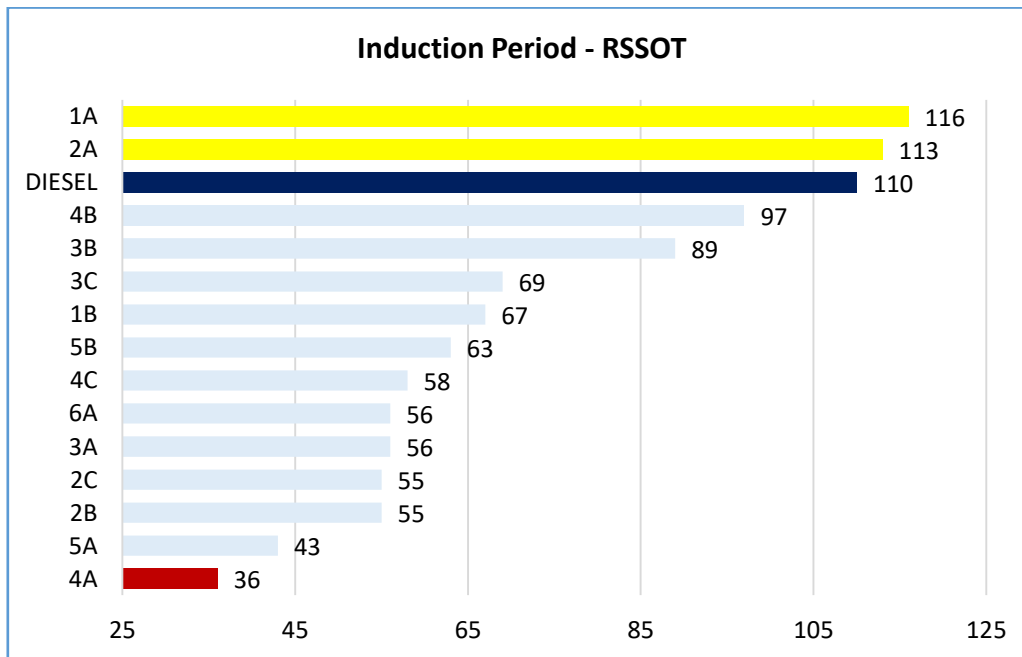


Figure 5: Change in Blend Oxidation Stability due to different compositions denoted by Induction Period – RSSOT.

1. RSSOT (Rapid Small Scale Oxidation test) conducted on above mentioned blends revealed that the oxidation stability is highest in Blend 1A containing 95% Diesel + 5% Ethanol + 0% Biodiesel. This means that presence of Ethanol in blend increases oxidation stability of Diesel fuel.
2. The RSSOT induction period of Diesel fuel was recorded as 110.08 minutes which shows high oxidation stability of the sample. High Induction Period (IP) value denotes stability of the samples against oxidizing agents. Higher the IP Value, higher is the stability of sample. This means the sample is less susceptible to oxidation when exposed to conditions such as temperature, sunlight, oxygen etc.
3. In Blend 1A, the induction period increased from 110.08 minutes to 116.5 minutes. This clearly showed positive effect of 5% Ethanol on Diesel fuel.

4. Above observation can be further confirmed by readings of Blend 4A containing 80% Diesel + 0% Ethanol + 20% Biodiesel. In this case the induction period decreased drastically from 110.08 minutes for neat diesel fuel to 35.93 minutes for Blend 4A. Biodiesel having initial oxidation stability of 15 minutes reduced the oxidation stability of blend drastically as it contains molecules which undergo oxidation when it comes in contact with oxygen present in air.

5. This denotes that Biodiesel is highly susceptible to oxidation and 20% Biodiesel having initial oxidation stability of 15 minutes is capable to drop induction point down to 35.93 minutes from 110.08 minutes. Also, ethanol is absent in this blend, which supports in enhancing Oxidation stability or Induction Period.

6. Readings observed in Blend 2B shows that when 10% Biodiesel (initial Oxidation stability 15.1 minute) is added to Diesel fuel with Induction period 110 minutes, its induction period drops to 55 minutes almost half from its initial reading. Similarly, in Blend 2C, 5% Biodiesel (initial Oxidation stability 15.1 minute) in presence of 5% Ethanol also has exactly same induction period of 55 minutes. This shows that presence of Biodiesel reduces oxidation improvement of Ethanol in blends.

7. Readings observed in Blend 3A shows when 85% Diesel + 10% Biodiesel + 5% Ethanol is blended, Induction period of Diesel drops from 110 to 56 minutes. This shows that presence of Biodiesel reduces oxidation stability and also that Oxidation Stability reduces due to decrease in percentage volume of Diesel fuel. But since Ethanol was present in the Blend it acted as Oxidation stability improver.

B. Oxidation Stability of Blends with synthetic Antioxidant

Table 11: Comparison of oxidation stability readings with 50 ppm phenolic antioxidant using RSSOT

Blend	1A	1B	2A	2B	2C	3A	3B
Oxidation stability	116	68	113	55	55	56	89
Changed O.S.	+50	+61	-11	+24	+74	+17	-16
Diesel	95	95	90	90	90	85	85
Ethanol	5	0	10	0	5	5	10
Biodiesel	0	5	0	10	5	10	5
Phenolic A.O.	50	50	50	50	50	50	50
Blend	3C	4A	4B	4C	5A	5B	6A
Oxidation stability	69	36	97	58	43	63	56
Changed O.S.	-1	+1	-18	+14	+4	+15	+4
Diesel	85	80	80	80	75	75	70
Ethanol	7.5	0	20	10	10	15	15
Biodiesel	7.5	20	0	10	15	10	15
Phenolic A.O.	50	50	50	50	50	50	50

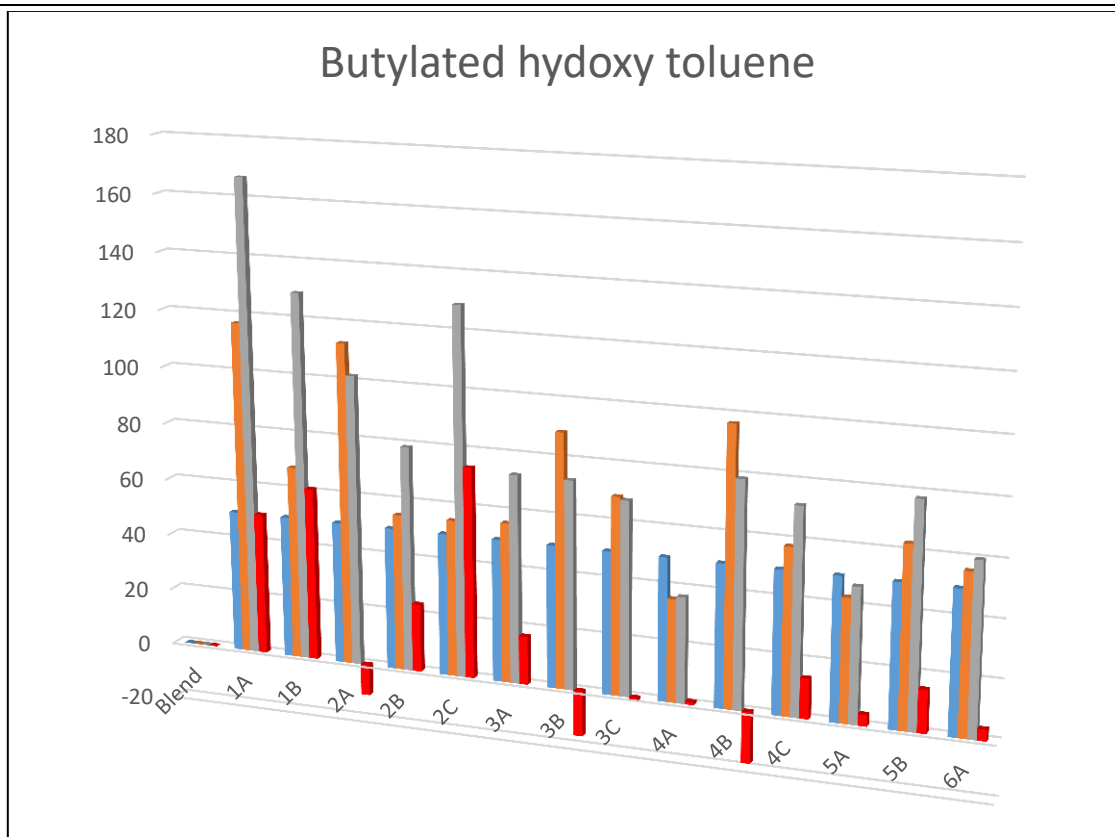


Figure 6: Graphical representation of results for Butylated hydroxy toluene synthetic antioxidant blends RSSOT (Rapid Small Scale Oxidation test) conducted on blends dosed with Butylated hydroxy toluene (BHT) anti-oxidant at 50 ppm dosage revealed below observations.

- 1) A sharp increase in oxidation stability clearly indicates that Butylated hydroxy toluene antioxidant additive is showing efficient antioxidant activity.
- 2) Our experiment clearly supports findings from Literature survey and it is evident that Butylated hydroxy toluene is preferred as an anti-oxidant for Biodiesel blends with Ethanol and Diesel fuel.
- 3) Out of 14 blends, 11 blends showed enhanced oxidation stability evident from higher degree of increase in induction point.
- 4) Two nos. blends 2A and 4B containing Diesel and Ethanol only without biodiesel content showed higher degree of decrease in induction point.
- 5) Blend 3C containing equal amount of Ethanol and biodiesel in diesel fuel showed slight decrease in induction point.

Table 12: Comparison of oxidation stability readings with 50 ppm aminic antioxidant using RSSOT

Blend	1A	1B	2A	2B	2C	3A	3B
Oxidation stability	117	68	113	55	55	56	89
Changed O.S.	+135	+59	+278	+46	+76	+74	+133
Diesel	95	95	90	90	90	85	85
Ethanol	5	0	10	0	5	5	10
Biodiesel	0	5	0	10	5	10	5
Aminic A.O.	50	50	50	50	50	50	50

Blend	3C	4A	4B	4C	5A	5B	6A
Oxidation stability	69	36	97	58	43	63	56
Changed O.S.	+83	+4	+391	+33	+7	+84	+58
Diesel	85	80	80	80	75	75	70
Ethanol	7.5	0	20	10	10	15	15
Biodiesel	7.5	20	0	10	15	10	15
Aminic A.O.	50	50	50	50	50	50	50

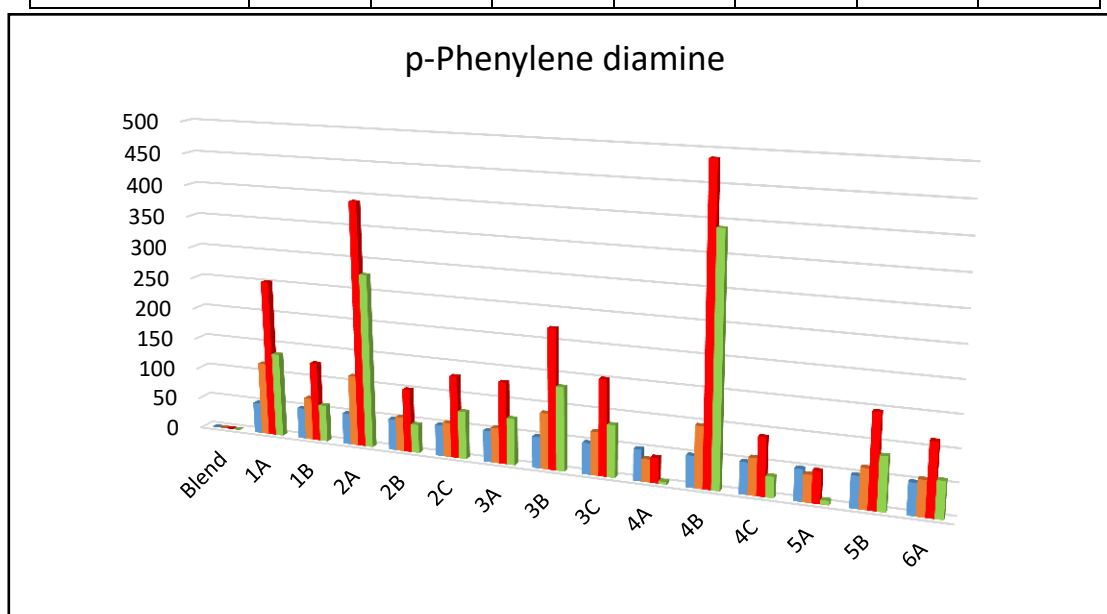


Figure 7: Graphical representation of results for p-phenylene diamine synthetic antioxidant blends

RSSOT (Rapid Small Scale Oxidation test) conducted on blends dosed with p-phenylene diamine anti-oxidant at 50 ppm dosage revealed below observations.

- 1) A sharp increase or enhancement in oxidation stability clearly indicates that p-Phenylene diamine anti-oxidant additive is showing all needed characteristics of anti-oxidant.
- 2) Blends containing Diesel and Ethanol only showed higher degree of increase in induction point.
- 3) Blends containing Biodiesel alongwith Diesel and Ethanol showed slight increase in induction point.
- 4) None of the cases showed reduction in Induction Point.

V. CONCLUSION

In this study the oxidation stability of 14 different blends prepared in laboratory; using biodiesel, ethanol and diesel with addition BHT; was evaluated by employing RSSOT method. The effects of the addition of phenolic synthetic antioxidant at 50 ppm concentration to biodiesel and ethanol in diesel blends on the oxidation stability were studied which led to conclusions as per following:

1. The addition of Butylated hydroxy toluene antioxidant in Laboratory blends drastically enhanced Oxidation Stability which was evident from higher induction points readings in minutes when compared with blank blend readings. Blank samples were prepared using Diesel fuel alongwith Ethanol and Biodiesel without dosage of Butylated hydroxy toluene antioxidant.
2. Blends containing ethanol showed negative response to BHT additive.
3. Blends containing biodiesel as one of the components, showed positive response and oxidation stability improved drastically.

In this study the oxidation stability of 14 different blends prepared in laboratory; using biodiesel, ethanol and

diesel with addition p-phenylene diamine; was evaluated by employing RSSOT method. The effects of the addition of phenolic synthetic antioxidant at 50 ppm concentration to biodiesel and ethanol in diesel blends on the oxidation stability were studied which led to conclusions as per following:

(1) The addition of p-phenylene diamine antioxidant in Laboratory blends drastically enhanced Oxidation Stability which was evident from higher induction points readings in minutes when compared with blank blend readings. Blank samples were prepared using Diesel fuel along with Ethanol and Biodiesel without dosage of Butylated hydroxy toluene antioxidant.

(2) All Blends showed positive response and oxidation stability improved drastically.

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