

Effect of L-Ascorbic Acid Antioxidant on Oxidation Stability of Biodiesel



Khushbu Yadav, Naveen Kumar, and Rajiv Chaudhary

Abstract Researchers are exploring alternative fuels due to decreasing fossil fuel reserves, increased prices, and environmental concerns. Biodiesel is found one of the possible solutions to utilize. For instance, biodiesel contains no sulfur or aromatics that contribute to air pollution or acid rain but has poor oxidation stability. Antioxidant additives enhance the stability of a fuel blend against thermo-oxidative degradation during storage through inhibition of free radical chain reactions between unsaturated compounds found in biodiesel. In the present research work, waste cooking oil biodiesel is used, containing a highly unsaturated compound, to evaluate the performance of L-ascorbic acid antioxidant. The induction period of antioxidant-treated biodiesel has been evaluated at different ppm levels to maintain standard of biodiesel. 200 ppm of L-ascorbic acid antioxidant enhance oxidation stability and meeting EN standard.

Keywords Biodiesel · Antioxidants · Oxidation stability · Induction time

1 Introduction

Biodiesel is one of the promising non-toxic and ecofriendly renewable alternative fuel made from vegetable oil or animal fats by transesterification process. Properties of biodiesel are similar to petro-diesel which makes it available to use in transportation sectors by blending it in conventional diesel. India is importer of vegetable oil for

K. Yadav (✉)

Mechanical Engineering Department, Amity University, Noida, Uttar Pradesh 201301, India
e-mail: khushbu.mnnit@gmail.com

K. Yadav · N. Kumar

Centre for Advanced Studies and Research in Automobile Engineering, Delhi Technological University, Delhi 110042, India

R. Chaudhary

Department of Mechanical Engineering, Delhi Technological University, Delhi 110042, India

consumption so production of biodiesel from edible vegetable oils cannot be considered as good choice Non-edible vegetable oil can be produced by harvesting of plants which helps in providing green cover to waste land and provide support to agriculture and rural economy [1]. Canada uses canola, The United States uses soybean, Japan uses animal fat, Europe uses rapeseed, and Malaysia uses palm oil for production of biodiesel. Non-edible oils such as neem, sal, kusum, mahua, pongamia, jatropha are easily available in many parts of India and could be utilized for production of biodiesel. Potential availability of oil source is Jatropha 3–4 MT/(ha year) Neem oil (100,000 tons/year), sal (180,000 tons/year), Mahua (180,000 tons/year), Pongamia (55,000 tons/year) per year [2]. Low oxidation stability is one of the drawbacks of biodiesel due to presence of unsaturated fatty present in the ester. Auto-oxidation of biodiesel leads to formation of oxidation product, gum formation, change in color, insoluble and sedimentation in the biodiesel. To overcome these stability problems various additives, synthetic as well as natural, used as an antioxidant [3]. Biodiesel consist of saturated fatty acid (SFA), monounsaturated fatty acid (MUSFA), and polyunsaturated fatty acid (PUFA). Unsaturated fatty acids with a higher percentage of unsaturated fatty acids are prone to oxidative degradation and highly saturated leads to low cold flow properties. Fuel properties are influenced by the fatty acid profile of the vegetable oil [4]. The methyl esters of highly unsaturated fatty acids have superior cold flow characteristics and low oxidation stability, whereas saturated fatty acids have significant high oxidation stability and poor cold flow properties. To get a high-quality fuel, the fatty acid profile of biodiesel must be optimized, which may be accomplished by mixing biodiesel from various feedstocks. Poor low temperature performance of biodiesel limits its use in cold climate [5].

Biodiesel produced by straight vegetable oil through chemical process know as transesterification or esterification. Vegetable oils and animal fats converted into Fatty Acid Methyl Esters (FAME) or mono alkyl esters of long chain. Vegetable oils (cottonseed oil, sunflower oil, peanut oil, coconut oil, soybean oil, canola/rapeseed oil, corn oil) and animal fats considered as edible feedstock's of 1st generation for production of biodiesel. Second generation non-edible feedstock's are plant waste biomass and agricultural waste (Jatropha oil, Pongamia oil, Mahua oil, Rubber seed, Caster oil, neem, sal, etc.). In this research article, 100 pound of biodiesel produced by 100 pound of vegetable oil reacted with 10 pound of alcohol (i.e., methanol and ethanol) in the presence of base catalyst [6]. Biodiesel can use in exiting engine without any modification. Utilization of biodiesel reduces Carbon monoxides, hydrocarbon, and sulfur emission. Only NO_x emission slightly risen up in comparison to diesel fuel. Nitrogen oxides and particulate matter were changed by changing chain length of concentration [7]. Shahir et al. [8] performed analysis on CRDI engine with pure diesel and several blends of animal fat biodiesel, brake thermal efficiency, exhaust gas temperature, and BSFC increases with lower value of CO, NO_x, and HC for 30% blend of biodiesel when compared to diesel.

Dutta et al. [9] investigated palm stearin biodiesel, Brake Thermal Efficiency slightly increases by adding Alcohols (Ethanol and Methanol) to biodiesel during synthesis of. Rising in alcohols maximum in-cylinder temperature decreases with decreasing the value of peak pressure rise, decrease in NO_x emission and increases

Table 1 Properties of diesel, biodiesel with their ASTM standards [12]

S. No.	Fuel properties	Testing methods	Diesel	Biodiesel	Units
	Fuel standard		ASTM D 975	ASTM D 6751	
1	Density @15 °C	D4052	848	878 min	Kg/m ³
2	Cetane number	D613	40–55	48–60	–
3	Cloud point	D2500	–15 to 5	–3 to 12	°C
4	Flash point	D 93	60–80	93.0 min	°C
5	Kinematic viscosity @40 °C	D445	1.3–4.1	1.9–6.0	mm ² /s
6	Pour point	D97	–35 to –15	–15 to 10	°C
7	Oxidation stability	EN14214	–	6	Hours

PM and Smoke. Imtenanet et al. [10] Investigates biodiesel-diesel blends performance and emission analysis with additives. Palm biodiesel-diesel blend with ethanol, n-butanol, and diethyl ether used as additives. Author used 80% of diesel, 15% of palm biodiesel with 5% of additives. The result shows improvement in brake power, brake thermal efficiency and decrease in brake specific fuel consumption. With diethyl ether additive brake power increase by 6.25%, brake specific fuel consumption by 3.28% and brake thermal efficiency by 4%. Ethanol and n-butanol enhance the performance like decrease NO and CO emission with slightly increase in HC emission. Sousaet et al. [11] used curcumin and β -carotene as antioxidant additives in methyl soybean biodiesel to control their oxidative process. Antioxidant activity checked against radical 2 of these two chemicals by DPPH (2-diphenyl-1-picrylhydrozyl) technique. Result shows that curcumin act as good antioxidant for soybean biodiesel because it increases induction period of biodiesel up to 83%. While β -carotene did not show any antioxidant activity for and concentration. The Petro-oxy and Rancimat techniques used to determine antioxidant activity.

Utilization of biodiesel in existing diesel engine should have similar physico-chemical properties to diesel. Biodiesel physico-chemical properties are viscosity, specific gravity, flash point, fire point, pour point, cloud point, and calorific value, cetane number, etc. these properties should meet ASTM standard given in Table 1.

2 Fatty Acid Composition

Physical and chemical structure of oil is greatly influenced by type and amount of fatty acid present. Fatty acids are classified into in two classes, saturated and unsaturated. Unsaturated fatty acid combines polyunsaturated and monounsaturated fatty acid. High degree of unsaturated acid present in oil leads to more susceptible to oxidative deterioration. Higher degree of unsaturation of fatty acids in vegetable oils, the more susceptible they are to oxidative deterioration [13, 14]. Most common form of saturated fatty acids (SFA) are Palmitic [C16:0] & Stearic [C18:0] and

Table 2 Fatty acid profile of different oil [9, 16, 17]

S. No.	Type of oil	SFA (%)	UFA (%)	[C16:0] (%)	[C18:0] (%)	[C18:1] (%)	[C18:2] (%)	[C18:3] (%)
1	Coconut	86.75	18.80	12.6	3.99	10.5	2.58	0.01
2	Cotton seed	27	73	24.4	2.2	17.2	55.0	0.3
3	Linseed	10.2	88.91	6.58	4.43	18.51	17.25	53.21
4	Palm Kernel	82.1	17.8	8.4	2.4	15.4	2.4	–
5	Olive	13.24	81.20	18.21	0.20	66.70	12.59	0.47
6	Soybean	15.1	88.4	11	4.0	23.4	53.2	7.8
7	Sunflower seed	9.4	90.7	6.2	2.8	28.0	62.8	0.16
8	Caster	1	98.1	1.3	1.2	5.5	7.3	0.5
9	Oleander	29	53.68	19.50	6.39	42.25	10.50	0.50
10	Neem	37	63	18.66	20.42	20.46	34.64	–
11	Kusum	53	40	8	2.3	42.6	9.5	–
12	Rapeseed	6.3	72	4.6	1.7	63.3	19.6	1.3
13	Rubber seed	6.3	72.8	4.6	1.7	63.3	19.6	1.3
14	Canola	7.45	92	-	-	61.8	18.6	9.1
15	Rice bran	22.5	77.6	20.0	2.1	42.7	33.1	0.45
16	Sesame	16.9	83.2	9.7	6.5	41.5	40.9	0.21
17	Sal	45–50	36–46	4–8	40–50	35–40	1–4	–
18	Karanja	26	54	11.65	7.5	51.59	16.64	–
19	Jatropha	21.6	78.4	14.2	7.0	44.7	32.8	0.2
20	Mahua	32.7	65.9	17.8	14.0	46.3	17.9	1.7
21	Palm seed oil	49.9	49.7	44.0	4.5	39.2	10.1	0.4

unsaturated fatty acids (UFA) are Oleic acid [C18:1], Linoleic acid [C18:2], and Linolenic [C18:3]. Fatty acid profile of different oils with saturated and unsaturated compound is given in Table 2. Highly unsaturated oil shows oxidation degradation can be overcome by utilization of antioxidants [8, 15]. Fatty acid composition of waste cooking oil biodiesel is given in Table 3, shows availability of higher amount of unsaturated fats.

3 Additives

Antioxidants are chemicals that slow down, regulate, or prevent the autoxidation of substrates, lowering the yields of undesirable secondary products. Chain breaking

Table 3 Saturated and unsaturated fatty acid compound of waste cooking oil biodiesel (WCOB)

Constituents type	Amount (% area)	Type
Hexadecanoic acid	22.11	saturated
Methyl stearate	4.32	Unsaturated
9,12-Octadecadienoic acid	68.22	Unsaturated
Docosanoic acid	1.53	Saturated
Pentacosanoic acid	0.07	Saturated
Hexacosanoic acid	0.07	Saturated
Tetracosanoic acid	0.74	Saturated
9,11-Octadecadienoic acid	0.07	Unsaturated
Eicosanoic acid	1.14	saturated
9,12-Octadecadienoic acid	0.08	Unsaturated
Heneicosanoic acid	0.11	Saturated
Methyl Tetradecanoate	0.29	Saturated
Gamma-Sitosterol	0.04	Saturated
Cis-Methyl 11-eicosenoate	0.37	Saturated
Tricosanoic acid	0.10	Saturated
9-Hexadecenoic acid	0.11	Saturated
(Z)-Methyl heptadec-9-enoate	0.17	Saturated
Hexadecatrienoic acid	0.02	Saturated
Heptadecanoic acid	0.34	Saturated
Unsaturated fatty acid	72.69	
Saturated fatty acid	27.21	

antioxidants (primary antioxidants) and hydroperoxide decomposers (secondary antioxidants) are the two types of antioxidants. By giving a hydrogen atom to a free radical (particularly the peroxy radical ROO*), primary antioxidants (AH) slow or stop the propagation process [10]. The hydrogen is liberated from main antioxidants' active OH or NH groups and subsequently given to free radicals. The most often used main antioxidants are substituted phenolic compounds, secondary aromatic amines, and thiophenols. Tocopherols and flavonoids, which are natural antioxidants, belong to this category as well [18, 19]. Light-induced photooxidation is not inhibited by primary antioxidants. Secondary antioxidants scavenge oxygen, metal ions, and pro-oxidative enzymes by decomposing hydroperoxides through chain-breaking. Because of their effectiveness in scavenging free radicals, hybrid or bifunctional antioxidants such as aminophenols, hydroxy hydroquinolines, and hydroxyl benzimidazoles have become popular in recent years. They have OH and NH groups in their molecular structure [19].

Additives can be divided into these categories are listed below.

1. Metal-based additives
2. Oxygenated additives

3. Cetane Number Improver Additives
4. Antioxidant additives.

4 Effect of Antioxidant Additives on Engine Performance and Emission

Nabi et al. [16] Experiment performed on biodiesel derived from waste cooking oil to check engine performance and emission under the 13-Mode European Stationary Cycle. Reduction in 13% blow by emission, 11–15% reduction in CO, 47–70% reduction in unburnt hydrocarbon emission, 84% reduction in PM, 88% reduction in PN and slightly increase in NO_x emission with reference fuel were observed. Nair et al. [17] investigated on diesel and blends of Neem biodiesel. By using Neem biodiesel brake thermal efficiency found to higher than diesel and brake power is approximately same. CO, HC, NO_x emission decreased and O₂ emission increases as compared to reference fuel. At B10 blend of neem biodiesel with diesel gives higher performance and lower emission than other blends. Oxygen-based emission caused by biodiesel reduced by using additives.

5 Properties of Waste Cooking Oil Biodiesel

Waste cooking oil was collected from local market. For converting waste cooking oil in to waste cooking oil biodiesel (WCOB) transesterification process has been done with methanol and NOH as catalyst. Properties of WCOB was tested as per ASTM standard and found be to in the range as given in Table 4.

Table 4 Waste cooking oil biodiesel Physico-chemical properties

Fuel properties	Measuring apparatus	Testing methods	Waste cooking oil biodiesel
Fuel standard	–	ASTM	ASTM D6751
Kinematic viscosity @40 °C (cSt)	Visco bath, Petrotest	D445	5.85
Density (Kg/m ³) @15 °C	Anton Par, DMA 4500	D4052	856
Lower heating value (MJ/Kg)	Oxygen bomb calorimeter Parr	D240	35.432
Flash pont °C	Pensky-Martens (AD0093-600)	D93	131
Oxidation stability	Rancimat	EN14112, D6751	2.49

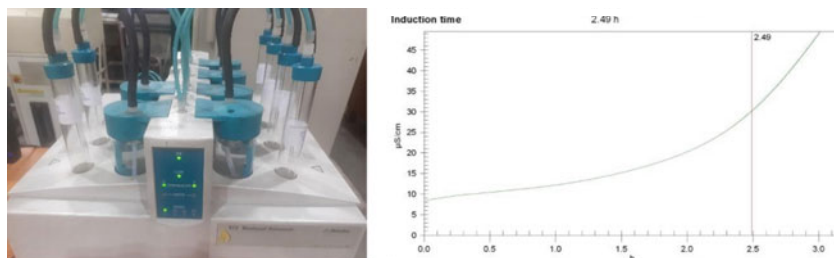


Fig. 1 Rancimat setup for oxidation stability and Induction time of waste cooking oil biodiesel

6 Oxidation Stability of Waste Cooking Oil Biodiesel

To achieve the oxidation stability standards, ASTM D6751 (3 h) or EN 14214 (6 h) [6, 7], the majority of biodiesel produced requires the application of antioxidants. Antioxidants added to biodiesel help to slow down the oxidation process. Rancimat is one of the method for determining the oxidation stability of biodiesel that is authorized by the EN 14214 standard. The induction duration is measured by tracking the steady increase in conductivity, which is mostly driven by volatile secondary oxidation products including formic and acetic acids [12–14]. The higher the oxidation stability, the longer the induction duration. In this investigation waste cooking biodiesel was used. Waste cooking oil biodiesel meets all properties of biodiesel as per standard but did not meet oxidation standard. Induction period was determined by Rancimat test methods and found to be 2.49 h. Figure 1, shows Rancimat setup and induction time of waste cooking oil biodiesel.

7 Effect of Antioxidant on Oxidation Stability of Waste Cooking Oil Biodiesel

Antioxidant additive helps to improve oxidation stability of biodiesel. L-ascorbic acid was used to evaluate oxidation stability. Antioxidant added in 100 and 200 ppm quantity in biodiesel. 100 ppm not able to meet EN14214. By adding 100 and 200 ppm of antioxidant, induction period increases to 3.24 and 6 h, respectively. Figures 2 and 3 shows representation of induction time evaluated by Rancimat method (Table 5).

8 Conclusion

In this paper, biodiesel was produced from waste cooking oil. Physico-chemical properties were evaluated and found in range as per ASTM. Fatty acid composition focusing on saturated and unsaturated compound of different oil have done.

Fig. 2 Induction time of waste cooking oil biodiesel with 100 ppm of L-ascorbic antioxidant

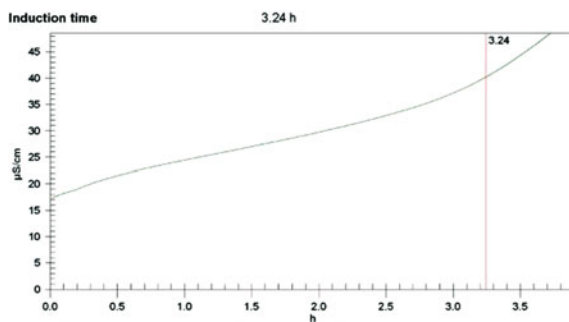
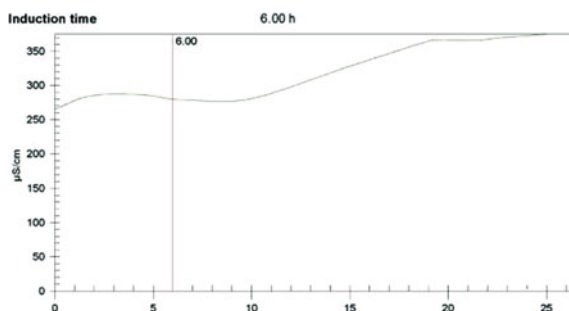


Fig. 3 Induction time of waste cooking oil biodiesel with 200 ppm of L-ascorbic antioxidant



Unsaturated fatty acid composition is found more in waste cooking oil biodiesel. Oxidation stability of pure waste cooking oil biodiesel was evaluated. Although, pure waste cooking oil biodiesel did not meet EN14214 standard. L-ascorbic antioxidant additive used in 100 ppm and 200 ppm quantity to evaluate Oxidation stability. 200 ppm of antioxidants were found effective to enhance oxidation stability to meet EN14214 standard.

Table 5 Effect of additives on engine performance and emission with feedstock

S. No.	Antioxidant	Feedstock	Amt	BSFC	BTE	NO _x	HC	CO	EGT	Smoke	References
1	PPDA	Annona methyl ester 20%	250 mg	<>	<>	↓	↓	↓	<>	↓	[20]
2	AT	Annona methyl ester 20%	250 mg	↑	↓	↓	↓	↓	↑	↓	[20]
3	LA	Annona methyl ester 20%	250 mg	<>	<>	↓	↓	↓	<>	↓	[20]
4	BHA	Lemongrass oil 25%	500 ppm	↓0.24%	↑0.47%	↓2.2%	↑2.2%	↑5.8%	↓2.54%	↑	[21]
5	BHA	Lemongrass oil 25%	1000 ppm	↓0.48%	↑0.94%	↓5.52%	↑4.3%	↑10.1%	↓4.1%	↑	[21]
6	BHA	Lemongrass oil 25%	2000 ppm	↓1.66%	↑1.29%	↓11%	↑10.2%	↑14.8%	↓7.1%	↑	[21]
7	BHT	Lemongrass oil 25%	500 ppm	↓0.01%	↑0.14%	↓2.1%	↑4.3%	↑8.5%	↓1.8%	↑	[21]
8	BHT	Lemongrass oil 25%	1000 ppm	↓0.65%	↑0.15%	↓3.6%	↑8.3%	↑13.1%	↓3.2%	↑	[21]
9	BHT	Lemongrass oil 25%	2000 ppm	↓0.96%	↑0.82%	↓9.1%	↑11.1%	↑16.6%	↓5.32%	↑	[21]
10	BHA	Beef Tallow oil 20%	1000 ppm	↑	↓1.5%	↓8.2%	↑10.6%	↑14.2%	↓1.9%	-	[22]
11	BHA	Palm Oil 20%	1000 ppm	↓	↑slight	↓	↑	↑	-	-	[23]
12	BHT	Palm Oil 20%	1000 ppm	↓	↑	<>	↑	↑	-	-	[23]

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