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Impact of Antioxidant and Metals on Biodiesel Stability-A Review

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Abstract

The rise in petroleum price and uncertainties in fossil fuel availability, there is renewed interest in vegetable oil fuels for diesel engines. The vegetable oil can be used as alternative fuel to diesel. But there are two problems associated with use of vegetable oil as fuel are oxidation stability and cold flow property. The use of vegetable oil as bio fuel is limited due to poor stability characteristics of this oil. The poor stability leads to gum formation which further leads to storage problem of these fuels for longer period of time. The high temperature engine performance is also affected due to poor thermal stability of the bio fuel obtained from vegetable oil. To overcome these stability related problems various chemical substances (natural as well as synthetic) in nature are used as antioxidants. These antioxidants improve the stability characteristics of bio fuels. The impact of various metals on the oxidation stability of various bio fuel sources is also investigated in the paper. The result of the investigation shows that Aluminium and Cast iron container are best for storage and transportation of biodiesel. The comparative study also shows that Pyrogallol is best antioxidant for improving the stability.

***Keyword**: Biodiesel; Stability; Antioxidant; Energy; Induction Period; Metal*

1. Biodiesel

Biodiesel has high potential as a new and renewable energy source in the future, as a substitution fuel for petroleum diesel and can be used in existing diesel engine without modification. Currently, more than 95% of the world biodiesel is produced from edible oil which is easily available on large scale from the agricultural industry. However, rapid and large-scale production of biodiesel from edible oil without proper planning may cause negative impact on the world, such as depletion of food supply leading to economic imbalance. Biodiesel, defined as the mono-alkyl esters of vegetable oils or animal fats [1-4]. The biodiesel fuel can be used in any mixture with petroleum diesel fuel as it has very similar characteristics but it has lower exhaust emissions. Biodiesel fuel has better fuel properties than that of petroleum diesel such as it is renewable, non-toxic in nature and essentially free of sulphur and aromatics and can be used in any diesel engine without modification [5, 6]. The table 1 shows the availability of modern transportation fuels.

Table 1. Availability of modern transportation fuels [6]

Nature of Fuel	Current Scenario	Future Availability
Gasoline	Excellent	Moderate-poor
Biodiesel	Moderate	Excellent
Compressed natural gas (CNG)	Excellent	Moderate
Hydrogen fuel cell	poor	Excellent

The above table shows that future availability of biodiesel is maximum as compared to other fuel. The main disadvantages of biodiesel are its higher viscosity, lower calorific value, higher cloud point and pour point, higher nitrogen oxide emissions, lower engine speed and power, injector choking, engine compatibility, and high price [6,7]. Biodiesel has similar combustion properties as compared to diesel. It is also inferred that the engine performance was poor when using vegetable oil/ diesel blend as the high viscous oil leads to injector choking and contaminated the lubricating oil. The tests with refined oil blends indicated that considerable improvement in engine performance. The emission of unburnt hydrocarbon from the engine was found to be more in other biodiesel and its blends as compared to diesel. The emission of nitrogen oxides from the engine is found to be higher on the all biodiesel blends as compared to diesel [8, 9]. The table 2 specify the ASTM and IS specification of diesel and biodiesel fuel.

Table 2. ASTM and IS specification of biodiesel [10]

Property (unit)	**ASTM (6751)**	**ASTM 6751 Limits**	**IS 15607**	**IS 15607 limits**
Flash point(°C)	D-93	Min.130	IS 1448	-
Viscosity at 40°C(cSt)	D-445	1.9-6.0	IS 1448	-
Water and sediment (vol%)	D-2709	Max.0.05	D-2709	Max.0.05
Free glycerin (% mass)	D-6584	Max.0.02	D-6584	Max.0.02
Total glycerin (% mass)	D-6584	Max.0.24	D-6584	Max.0.24
Oxidation stability of FAME, hrs	-	3	EN 14112	Min. 6
Oxidation stability of FAME blend, hrs	-	-	EN 590	Min. 20

The oxidation and polymerization of biodiesel fuel during combustion and storage is major concern in terms of the quality of biodiesel. These problems lead biodiesel fuel to become acidic, form un-dissolvable gum and sediments that can plug fuel filters. However, oxidation and polymerization occurs due to presence of unsaturated fatty acid chains and the double bond in the parent molecule, which immediately react with the oxygen as soon as it is being exposed to air [11].

2. Stability of Biodiesel

Biodiesel consists of long chain fatty acid esters derived from feed stocks such as animal fats, vegetable oils, and used cooking oil, etc. which contains saturated and unsaturated fatty acids which are prone to oxidation accelerated by exposure to air during storage and at high temperature may result in polymerized compounds as product. Auto oxidation of biodiesel can leads to degradation of fuel quality by affecting the stability characteristics. Biodiesel stability parameter includes oxidation, thermal and storage stability. Oxidation instability can lead to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, gum, insolubles, and sediment in the biodiesel.

Thermal instability is related to the increased rate of oxidation at higher temperature which will result in, increases the weight of oil and fat due to the formation of gums and insolubles. Storage stability is the ability of liquid fuel to resist change in its physical and chemical characteristics brought about by its interaction with its environment and may be affected by exposure with contaminants, sunlight light, factors causing sediment formation, changes in colour and other changes that reduce the purity of the fuel. These fuel instabilities give rise to formation of undesirable substances in bio fuel and its blends beyond acceptable limit as per specifications and when such fuel is used in engine, it effects the engine performance due to injector fouling, fuel filter plugging, deposit formation in engine chamber during combustion and various components of the fuel system [12].

2.1 Mechanism of Oxidation

The oxidation of fatty acid chain is a complex process proceeded by a variety of mechanisms. The oxidation of biodiesel is due to the unsaturation in fatty acid chain and presence of double bond in the molecule which offers high level of reactivity with O_2, especially, when it is placed in contact with air/ water. The primary oxidation products of double bonds are unstable allylic hydroperoxides which are unstable and easily form a variety of secondary oxidation products. This includes the rearrangement of product of similar molecular weights to give short chain aldehydes, acids compounds and high molecular weight materials.The oxidation reactivity is related to the degree of C=C bonds in the fuel, increased content of the C=C bonds correlates to decreased oxidative stability of the fuel. The increase in instability of a given diesel fuel molecule is generally directly proportional to the number of C=C bonds in the molecule (i.e., a molecule containing two C=C bonds has half the stability of a molecule containing one C=C bond) [13]. The methylene groups adjacent to double bonds have turned out to be particularly susceptible to radical attack as the first step of fuel oxidation [14]. The rate of oxidation of fatty compounds depends on the number of double bonds and their position [1]. The oxidation chain reaction is usually initiated at the positions allylic to double bonds. Thus, fatty acid with methylene-interrupted double bonds, for example, linoleic acid [(9*Z*, 12*Z*)-octadecadienoic acid], are more susceptible to oxidation because they contain methylene groups that are allylic to two double bonds. FA with two such methylene groups, for example, linolenic acid [(9*Z*, 12*Z*, 15*Z*)-octadecatrienoic acid], are even more susceptible to oxidation. oleic and linoleic acids had decreased oxidative stability compared with their alkyl esters [15].

2.1.1 Primary oxidation

Peroxidation occurs by a set of reactions categorized as initiation, propagation, and termination which shows that first set involves the removal of hydrogen from a carbon atom to produce a carbon free radical. If diatomic oxygen is present, the next reaction will result in formation of peroxy radical becomes extremely fast even not to allow significant alternatives for the carbon-based free radical. The peroxy free radical is not reactive as compared to carbon free radical, but is sufficiently reactive so that it rapidly extract hydrogen from a carbon to form another carbon radical and a hydroperoxide (ROOH). The new carbon free radical can then react with diatomic oxygen to continue the propagation cycle. This chain reaction terminates when two free radicals react with each other to yield stable products [10].

Initiation: RH + I » R· + IH
Propagation: R· + O_2 » ROO·
ROO· + RH » ROOH + R·
Termination: R· + R· » R-R
ROO· + ROO· » Stable Products

2.1.2 Secondary oxidation

Once the fatty oil hydroperoxides are formed, they ultimately decompose and results in formation of aldehydes such as hexenals , heptenals, and propanal. Hexanal, pentane, and 2, 4-heptadienal. Increased acidity is always a result of oxidation of fatty oils and biodiesel leading to the formation of shorter chain fatty acids. The fig 1 shows the secondary oxidation reaction.

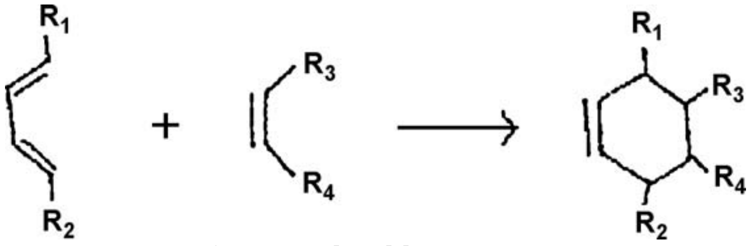


Fig. 1: Diels Alder reaction.

3. Impact Assessment of Stability on Biodiesel

Oxidation Stability is one of the most important properties of fatty acid alkyl esters (biodiesel fuel) and primarily affects the stability of biodiesel during extended storage. Degradation by oxidation yields products results in compromise of fuel properties, impair fuel quality and effect the engine performance. In Europe, standardization and fuel quality parameter assurance are crucial and deciding factors for biodiesel market acceptance, and storage [16]. The parent vegetable oil, biodiesel is suspectible to the oxidation of its unsaturated fatty acid esters. Sunlight, metal contamination, humidity, pigments, some enzymes and high temperature can change biodiesel quality, deteriorating its fuel performance when exposed to oxygen. Both oxygen content and exposition time play an important role in the formation of undesirable compounds, which can corrode the engines or clog the fuel filters and injection systems of the engines. Thus, oxidation stability has to be considered as an essential characteristic in the control of the biodiesel fuel properties. [17]

The presence of air, elevated temperatures or sunlight, presence of metals facilitates oxidation. Studies performed with the automated oil stability index (OSI) method confirmed the catalyzing effect of metals on oxidation with copper showing the strongest catalyzing effect however, the impact of compound structure of the fatty esters, especially unsaturation. A European standard (pr EN 14112) has been established for potential inclusion of an oxidative stability parameter in the European biodiesel standard EN 14214. The biodiesel standard EN 14214 leads to determination of oxidation stability at 110°C with a minimum induction period of 6 h by the Rancimat method. The Rancimat method is nearly similar to the OSI method, which is an AOCS (American Oil Chemists' Society) method. The fuel properties of biodiesel are strongly affected by the properties of the individual fatty esters present in the biodiesel. Both *moieties*, the fatty acid and alcohol, can have considerable impact on fuel properties such as cetane number with relation to combustion and exhaust emissions, oxidative stability, cold flow, lubricity and viscosity. Generally, cetane number, heat of combustion, viscosity and melting point of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation. It therefore appears reasonable to increase (a) certain fatty ester(s) with desirable properties in the fuel in order to improve the properties of the whole fuel [1].

Sarin et al. [2] states that biodiesel fuel containing large amounts of esters of oleic, linoleic or linolenic acids. The order of increasing stability was linolenic < linoleic < oleic. These esters undergo auto-oxidation with different rates depending upon the number and position of the double bonds and results in formation of a series of by-products, like acids, esters, aldehydes, lactones, ketones , etc. During the oxidation process, the fatty acid methyl ester result in formation of radical next to the double bond. These radical quickly binds with the oxygen in the air, which is a biradical. This results in peroxide radical. The rapid radical destruction cycle begins after that. This peroxide radical immediately forms a new radical from the fatty acid methyl ester, which in turn binds with oxygen in the air. Then the destructive radical auto-oxidation cycle starts. During this process, up to 100 new radicals are created rapidly from a single radical.

Bouaid et al. [18] performed transesterification from different vegetable oils: high oleic sunflower oil (HOSO), high and low erucic Brassica carinata oil (HEBO and LEBO) respectively and used frying oil (UFO) to produce biodiesel. These biodiesels, produced from various sources, were used to determine the effects of long term storage under different conditions on oxidation stability. The results showed that acid value, peroxide value, and viscosity increased, while iodine value decreased with increase in storage time of biodiesel. Oxidation of unsaturated esters of biodiesel is due to contact with air and other pro-oxidizing conditions during the long term storage.

Knothe [19] find out that biodiesel is prone to oxidation upon exposure to oxygen in ambient air. This susceptibility is due to presence of unsaturated fatty acid chains, especially those with bis-allylic methylene moieties. McCormick [20] et al. states that biodiesel is less stable as compared to petroleum diesel. The stability of biodiesel is measured by using the ASTM D2274 test for insoluble formation and the OSI method (via Rancimat apparatus) for induction period. Additionally, the samples were characterized for fatty acid make up, relative antioxidant content, metals content, and total glycerin content (free glycerin plus glycerin bound as mono-, di-, and triglycerides). The samples containing the polyunsaturated content (or oxidizability) have the largest impact which results in increasing insoluble formation and reducing the induction period. However, the formation of insolubles is also measurably decreased by increasing relative antioxidant content and increased by increasing the total glycerin content.

Knothe performed oxidation stability tests: ASTM D2274 and EN14112. These tests are designed to predict storage stability characterstics. In the D2274 method, developed for petroleum products, the sample is heated to 95 °C and exposed to oxygen for 16 h. The sum of sediment (filterable insolubles) and gum (adherent insolubles) is reported in mg/ 100 ml of sample. The EN14112 method is known as Oil Stability Index (OSI) in the oleochemical industry.

Xin et al. [21] produced biodiesel, by alkali-catalyzed method and supercritical methanol method. Then stability phenomenon is analyzed for these biodiesel. It was found that the tocopherol in biodiesel is not stable at a temperature higher than 300°C. After the supercritical methanol treatment, hydroperoxides were greatly reduced from biodiesel with initially high in peroxide value, while the tocopherol slightly decreased in its content. As a result, the biodiesel prepared by the supercritical methanol method was enhanced for oxidation stability as compared with that prepared by alkali-catalyzed method from waste oil. Therefore, supercritical methanol method is useful especially for oils/fats having higher peroxide values.

Tang et al [22] states that precipitates of biodiesel blends may have serious impact on diesel engine fuel delivery systems. Precipitates were observed in Soybean oil (SBO), cottonseed oil (CSO), and poultry fat (PF) based biodiesel blends after storage at 4^{o}C. CSO and PF based biodiesel had a lower mass of precipitates observed than the SBO based, since steryl glucosides are the major reason of precipitate formation in SBO based biodiesel, while for PF based biodiesel, the precipitates are due to the presence of monoglycerides.

The Rancimat and AOCS Oil Stability Index methods are used for determining the oxidative stability of biodiesel in inclusion of specification for this measurement in EN 14214, the iodine value will not be necessary anymore. Different types of biodiesel obtained from sunflower, *Brassica carinata*, and used frying oils were stored in white and amber glass containers at room temperature for a period of 30-months. The physicochemical parameters such as acid value, peroxide value, viscosity, iodine value and insoluble impurities were measured after regular interval. The results showed that the iodine value decreased with increasing storage time, but the other parameters increased through the storage. Therefore, all kinds of biodiesel were very stable because the increase of the three parameters was not rapid. However, there is deterioration in biodiesel quality after 12 months of storage and the specification limits of the parameters studied was exceeded after this period of time [23].

Park et al .[24] improved the oxidation stability and the cold flow properties of a biodiesel mixture, the dependence of the oxidation stability and the cold filter plugging point (CFPP) on the fatty acid compositions was evaluated. Three different kinds of biodiesels, palm, rapeseed, and soybean biodiesels, were blended with the different weight ratios. The oxidation stability and the CFPP of the biodiesels blended had a close relationship with the percentage compositions of the major fatty acid components.

The correlation was obtained by Serrano et al [25] as

$$IP = 0.27\,[SAT] + 0.13\,[MONOUNSAT] - 0.09\,[POLYUNSAT]$$

Where [SAT], [MONOUNSAT] and [POLYUNSAT] are the content of the saturated, monounsaturated and polyunsaturated fatty acids (% wt). The induction period is calculated for various biodiesel is given in table 3.

Table 3. Induction Period of Biodiesel [26-30]

Biodiesel	Saturated Fatty Acid	Monounsaturated Fatty Acid	Poly Unsaturated Fatty Acid	Induction Period (Hours)
Canola	7.78	62.6	30.43	7.5
Rape seed	6.87	64.27	29.33	7.5
Jatropha	22.17	43.6	35.61	8.5
Karanja	26.04	54.71	23.43	12.03
Mahua	45.88	39.01	14.97	16.11
Neem	36.08	45.83	18.51	14.03

The above table shows that induction period of *canola* and *rapeseed* biodiesel is lowest and *Mahua* biodiesel has maximum induction period. The relation between induction period and % mono unsaturated fatty acid is shown in Figure 2.

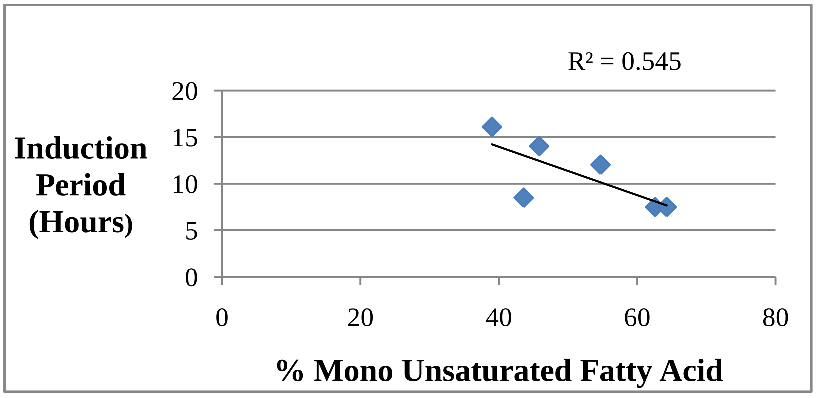


Fig. 2: Variation of Induction period with % Mono Unsaturated Fatty acid

The value of R^2 (0.545) is significant and it indicates that the relation is applicable to all biodiesel. The relation between induction period and % saturated fatty acid is shown in Figure 3.

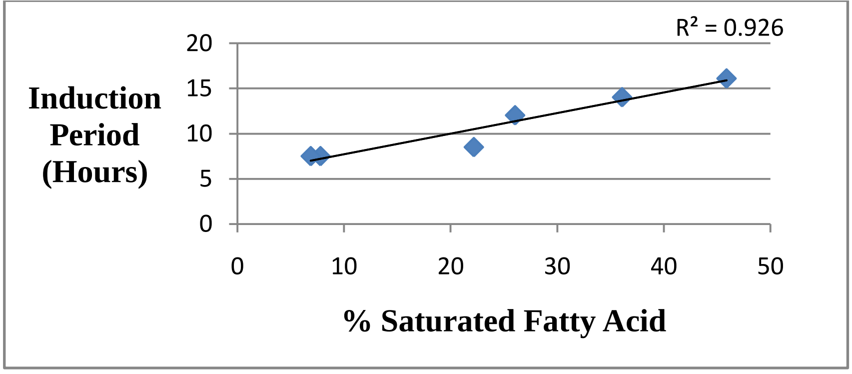


Fig. 3: Variation of Induction period with % Saturated Fatty acid

The value of R^2 (0.926) is very significant and it indicates that the relation is applicable to all biodiesel. The relation between induction period and % Poly unsaturated fatty acid is shown in Figure 4.

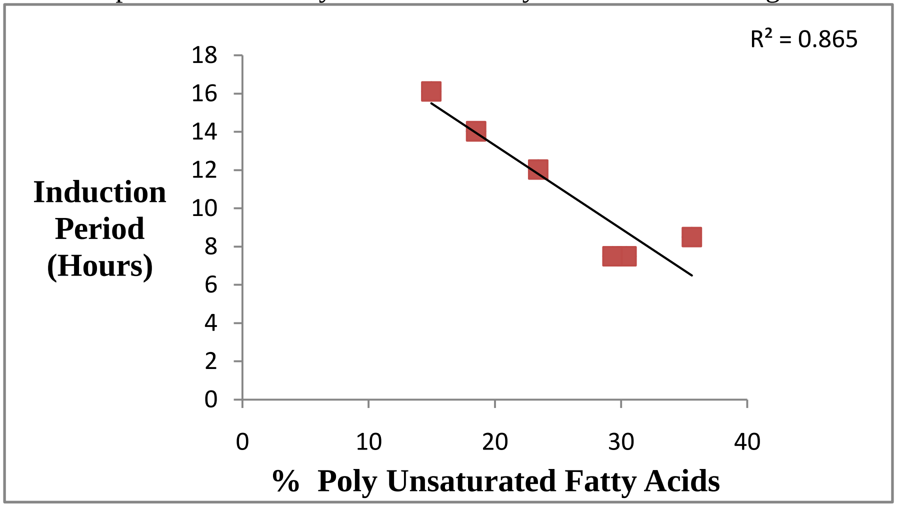
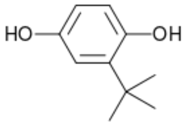
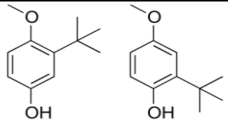
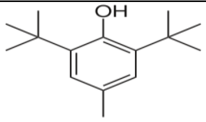
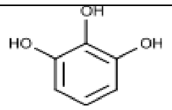
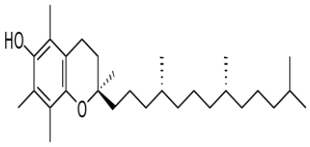
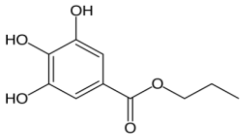
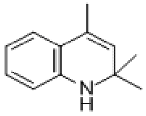
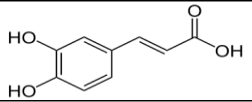
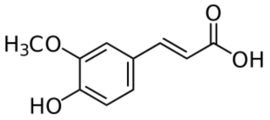
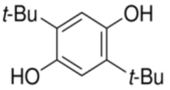
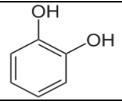


Fig. 4: Variation of Induction period with % Polyunsaturated Fatty acid

The value of R^2 (0.865) is very significant and it indicates that the relation is applicable to all biodiesel. Oxidation stability of biodiesels decreased as the content of the linoleic and linolenic acids increased [24].
Sarin et al. [31] states that stability of biodiesel is less as compared to petro diesel and therefore doping of biodiesel in petro diesel will affect the fuel stability. The poor stability of biodiesel is further due to presence of the double bonds in the fatty acids, which may lead to insoluble and gum formation. Therefore, it was decided to include a limit for oxidation stability in the quality standards of biodiesel. The major problem associated with the use of biodiesel, especially prepared from palm oil is its poor cold flow property, measured in terms of cloud point, pour point and CFPP. The cold flow property is very important for application of biofuels for aviation application. The cold flow properties of biodiesel can be improved by blending it with unsaturated feed stocks. The efforts have been made to improve cold flow properties by alteration in chain of alkylesters. Sarin et al. [32] showed that neat Jatropha biodiesel (JBD) exhibited the oxidation stability of 3.95 h and research was conducted to investigate the presence of transition metals, likely to be present in the metallurgy of storage tanks and barrels, on oxidation stability of JBD. It was found that impact of metal was detrimental to oxidation stability and catalytic. Even small percentage of metal contaminants showed nearly same effect on oxidation stability as large amounts. Copper showed strongest detrimental and catalytic effect. The dependence of the oxidation stability on the type of metal showed that long-term storage tests in different types of metal containers for examining the influence of material container on oxidation stability of biodiesel is replaced by Rancimat test serving as an accelerated storage test. The table 4 shows the various antioxidant and their structure.

Table 4: Antioxidant and their structure [33-36]

S.No	Name	Molecular Formulae	Symbol	Molecular Mass (g /mol)	Molecular Structure
1-	Tertiary Butylhydroquinone	$C_{10}H_{14}O_2$	TBHQ	166.22	
2-	Butylated hydroxyanisole	$C_{11}H_{16}O_2$	BHA	180.24	

S.No	Name	Molecular Formulae	Symbol	Molecular Mass (g /mol)	Molecular Structure
3-	Butylated hydroxytoluene	$C_{15}H_{24}O$	BHT	220.35	
4-	Pyrogallol	$C_6H_6O_3$	PY	126.11	
5-	alpha-Tocopherol	$C_{29}H_{50}O_2$	α-Tocopherol	430.71	
6-	Propyl Gallate	$C_{10}H_{12}O_5$	PG	212.20	
7-	1,2-dihydro- 2,2,4-trimethylquinoline	$C_{12}H_{15}N$	Orox PK	173.25	
8-	Caffeic acid	$C_9H_8O_4$	-	180.16	
9-	Ferulic acid	$C_{10}H_{10}O_4$	-	194.18	
10-	2,5-Di-*tert*-butylhydroquinone	$[(CH_3)_3C]_2C_6H_2\text{-1,4-}(OH)_2$	DTBHQ	222.32	
11-	Catechol	$C_6H_6O_2$	C	110.1	

The above table show the structure, molecular mass of natural and synthetic antioxidant. These antioxidant are used to increase the storage stability of various biodiesel. The long term use of biodiesel is possible only due to use of these antioxidant. Araujo et al. [37] evaluated the oxidation stability of castor oil fatty methyl ester (FAME), doped with four different phenolic antioxidants, using rapid method of thermal and air-contact degradation. The methodology is based on the induction period observed when the samples are kept in contact with pure oxygen at elevated temperatures and pressures. The results indicated that there is performance variation of the antioxidants is observed with biodiesel. The table 5 shows the impact of various antioxidants on biodiesel stability.

Table 5: Role of Antioxidant on Biodiesel Stability

S.No	Biodiesel	Antioxidant	Measurement Methodology/Standard	Findings	Ref.
1-	Soybean biodiesel	Tert-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PrG)	Pressurized differential scanning calorimetry (P-DSC	PrG, BHT and BHA were most effective and a-Tocopherol least effective	[38]

S.No	**Biodiesel**	**Antioxidant**	**Measurement Methodology/Standard**	**Findings**	**Ref.**
		and a-Tocopherol			
2-	Safflower biodiesel	Propyl gallate	Rancimat method	Induction period of biodiesel increases with the increase of antioxidant concentration and decreases with increase of temperature	[39]
3-	Jatropha biodiesel	α-tocopherol, tert-butylated hydroxytoluene, tert-butylated phenol derivative, octylated butylated diphenyl amine, tert-butylhydroxquinone	-	Synthetic antioxidants were found to be more effective	[40]
4-	Jatropha biodiesel	butylated hydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA), propyl gallate (PG), and pyrogallol (PY)	-	PY is found to be the best antioxidant	[41]
5-	Biodiesel	BHT,BHA,PG, PA	Modified Rancimat	Butylated hydroxytoluene (BHT) and butylated hydroxyanisol (BHA) displayed the lowest effectiveness in neat biodiesel. Propyl gallate (PG) and pyrogallol (PA) additives showed the strongest effectiveness in both the neat biodiesel and the biodiesel blends.	[42]
6-	Croton Biodiesel	1, 2, 3 tri-hydroxy benzene (Pyrogallol, PY), 3,4,5-tri hydroxy benzoic acid (Propyl Gallate, PG) and 2-tert butyl-4-methoxy phenol (Butylated Hydroxyanisole, BHA)	Rancimat and Thermogravimetry Analysis	effectiveness of these antioxidants was in the order of PY>PG>BHA	[43]
7-	Canola biodiesel	Di-tert-butylhydroquinone (DTBHQ) or poly(1,2-dihydro- 2,2,4-trimethylquinoline) (Orox PK)	EN 14214, Rancimat method	Stability was enhanced with antioxidant	[44]
8-	T. belerica biodiesel	Vitamin E (α-tocopherol), butylated hydroxyanisole (BHA), Pyrogallol (PY), Propyl gallate (PG), tert-butylhydroxytoluene (BHT) and tert-butylhydroxyquinone (TBHQ) at varying concentration levels (100 ppm, 500 ppm, 1000 ppm and 1500 ppm)	EN 14214	Antioxidants could be ranked as PG>PY>TBHQ>BHT>BHA>α-tocopherol	[45]
9-	Pongamia biodiesel	BHT, BHA, PY, GA and TBHQ	ASTM D4625 at 30 °C/50 weeks and 2) ASTM D4625 at 43	Pyrogallol as an antioxidant for PBD	[46]

S.No	Biodiesel	Antioxidant	Measurement Methodology/Standard	Findings	Ref.
			°C/12		
10-	Soybean Biodiesel	caffeic acid, ferulic acid, and terthydroquinone	Rancimat, PetroOXY and P-DSC	The efficiency of the antioxidant took the following efficiency order: caffeic acid > ferulic acid > tert-butylhydroquinone	[47]
11-	Soybean methyl ester (SBME), Rapeseed methyl ester (RME), High oleic sunflower methyl ester (HOSME) Palm methyl ester (PME)	Commercial Synthetic (AO1, AO2 and AO3) and one natural (AO4) antioxidants	EN 14214	Antioxidants can improve the oxidation stability and the antioxidant effect increases as a function of its concentration	[48]
12-	Pongamia Biodiesel	Five antioxidants viz. 2,6-di-tert butyl-4-methyl phenol (BHT), 2-tert butyl-4-methoxy phenol (BHA), 2-tert butyl hydroquinone (TBHQ), 1,2,3 tri-hydroxy benzene (PY) and 3,4,5-tri hydroxy benzoic acid (PG)	EN14214	-	[49]
13-	Biodiesel	tert-butylhydroquinone (TBHQ) propyl gallate (PG), butylated hydroxyanisole (BHA), 3,5-di-tert-butyl-4-hydroxyltoluene (BHT), and α-tocopherol	EN-14112	Pyrogallol (PY) was the best in enhancing IP with a concentration of less than 3000 ppm, however, tert-butylhydroquinone (TBHQ) was the best after 3000 ppm, followed by propyl gallate (PG), butylated hydroxyanisole (BHA), 3,5-di-tert-butyl-4-hydroxyltoluene (BHT), and α-tocopherol	[50]

The above table shows that out of various natural and synthetic antioxidants Pyrogallol is best antioxidant for long term storage of biodiesel. Pyrogallol gives the highest induction period as compared to other antioxidants. Jain and Sharma [51] compared the ASTM 2274 and 743 Rancimat tests and showed that these two tests may be used alternatively. Most commonly used methods to find the thermal stability is Rancimat test, ASTM D 6408-08, D 5304-06 and TGA/DTA. The important method to measure the thermal stability of oils and fats is Rancimat test. Sarin et al. [52] used neat Jatropha biodiesel, and find out that oxidation stability of 3.95 h. It is possible to meet the desired EN specification for neat Jatropha biodiesel and metal contaminated Jatropha biodiesel by using antioxidants, it will have cost implications, as antioxidants are costly chemicals. The research was conducted to increase the oxidation stability of metal contaminated Jatropha biodiesel by doping metal deactivator with antioxidant, with varying amount in order to meet the standard required for oxidation stability. The result showed that usage of antioxidant can be reduced by 30-50%, therefore the cost is reduced, even if very small amount of metal deactivator is doped in Jatropha biodiesel to meet EN-14112 specification. Meira et al. [53] use spectrofluorimetry, a fast analytical technique associated with multivariate data analysis as a powerful analytical tool for predicting the oxidation stability. The prediction of the oxidation stability value showed a agreement with the results obtained by the EN14112 (Rancimat). The models show high correlation (0.99276 and 0.97951) between real and predicted values. The R^2 values of 0.98557 and 0.95943 show the accuracy of the models to predict the oxidation stability of soy oil and soy biodiesel. Dantas et al. [17] states that important factors responsible for the oxidative processes of biodiesel are oxygen, metal traces, high operating temperature and the amount of unsaturated fatty acids. The biodiesel quality is deteriorated by the oxidation products, which are corrosive to engine parts (engine chambers) and may lead to clogging of the injection pumps and filters, besides increasing the biodiesel viscosity. The oxidative stability of corn biodiesel, obtained by base-catalyzed transesterification reaction, using the ethanol route. As-synthesized, stored and heated biodiesel samples were characterized by peroxide value, iodine value and dynamic viscosity. UV/Vis absorption was used to investigate the oxidative degradation of biodiesel, by means of the 232 and 272 nm absorption peaks, ascribed to double bonds and carbonyl groups, respectively. The TG and PDSC thermal analysis techniques were also employed to calculate the oxidative stability. The oxidative decomposition was confirmed by the increase of the dynamic viscosities. PDSC curves showed that the oxidation onset temperature was reduced as the sample was exposed to degradation factors during storage and heating. These results were in agreement with the peroxide and dynamic viscosity, as well as with iodine values.

Jain and Sharma [54] studied the effect of metal contaminants on the oxidation stability of Jatropha curcas biodiesel (JCB). JCB was mixed with different transition metals – Fe, Ni, Mn, Co and Cu in different amounts. Induction period (IP) was measured using Rancimat method (EN 14112). Based on the results, several relations are developed for assessing the oxidation stability in terms of IP as a function of antioxidant and metal concentration. A comparison between the experimental IP values and those predicted by the relation shows that about 95% of the predicted data points lie within ±10% deviation lines of the experimental results.

Jain and Sharma [12] states that biodiesel is more affected to oxidation when exposed to higher temperature due to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, insolubles, gum and sediment in the biodiesel, which are responsible for fuel filter plugging, injector fouling, deposits formation in engine combustion chamber and various components of the fuel system. Most commonly used methods to investigate the thermal stability are Rancimat test, ASTM D 6408-08, D 5304-06 and TGA/DTA. Rancimat test has been suggested as an important method to measure the thermal stability of oils, fats and biodiesel fuels. Further the KF Coulometer has also been suggested as suitable method to measure the thermal as well as oxidation stability of vegetable oils.

Jain and Sharma [55] show that the thermal decay of all JCB samples can be treated as a first order reaction. The pyrogallol (PY) has been found to have more pronounced effect on the onset temperature (T_{on}) as well as on the Ea followed by propyl galate (PG) > tert-butyl hydroquinone (TBHQ) > butylated hydroxytoluene (BHT) > butylated hydroxyanisole (BHA). The results may have important applications in the development of JCB as engine fuel.

Lapuerta et al. [56] showed a drastic decay in the induction period when the test temperature increases from 110 °C to 130 °C. The result suggests that, its impossible to achieve the threshold, currently imposed in the standards at 130 °C, even after a massive additive addition.

Freire et al. [57] used transesterification reaction process for producing biodiesel using alkaline catalysts, due to their high reaction rates and high conversion rates. Low cost catalysts (alkali, alkaline earth and transition metal hydroxides) are often used. The catalytic activity of sodium hydroxide (NaOH) in the synthesis of Jatropha curcas ethanol biodiesel was studied. Ethoxide ions, recently prepared (BINaOH) and stored under refrigeration for 12 (B12NaOH) and 24 (B24NaOH) hours were used in transesterification reactions. Each of these reactions was also conducted by means of newly produced ethoxide ions (BINaOH). The yields of each reaction condition were calculated as B12NaOH – 86.7%, B24NaOH – 99.3%, and BINaOH – 82.8%. It can be concluded that the transesterification reaction of J. curcas oil is not only severely affected by hydroxyl ions but also affected by ethoxide ions. The oxidative stability of biodiesel is another important parameter in places with warm climate, as this property provides an estimation of storage time of biodiesel in normal conditions.

Fernandes et al. [58] reports the preparation and characterization of methylic and ethylic biodiesel from cotton seed oil. Biodiesel was prepared by a transesterification process involving the reaction of the oil with methanol or ethanol using KOH as catalyst. The conversion of triglycerides to the corresponding methyl and ethyl ester was 91.5 and 88.5 (wt %). All the physical–chemical properties of the obtained biodiesels met the limits of the EN 14214. The addition of the synthetic antioxidant tert-butylhydroquinone at the concentration of 300 mg/kg was enough to obtain acceptable oxidation stability values (>6 h). Thermogravimetric analysis was also performed and similar profiles were verified for both ethylic and methylic biodiesels.

Thompson et al. [59] explores the long-term effects of biodiesel fuel blended with low sulphur diesel fuel at concentrations of 0%, 15%, 50%, 85%, and 100% (v/v) can have on polyethylene materials. Rotationally moulded fuel tanks made of linear low density polyethylene or cross linked polyethylene were used to appropriately mimic the storage environment of fuels. The extent of oxidation for the fuels was governed by determination of its acid number and peroxide value over time, with both values being consistently higher for blends with higher biodiesel content. Storage at 80°C for up to 56 days resulted in significant oxidation of the fuel while testing up to 380 days at 23°C produced no change in peroxide or acid concentration. The change in mechanical properties for the polyethylenes due to fuel was determined by tensile testing. Comparing the tensile data to the oxidation species in the stored fuels revealed that mechanical losses did not correspond with higher concentration of hydroperoxides or acid species but rather occurred as a result of fuel absorption. No difference was found in this regards between the two polyethylene species. Shahabuddin et al. [60] evaluated the oxidation and storage stabilities of various biodiesel fuels. The biodiesel fuels are Palm methyl ester (PME), Jatropha methyl ester (JME), Coconut oil methyl ester (COME), 20% blends of PME with diesel fuel and 20% blends of JME with diesel fuel. The ASTM standard methods were used to evaluate all the samples at the interval of 180 h over a 2160 h (three months) duration. The result shows that almost all fuel samples meet the standard regulation regarding IP. The trends for density, viscosity and TAN increased, while the TBN decreased due to oxidation.

Fernandes et al. [61] found out the storage stability and corrosive character of soyabean biodiesel stabilised with tert-butylhydroquinone (TBHQ), through static immersion corrosion tests. Wire of carbon steel and galvanised steel were immersed in soybean biodiesel with and without TBHQ for 12 weeks. Measurements of total acid number, peroxide value, oxidation stability (Rancimat induction period), metal, and TBHQ consumption at different stages of corrosion were analyzed. After 12 weeks of the static immersion test with both steels, the non-stabilised biodiesels show induction period below the EN 14214 limit (6 h) these results were in agreement with increase in the peroxide values. Zinc release was only detected in the non-stabilised biodiesel exposed to galvanised steel, while iron was not detected in any biodiesel samples exposed to carbon steel. The absence of zinc in the TBHQ-doped biodiesel exposed to galvanised steel indicates that TBHQ may have acted as a corrosion inhibitor. Additionally, TBHQ was rapidly consumed in the first 3 days of experiments. For a storage period of up to 56 days, both galvanised and carbon steels were shown to be compatible with biodiesel even in the absence of an antioxidant. The impact of various metal container on biodiesel is given in table 6.

Table 6: Impact of Various Metals on Biodiesel

S.No.	**Fuel**	**Metal**	**Findings**	**Ref.**
1-	*Jatropha Curcas Biodiesel (JCB)*	Iron, Nickel, Manganese, Cobalt, Copper	1-Copper has strongest catalytic effect followed by Cobalt, Manganese, Nickel and Iron. 2-Influence of Metal was catalytic for small and large concentration of metals on the Oxidation stability.	[54]
2-	*Soybean Biodiesel (SB)*	Carbon Steel, Galvanised Steel	1-Carbon steel and Galvanised steel both are selected due to their resistance to corrosion and relatively low cost for the manufacture of container. 2-In contact with Carbon steel the peroxide value increased constantly throughout the experiment while in contact with Galvanised steel it increases only after 84 days of exposure. 3-Galvanised steel container have been used for transport/storage of diesel fuel .But due to presence of water/moisture content in biodiesel it may trigger corrosion process in Galvanised steel. 4-Carbon steel is more prone to corrosion than Galvanised steel. 5-Both steel have shown compatibility with biodiesel over storage period of 56 days.	[61]
3-	*Jatropha Curcas Biodiesel (JCB)*	Iron, Nickel, Manganese, Cobalt, Copper	1-Copper has strongest catalytic effect followed by Cobalt, Manganese, Nickel and Iron. 2-It was also found that beyond a concentration of 2mg/litre, Induction Period became constant as concentration of metal is increased.	[62]
4-	*Diesel,*	-	1-Diesel with high sulphur content was found to be most	[63]

	Pongamia Biodiesel (PB)		suitable for blend preparation in respect of Oxidation stability.	
5-	*Diesel, Palm Biodiesel*	Mild Steel	1-Corrosion of Mild Steel is increases with increase in temperature for Diesel as well as Biodiesel. 2-Degardion of fuel properties upon exposure of Mild Steel in Palm Biodiesel increases with increase in temperature. 3-Exposure of Mild Steel in biodiesel can increase its oxidation and instability. 4-Corrosion attack on metal surface is more in case of Biodiesel as compared to diesel.	[64]
6-	*Palm Biodiesel*	Copper, Brass, Aluminium, Cast Iron	1-Upon exposure the degradation order is of: **Copper> Brass> Aluminium> Cast Iron.** 2-Copper Metal is less resistant in Biodiesel and also cause more degradation of fuel Properties.	[65]
7-	*Palm Biodiesel*	Aluminium, Magnesium	1-Magnesium exhibit higher corrosion rate in Biodiesel compare to Aluminium. 2-Biodiesel undergoes significant degradation upon exposure to Metal. 3-Magnesium surface is seen to be covered by yellowish gel like sticky mass while Aluminium surface remained clean.	[66]
8-	*Pongamia oil, Pongamia Biodiesel*	Aluminium, Copper, Mild Steel-I, Mild Steel-II, Brass	1-Corrosion rate for Pongamia Biodiesel: **Copper> Mild Steel-I> Mild Steel-II > Brass > Aluminium** 2-Aluminium was least corroded in both oil as well as Biodiesel since the water present in the fuel might mitigate the corrosion by contributing to the formation of protective hydroxide surface film. 3-Copper was highly reactive in B-100 Mild Steel-I was highly reactive in Oil. Aluminium has negligible effect in both the medium.	[67]

The above table shows that Aluminium and Cast iron container are best for storage and transportation of biodiesel while poor performance is shown by copper for all the bio fuel sources.

4. Future Scope of Study

The study shows that oxidation stability is the important parameter to determine the storage of biodiesel for longer period of time. The study also shows that out of various natural and synthetic antioxidants Pyrogallol is best for storage of biodiesel. There are various type of metal and alloys containers are used for storage of biodiesel. Out of various metal and alloys Iron and Aluminium alloy is best for storage of biodiesel. The future scope of study includes the thermal stability of various biodiesel and the long term effect of various antioxidant, metal and alloys on biodiesel.

Conclusion

The literature review shows that biodiesel stability is affected by various parameters such as oxidation, thermal and storage stability. The present work has covered the different types of the fuel stabilities, mechanism of occurrence and various correlations developed to investigate the impact of various stability parameters on the stability of the fuel. Various correlations have been developed between these parameters, collected from literature, to check the effect of these parameters on the stability of biodiesel. The relation between IP and % Saturated Fatty acid and % Poly unsaturated acid is found to be good with value of R^2 being 0.926 and 0.865 respectively. The comparative study of different types of natural and synthetic antioxidants shows that Pyrogallol being very sensitive to biodiesel stability as compared to other antioxidant. The stability of Pyrogallol is highest as compared to other natural and synthetic antioxidant. The impact of various metals on the stability of various bio fuel sources shows that Aluminium and Cast iron container are best for storage and transportation of biodiesel while copper container show poor stability characteristics for all type of biodiesel.

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