

An Overview on the Biodiesel Oxidative Stability: Its Causes, Consequences, and Inhibition

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ABSTRACT

Poor oxidative stability of biodiesel has been considered one of the major threat for its sustainable production and commercialization. Due to poor oxidative stability, degradation of biodiesel occurs on storage as well as its applications. The storage stability of biodiesel varies with the nature and proportions of chemical functional groups present in the fatty acid esters (FFAs) constituting the biodiesel. The chemical composition of biodiesel imparts crucial role on its storage behavior. The degree of unsaturation and the available allylic and bis-allylic positions are highly prone to oxidation, which leads to the formation of gums, acids, and polymer deposits that causes fouling or plugging problems in the engine and filter. Although, the auto-oxidation of biodiesel cannot be prevented completely, however, it can be slowed down by using additives called antioxidants. These additives prevent the propagation of oxidation processes by scavenging the free radicals that are formed by the attack of oxygen on reactive sites of fatty acid esters (FFAs). The present mini review emphasizes on the major causes that are primarily responsible for poor oxidation stability of biodiesel, its impact on the fuel characteristic of biodiesel, and available techniques for its prevention.

1. Introduction

The 'fuel stability' is the virtue of resistance of its degradation under storage, engine operating and environmental conditions. Degradation can changes the fuel properties and also form undesirable species that cause the formation of gums, acids, and polymer deposits that causes fouling or plugging problems in the engine and filter. [1-3] Any fuel that readily undergo such changes is considered as unstable. Biodiesel is also an unstable fuel since it can degrade by one or more of the following reasons: (i) oxidation or auto-oxidation caused by its contact with oxygen present in air; (ii) thermal oxidative decomposition

caused by excess of heat; (iii) hydrolysis caused by the presence of water or moisture in tanks and fuel lines; (iv) microbial contamination in fuel caused by the dust and water droplets containing bacteria or fungi. [1-3]. Among those, the oxidation or auto-oxidation processes are the most frequent processes that involve degrading the biodiesel. The oxidation stability is the affinity of fuel towards oxygen at ambient temperatures and describes the relative susceptibility of the fuel to degradation by oxidation. The storage stability is the commonly used term that refers to the general stability of a fuel during long-term storage. The oxidative degradation is one of the primary degradative process of concerns of storage stability along with others as stated above. [4] Biodiesel is obtained by the transesterification of fatty acid or oils using methanol or ethanol in the presence of homogeneous/heterogeneous acidic or basic catalysts.[5,6] During the transesterification process, the fatty acid chain remains unchanged in the biodiesel obtained. Therefore, the oxidation chemistry of

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biodiesel will also be similar to that of the fatty acid from which it is derived. Thus the good knowledge of chemical composition and structure of fatty acids and their corresponding alkyl esters is highly desirable for the proper understanding of their oxidation phenomenon. The fatty acid chain present in the biodiesel are primarily of two types i.e., saturated and

unsaturated fatty acids. The unsaturated fatty acids are further classified as monounsaturated fatty acid (MUFA) and polyunsaturated fatty acid (PUFA).[7] The unsaturated fatty acids are highly susceptible for oxidation. Prior to use biodiesel as a fuel for combustion engines it is necessary for biodiesel to qualify the minimum values of fuel standards (Table 1).

Table 1: Fuel standards for biodiesel and diesel [8]

| Specification applies to all Standards (Units) | BIODIESEL | | | |
|--|-------------------|-------------------------------------|-----------------|-------------|
| | EUROPE | GERMANY | USA | INDIA |
| | EN 14214:2003 | DIN V 51606 | ASTM D 6751-07b | BIS (P) |
| Density 15°C (g/cm ³) | 0.86-0.90 | 0.875-0.90 | 0.85-0.90 | 0.87-0.90 |
| Viscosity 40°C (mm ² /s) | 3.5-5.0 | 3.5-5.0 | 1.9-6.0 | 3.5-5.0 |
| Flashpoint (°C) | 120 min | 110 min | 93 min | > 100 |
| CFPP (°C) | *Country specific | summer 0, spr/aut -10 winter -20 | ----- | ----- |
| Cloud point (°C) | ----- | ----- | * report | ----- |
| Sulphur (mg/kg) | 10 max | 10 max | 15 max | 0.035 |
| Water(mg/kg) | 500 max | 300 max | 500 max | 500 max |
| Oxidation stability (hrs;110°C) | 6 hours min | ----- | 6 hours min | 6 hours min |
| Cetane number | 51 min | 49 min | 47 min | > 51 |
| Acid value (mgKOH/g) | 0.5 max | 0.5 max | 0.5 max | < 0.8 |
| Iodine value | 120 max | 115 max | | < 115 |

As, the physical properties of a fuel such as density, viscosity, flash point, cloud and pour- point oxidation behavior etc. are affected by the environmental or climatic conditions of the different geographical regions. Thus, these fuel standards/specifications are set by authorized agencies keeping in mind the environmental or climatic conditions of the geographical regions where the biodiesel fuel or any

fuel has to be utilized. Thus, biodiesel must retain its physico-chemical properties during its storage and application in combustion engine. Any changes in physico-chemical properties of biodiesel is not allows it to be used as fuel. The important physical properties of biodiesel obtained from various feedstocks along with recommended fuel specification are summarized in Table 2.

Table 2: Important fuel characteristics of biodiesel derived from various feedstocks as per ASTM D 6751-07b standards [9-16]

| Feedstock | Density @15°C, g.cm ³ | Viscosity @40°C, mm ² /s | Oxi. Stab. (h, @ 110°C) | CFPP (°C) | Pour point (°C) | Cloud point (°C) | Flash point (°C) | Calorific values (kJ/kg) |
|-------------------|----------------------------------|-------------------------------------|-------------------------|-----------|-----------------|------------------|------------------|--------------------------|
| Edible Oil | | | | | | | | |
| Sunflower Oil | 0.879 | 4.14 | 4.7 | -6 | -7 | -4 | 174 | 39995 |
| Soybean Oil | 0.882 | 4.26 | 2.1 | -4 | 3 | 2 | 159 | 34113 |
| Palm Oil | 0.864 | 4.5 | 10.3 | 12 | 15 | 16 | 135 | 38400 |
| Canola Oil | 0.880 | 4.29 | 15 | -9 | -6 | -2 | 182 | 39490 |
| Cotton seed | 0.887 | 4.5-5.3 | 4.9 | - | 7 | 9 | 117 | 41800 |

| | | | | | | | | | |
|-------------------------|----------------|---------------|--------------|-------|-----------|----------|---------------|-------------|-------|
| Oil | | | | | | | | | |
| Rice barn Oil | - | 3.5 | 1.7 | 0 | -10 | -11 | 169 | 38853 | |
| Non-edible Oil | | | | | | | | | |
| Castor Oil | 0.889 | 13.3 | 29.8 | -- | 2.7 | -3 – 12 | 229 | 37500-42800 | |
| Rapeseed Oil | 0.882 | 4.44 | 7.6 | -13 | -12 | -3.3 | 170 | 37600 | |
| Jatropha Oil | 0.8642 | 4.3 | 2 – 8 | | 3 | 3 | 169 | 39698 | |
| Karanja Oil | 0.8690 | 4.65 | 2 – 5 | -7 | -1 | -6 | 180 | 38960 | |
| Microalgae oil | | | | | | | | | |
| Chlorella protothe. Oil | 0.841 0.860 | - 4.0 – 4.6 | -- | -- | -8 – 13 | -2 – 2 | 143 | 41400 | |
| Chlorella vulgaris Oil | 0.841 0.860 | - 4.0 – 4.6 | -- | -- | -8 – 13 | -2 – 2 | 143 | 45630 | |
| Spirulina Oil | 0.863 | 12.4 | - | - | -9 | -3 | 189 | -- | |
| Waste oil | | | | | | | | | |
| Waste cooking Oil | 0.875 0.888 | - 3.66 – 6.8 | 0.43 15.9 | - | -5 – 12 | -2.5 – 9 | -12 – 13 | 71 – 190 | 35400 |
| Waste sunflower Oil | 0.680 | 1.9 – 6.5 | -- | -- | -- | -- | -- | -- | -- |
| Waste chicken fat | 0.832 0.890 | - 4.94 – 6.27 | 6 | 2 – 3 | -6 – 12.3 | -5 – 14 | 169 – 174 | -- | |
| Waste Tallow | 0.832 0.872 | - 4.89 – 5.98 | 1.6 | 14 | -5 – 15 | -4 – 16 | 152 – 171 | 38500 | |
| Waste Lard | 0.873 0.877 | - 4.59 – 5.08 | | | 5 – 7 | | 143 – 14 7 | | |

2.Oxidation Stability of Biodiesel: Causes, Consequences and Inhibition

Causes and consequences: The oxidation stability of biodiesel is one of the important criteria concerning of

its fuel properties. Due to the presence of unsaturated fatty acid(s) in biodiesel (irrespective of the feedstock and methods used for biodiesel preparation, the stability of biodiesels (Table 2) is lower than its prescribed value (Table 1).

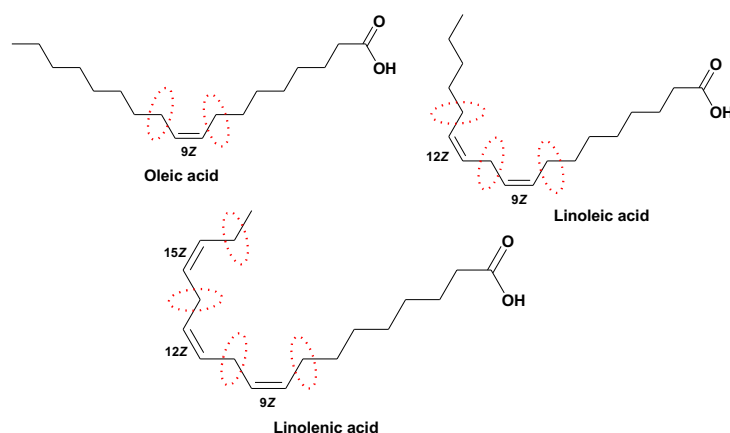


Fig. 1: Active allylic and bis-allylic positions in unsaturated fatty acids present in biodiesel

The presence of these unsaturated fatty acids lead to the formation of deposits and darkening of fuels as a result the formation of contaminants, such as alcohols, aldehydes, acids, peroxides, etc., occur during long term storage of biodiesel fuel. [7] Various processes such as auto-oxidation, photo-oxidation, hydrolysis, thermal decomposition, contamination of impurities, storage tank material, presence of trace metal, and exposure to the light etc., are primarily responsible for these side reactions or byproduct formation that change the fuel properties considerably during long term storage of biodiesel [8], and references their-in.

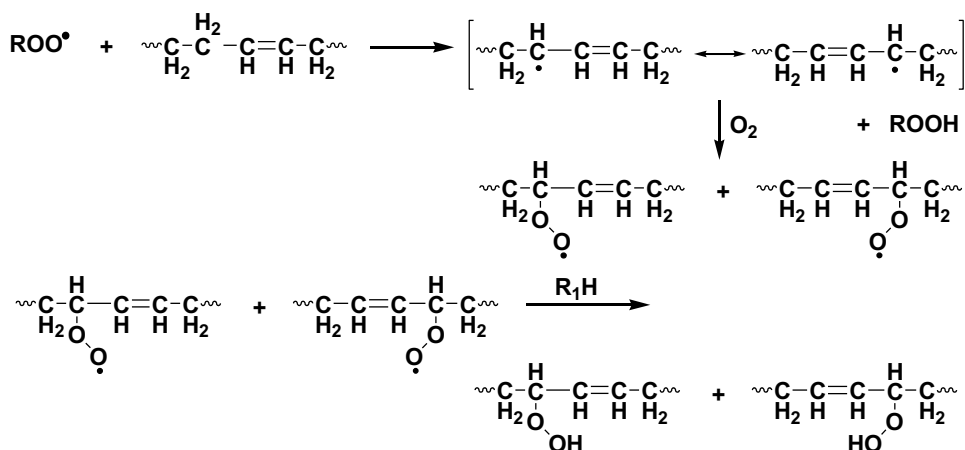
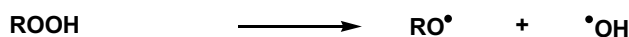
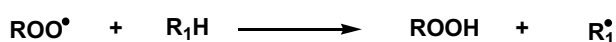
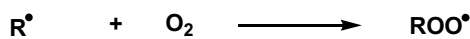
Among these, the oxidation process are the most significant process responsible for the deterioration of biodiesel. Primarily two types of oxidation processes are observed in biodiesel oxidation include auto-oxidation and photo-oxidation. Among these oxidation processes, auto-oxidation is one of the most significant problem associated with the stability of biodiesel. The greater degree of unsaturation in biodiesel makes is highly susceptible for auto-oxidation of biodiesel hence lower oxidation stability of the biodiesel. The oxidation stability of biodiesel usually correlates with the total

number of allylic and bis-allylic carbon (**Figure 1**) that are adjacent to double bond [17]. The polyunsaturated methyl esters are more vulnerable to oxidation processes when compared to monounsaturated methyl esters, because of the presence of additional number of bis-allylic methylene groups in it. Thus, the relative rates of oxidation of commonly observed unsaturated fatty acid esters (FAE) in biodiesel can be ordered as linolenic acid esters > linoleic acid esters > oleic acid esters. The auto-oxidation of biodiesel free is a radical chain reaction which involves the three common steps of chain reaction i.e., chain initiation step, chain propagation step and chain termination step [18]. In chain initiation step the initiator decomposes into free radicals, which interact with the active molecule and transformed it into reactive radical. These reactive radicals under propagation step combine with various other molecules to form different stable products and other reactive radicals. These reactive radicals are converted into respective stable products in termination step. The general mechanism of radical chain reaction is shown below [18, 19].

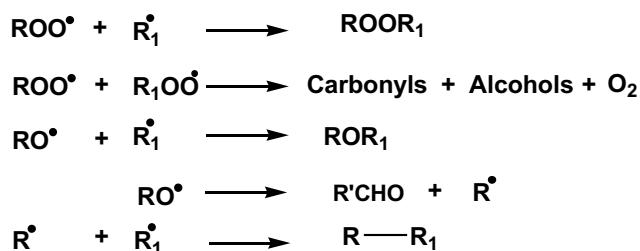
1) Chain Initiation



2) Chain Propagation



3) Chain Termination

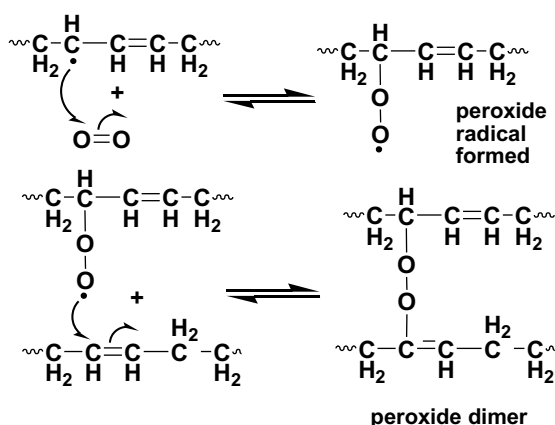


(R = unsaturated fatty acid
R and R₁ may be similar or different)

In case of auto-oxidation of fatty acid esters (FAE) the highly active hydrogen of methylene group at allylic and bis-allylic position is abstracted by the radical initiator and generate resonance-stabilized carbon

Addition-elimination reaction

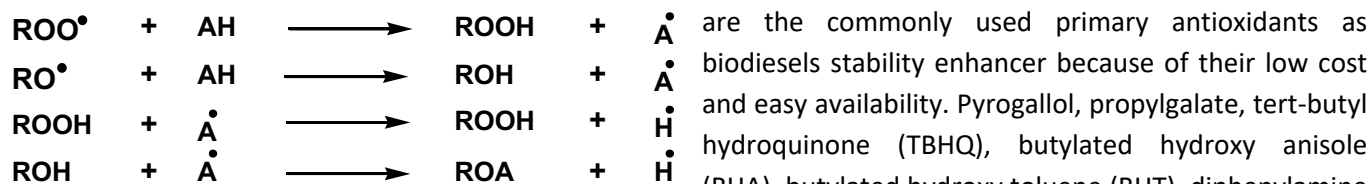
These new radicals may also undergo cyclization and polymerization reactions. The allylic radicals formed during addition-elimination reactions may react with the O₂ molecule to lead the formation of peroxide radicals.



These peroxy radicals can further react with double bond of unsaturated fatty acid and results in formation of respective peroxide linked dimers. [20] Thus, it is necessary to restrict these oxidative processes in biodiesel for its applications as fuel. Therefore, the oxidation stability of biodiesel is a parameter of great importance for its commercialization and application as fuel. It is an inherent capacity of the biodiesel to resist the various chemical changes that occur during the long storage and deteriorates its fuel characteristics. It is noticeable from the **Table 2**, that the neat biodiesel does not meet the minimum prescribed value for induction period (*i.e.*, 6 h min as per ASTM). The poor

radicals – it corresponds to the chain initiation step. In propagation step, the carbon radicals formed by initiator combine with oxygen molecule results in the formation of peroxides. These peroxides further abstract the active methylene hydrogen, which lead to the formation of hydroperoxides and generate fresh stabilized carbon radicals and continues the propagation step until the its termination. The termination step lead to the formation stable products. Beside, some other parallel reactions (such as addition-elimination reactions, rearrangement reactions, fragmentation reactions, disproportionation reactions, etc.) are also take place during the auto-oxidation of fatty acid esters (FAE). [20]

oxidation stability of biodiesel can be improve by addition of natural or synthetic chemical additives into biodiesel. [1, 21] These antioxidants retards, controls or inhibits the auto-oxidation processes of fatty acid alkyl esters and reduce the formation of the formation of oxidized side products.[22] Depending upon their oxidation inhibition characteristics the antioxidants can be classified into two categories: the primary antioxidants (or chain breaking antioxidants), and secondary antioxidants (or hydroperoxide decomposer antioxidants). The primary antioxidants do not inhibit the radical initiation reaction of the biodiesel degradation; however, they act as free radical scavenger that inhibits the oxidation during the propagation step. The allylic or bis-allylic carbon radicals formed after in the initiation steps are highly reactive, and react with O₂ molecule to result in the formation of reactive peroxy radicals, which on subsequent abstraction of active proton from bis-allylic carbon results in the formation of hydroperoxide radicals. The antioxidants react with these peroxy and hydroperoxide radicals and discontinue the further propagation processes by forming stable molecules. [22] The general mechanism of retardation of oxidation processes in biodiesel can be shown as:



Inhibition: Phenolic and substituted phenolic compounds, secondary aromatic amines, thiophenols, natural antioxidants (tocopherols and flavonoids) etc.,

are the commonly used primary antioxidants as biodiesels stability enhancer because of their low cost and easy availability. Pyrogallol, propylgallate, tert-butyl hydroquinone (TBHQ), butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), diphenylamine (DPA), dodecylgallate (DG), etc. (**Figure 2**) are some of the most commonly used synthetic antioxidants studied for the improvement of biodiesel storage stability. [21-23]

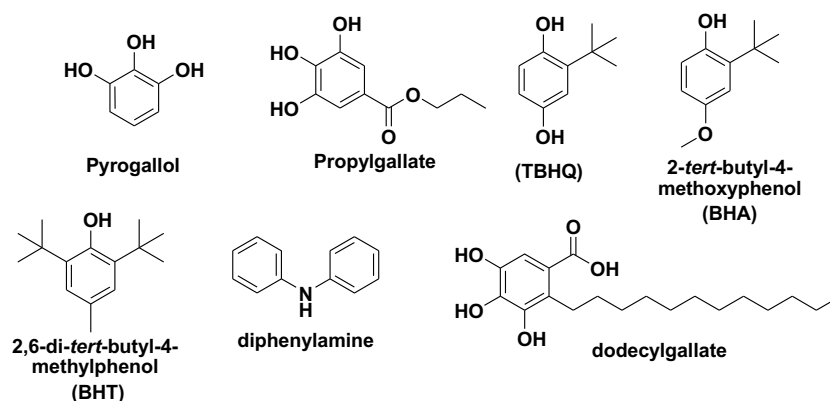


Fig. 2: Commonly used synthetic antioxidants

These additives can be used individually or in various proportion of their binary mixtures. [21,23] **Figure 3** represents the mechanism for inhibition of auto-oxidation of unsaturated fatty acid in propagation step using pyrogallol as antioxidant. Rawat et al., reported that in comparison to the individual antioxidants, the binary combinations of antioxidants not only have shown their greater effectiveness to slow down the rate of auto-oxidation, but also due to effective synergism between the antioxidants used they improved the long-term storage stability of biodiesel significantly. [21,23] The general mechanism of the synergistic relationship between the binary antioxidant systems has also discussed in these reports (**Figure 4**). The effectiveness of synthetic antioxidants towards biodiesel stabilization is also depend upon their

solubility in the biodiesel in which they are tested. It is observed that the antioxidants those are completely soluble in fatty acids esters are found relatively less effective in comparison to partially soluble antioxidants.[24] This may be because, due to their lower solubility these antioxidants concentrated gradually from top to bottom in the biodiesel and thus, it prevents the oxidation process at initiation stage in the surface and reduces the rate of propagation to the inner part of biodiesel.[25] Another method to improve the oxidation stability is the blending of biodiesel of different induction periods. In this method, the oxidation stability of the biodiesel with low induction period could be improved without addition of any antioxidant. [26]

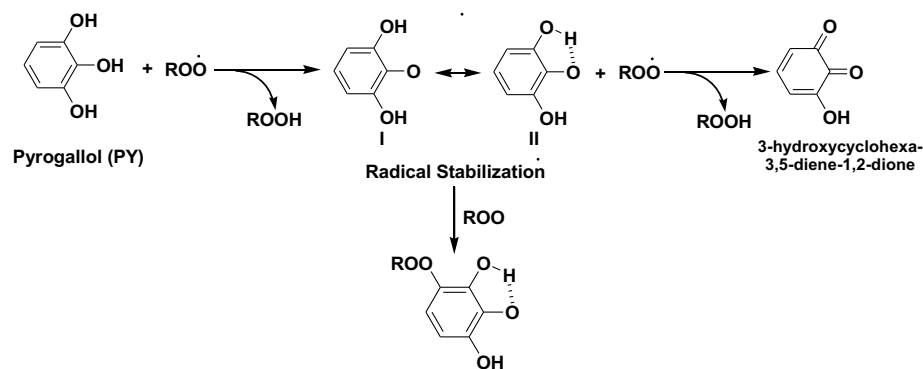


Figure 3: Mechanistic representation of antioxidant behaviour of pyrogallol. [21]

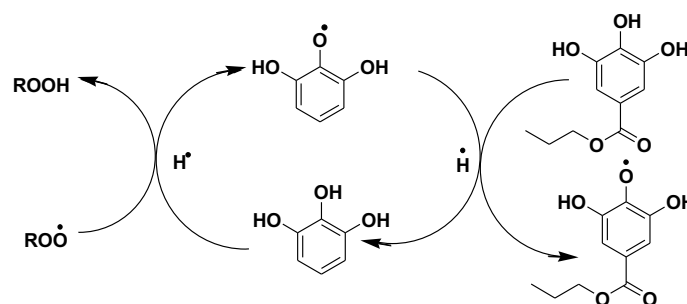


Figure 4: Mechanistic representation of synergistic relation between antioxidants (pyrogallol and propylgalate). [21]

4. Conclusions

The present review insights the various oxidation processes involved, their causes and potential inhibition techniques for sustainable application of biodiesel as fuel. The oxidation stability of biodiesel is one of the most important parameter that affect its asin increasing the oxidation stability of biodiesel by inhibiting the various oxidation processes involve in it.

This review would be helpful in development of biodiesel production and application technologies in order to make them more sustainable.commercial production and its uses as an alternative of fossil diesel. The degree of unsaturation, position of C-C double bonds and total number of allylic and bis-allylic position play the significant role in promoting the oxidation processes in fatty acid chains of biodiesel. Chemical additives *i.e.*, antioxidants are very effective.

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