Investigation on The Effects of Tbhq on Oxidation Stability of Citrus Sinensis Biodiesel

Manivannan P[1], Ramesh K[2], Sakthivel R[3], Baranitharan P[4]
[1, 3, 4] Dept of Mechanical Engineering
[2]Assistant Professor, Dept of Mechanical Engineering
[1, 2] Government College of Technology, Coimbatore 641013, India

Abstract- *Biodiesel from orange oil is one of the promising non-edible sources in India. But the storage stability of biodiesel is one of the main problems while using biodiesel. Poor oxidation stability causes the formation of gum which leads to problems in storage of fuels for long time. In the present study, the method of improving the stability characteristics of orange oil methyl ester with the addition of anti-oxidant TBHQ is investigated. The FTIR spectroscopy was used for characterize the oxidation stability of biodiesel. The investigation shows that the TBHQ improves the oxidation stability of orange oil methyl ester significantly. The results show that the optimum amount of TBHQ for pure biodiesel to maintain the oxidation stability for long time is 1000 ppm concentration. Above that concentration the stability of biodiesel starts to decrease due to the deterioration of hydrophobic and hydrophilic clusters formed in between the biodiesel and anti-oxidant. It is concluded that TBHQ at 1000 ppm concentration in biodiesel can be used for the storage of orange oil methyl ester for long period.*

Keywords- Citrus Sinensis, FTIR, Oxidation stability, TBHQ

I. INTRODUCTION

In the field of heavy transportation and agriculture, Compression ignition engines are employed due to their higher thermal efficiency and durability. However oxides of nitrogen and particulate emission from the engine are harmful to environment. Hence strict standards are imposed on exhaust emissions. After the global energy crisis in the 1970s and strict standards, the search for alternate fuel has increased.

Vegetable oils have been used as potential alternative to diesel. Those properties of vegetable oils are comparable to diesel and it can be used in CI engines without major modification [2, 3]. To evolve suitable methods for using vegetable oils in diesel engine, there are attempts have been made in the past. For example to improve the performance andlowering emissions from engine, transesterification process is used. Methyl esters of vegetable oils give higher thermal efficiency with lower emissions. Zoobik J et al reviewed that the sunflower oil methyl ester in diesel engine shows that increased pressure and high pressure rate [4]. There is also same results were found for soybean ester as well [5].

India has producing orange peel oil of 27,600 ton (based on 0.6% recovery of oil from 46 lakhs ton fruits by cold press process) from the orange fruits. There is only 2-3 tons of orange oil are used for food and cosmetic industries. There is no other demand for orange oil. The requirement for orange peel may be higher, if the demand increased for orange oil to fuelling in internal combustion engines [6,7].Orange oil is a renewable oil obtained from orange skin, peel in which 90% of D- limonene is present. It can be used in several applications. It is used as hand cleaner, furniture polish, and soap and shampoo production [8]. Furthermore it can be used as a fuel to gasoline engine in the form of blends.

Table 1.Average composition of Orange oil

Components	**Percentage of Composition (%)**
Moisture	Nil
Mineral matter	Nil
Carbon	84.28
Hydrogen	12.47
Nitrogen	0.19
Sulphur	0.007
Oxygen	3.05

The main problems associated with the biodiesel are its lower stability and cold flow property. The oxidation, thermal, and storage stability are included in stability parameter. The oxidation products like alcohols, aldehydes, shorter chain carboxylic acids, insolubles, gums and sediment are the byproducts of oxidation of biodiesel. Thermal instability leads to increase in weight of fat and oil because of the formation of insolubles and gums. It is related to rate of oxidation at high temperature.

Storage stability is the tendency of fuel to resist change in its chemical and physical characteristics. The undesired properties are brought by environment, sunlight, storage vessels etc. the fuel may be affected by exposure to contaminants leads to change in color, sediment formation and others that reduce the desired property of fuel [9]. These properties are the factors in the formation of substances in biodiesel which are undesirable as per the specifications. Such fuels used in engine affects the engine performance by fuel filter plugging, injector fouling, deposit formation in combustion chamber and other fuel delivery system [10-11]. The addition antioxidant additives can improve the stability of biofuel. The additives can be natural or synthetic. There are various research have been conducted on the biodiesel with the addition of additives. Results of those study show that the stability of biodiesel is increased with the addition of antioxidants. And it decrease with increase in temperature [12-13]. The investigation shows that butylated hydroxytolune(BHT), tert-butyl hydroquinone (TBHQ), propyl gallate (PG), butylated hydroxyanisole (BHA), and pyrogallol (PG) are the best antioxidants among various antioxidants [14-15]. The objective of the paper is to investigate the oxidation stability of Orange oil methyl ester with the addition of TBHQ at various concentrations.

II. MATERIALS AND METHODOLOGY

2.1 Test fuel

The major component of orange oil is D-limonene. The orange oil is extracted from orange peel of fruits by means of (i) juice extraction process (ii) steam distillation process and (iii) cold press.

There are three grades of orange oil are available in market. They are (i) natural or raw oil (ii) two fold orange oil (iii) fivefold orange oil. Number of folds means no of distillation process carried out on the raw orange oil. It is to increase the purity of orange oil. Raw orange oil is the cheapest one in the market. So it is used in the present study. The chemical composition of orange oil is given in table 1.

Orange oil is transesterified by the traditional method to convert it into orange oil methyl ester. Synthetic antioxidant tert-butyl hydroquinone (TBHQ) was added with pure biodiesel at different concentrations (375, 750, 1000, 1125 ppm). The additive TBHQ is completely soluble in biodiesel at all concentrations. Five test fuels are prepared and being tested. The properties of all test fuels were listed in table 2.

Test fuel blends:

(i) Pure Biodiesel (B100),
(ii) B100 + 350 ppm of TBHQ (B100A1),
(iii) B100 + 700 ppm of TBHQ (B100A2),
(iv) B100 + 1000 ppm of TBHQ (B100A3),
(v) B100 + 1125 ppm of TBHQ (B100A4).

2.2 Stability Measurement

Oxidation stability of biodiesel was quantified by the induction period (IP). The rancimat method EN 14112 was used for evaluating the induction period of biodiesel. The metrohm 873 biodiesel rancimat instrument was used for all measurements. Samples of 5g of biodiesel were analyzed in the constant air flow passing through the biodiesel and into a vessel containing double distilled water. The electrode presents in the vessel measure the conductivity through the test continuously. It is connected with recording device. When the conductivity increased rapidly it is indicated as end of induction period. The dissociation of volatile carboxylic acids created during the oxidation process is the reason for accelerated increase in conductivity. As the conductivity of the water is monitored continuously, a conductivity curve is obtained whose inflection point is called as induction period. It is the good characteristic value for the oxidation stability. All test fuels were measured at temperature of 140^{o}C, 145^{o}C and 150^{o}C. The biodiesel should have 6 hours of IP at 110^{o}C as per EN14214 standard.

Table 2.Properties of fuel blends

Properties / samples	Kinematic viscosity at 40°C	Density	Flash point	Fire point	Oxidation stability at 110°C
Units	cSt	Kg/m^3	°C	°C	h
Diesel	2.7	0.8284	52	65	-
B100	2.9	0.7569	62	76	1.53
B100A1	2.9	0.7569	62	76	5.86
B100A2	2.9	0.7569	63	76	6.69
B100A3	3.0	0.7572	63	77	9.47
B100A4	3.0	0.7572	63	77	8.47

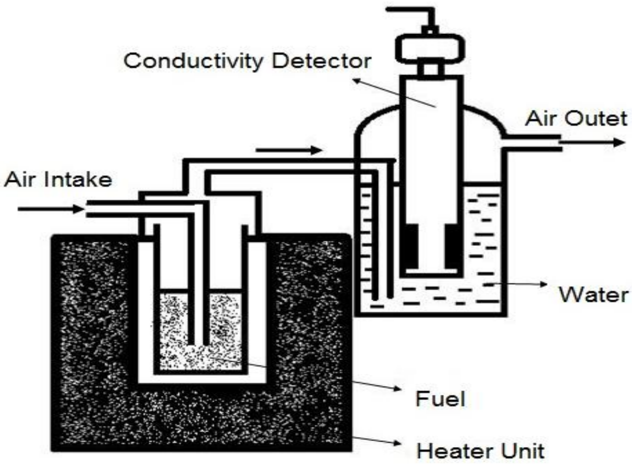

Fig 1.Rancimat instrument

2.3. FTIR SPECTROSCOPY

FTIR (Fourier transform infra-red spectroscopy) method is used for identifying the organic and inorganic molecular present in the given sample. In this study Perkin Elmer spectrum 2 instrument is used. The molecules present in the sample absorb the infra red spectrum of electromagnetic waves that corresponds to the chemical bond present in the molecule. FTIR matches the emission spectrum of the sample with the default emission spectrum present in the database. The ratio between the sample spectrum and the background emission spectrum is indirectly proportional to the transmission percentage of the sample. With respect to the frequency range from 600 to 4000 cm^{-1}, the automated software will depict the molecular compounds present in the sample. In the present study, all the samples were analyzed at wave number range 3000-3700 cm^{-1} and 2700-3000 cm^{-1}, which represents the presence of O-H and C-H molecules respectively present in the sample.

Based on the transmission percentage of the sample in specific regions, the oxidation characteristics of the test fuels were validated with respect to the presence and absence of O-H and C-H molecular groups in the sample which are the main criteria for oxidation.

III. RESULTS AND DISCUSSIONS

3.1 Analysis of oxidation stability

The induction period variation for pure biodiesel and effects of TBHQ addition on oxidation stability of biodiesel were studied by evaluating the samples at 140°C, 145°C, and 150°C (Fig 2). The induction period at 30°C was calculating by extrapolating the measured values in the automated rancimat software for the corresponding test samples in terms of hours. From the extrapolated curve it is found that B100 can be stored for 457.7 hours (0.03 years) at a temperature of 30°C without any change its physical and chemical property. And also for the other blends the storage period are extrapolated in the software for the same temperature condition. (Table 3)

Table 3.Rancimat measurement (IP @ 30°C) for fuel blends

Samples	Extrapolated IP at 30°C	
	(h)	(Year)
B100	377.8	0.03
B100A1	2500	0.28
B100A2	3492	0.39
B100A3	5487	0.62
B100A4	4683	0.53

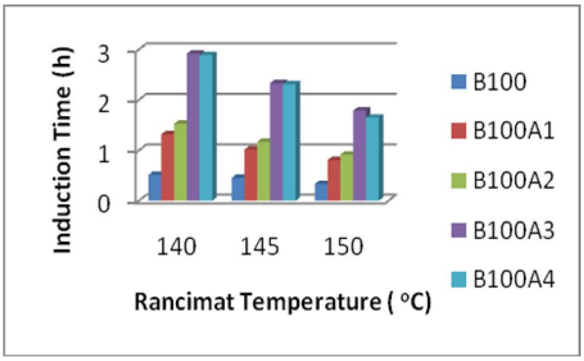

Fig 2.Induction period for all blends at various temperatures

In the FTIR image, the graph is plotted between wave number (cm^{-1}) v_s transmittance percentage (%T) of the emission spectrum of the sample containing the molecules which absorb the portion of the infra-red spectrum passed through it. In the given image transmittance percentage and wave number are marked for the regions of (3000-3700 cm^{-1}) and (2700-3000 cm^{-1}) which corresponds to the O-H and C-H bonds respectively. The O-H and C-H bonds present in the sample plays the vital role in the oxidation stability. The higher percentage of molecules can be identified with the lower percentage of transmittance at the corresponding wave number regions.

3.1.1 Pure Biodiesel (B100)

The oxidation stability of pure orange oil methyl ester transesterified from orange peel oil without any mixture concentration of petro diesel is one of the important parameter in commercialization. The pure biodiesel should display 6 hours of induction period at 110°C, as per EN 14214 standard. Orange oil methyl ester (B100) shows only 1.47 hours of induction time that means it did not meet the biodiesel standard provided by the European Norms without any Antioxidant. Orange oil methyl ester shows much lower IP as compared to diesel. By using the FTIR image, the inferior stability of pure biodiesel can be characterized. The C-H chain in the wave number of 2922.1 cm^{-1} (30.123% T) represents the presence of lower C-H molecules in the sample which causes the lower stability of biodiesel. The reason for decreased stability in biodiesel is the lower presence of C-H bonds in the sample. Further that the microorganisms exist in the atmosphere consumes the organic compound present in the biodiesel that generates free radicals which is also the cause for inferior oxidation stability.

3.1.2 Effect of anti-oxidant on stability of biodiesel

Initially all samples were tested at 110°C to find out the induction time as per the EN 14214 method. The biodiesel displays only 1.53 hours of induction time at 110°C, so it does not meet the EN 14112 standard. B100A1 blend shows 5.86 hours of induction time that meets the ASTM 6751 standards for oxidation stability. B100A2 have 6.69 hours of induction time that fulfills both ASTM 6751 and EN 14112 standard. 1000 ppm of TBHQ additive in biodiesel has highest induction time of 9.47 hours among the other blends (fig 3). After 1000 ppm the oxidation stability of biodiesel starts to decrease due to the brakeage of its chemical structure that means the deformation of hydrophobic and hydrophilic cluster. That mechanism can be clearly revealed by the C-H bonds present in the sample. Anti- oxidant TBHQ improves the oxidation stability of biodiesel significantly. From the extrapolated curve it can be see that TBHQ at 375, 750, 100, 1125 ppm in biodiesel have 0.28, 0.39, 0.62, 0.53 years of storage time respectively at normal temperature of 30°C. The extrapolated curve for the B100A3 blend by the rancimat software in shown in Fig 4.

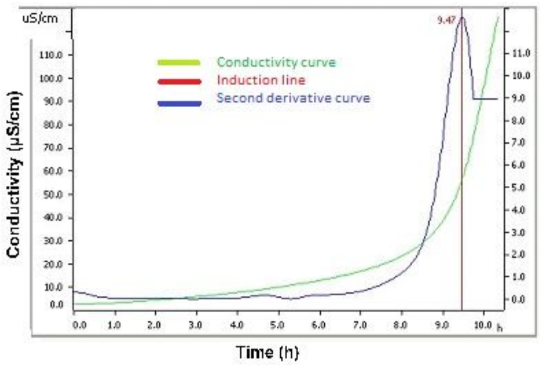

Fig 3.Induction period of B100A3 blend at 110°C

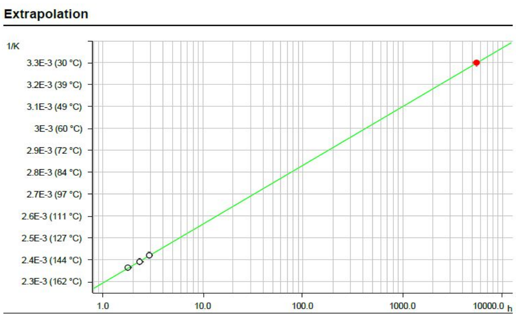

Fig 4.Extrapolated curve for the blend B100A3 at 30°C

4. FTIR evaluation

FTIR spectrum for all the blends is shown in fig 5. As stated above wave number ranges 2700-3000 and 3000-37000 cm^{-1} represents the presence of C-H and O-H bond respectively. The increase of O-H molecules in the sample due to the moisture and water content present in the sample that increases the rate of oxidation. It causes rapid degradation of biodiesel. Water and moisture content can be characterized by means of the presence of O-H bonds in the FTIR spectrum images.

Thus the oxidation of biodiesel is organized by the C-H and O-H bonds present in the sample [16]. Pure biodiesel have lower oxidation stability due to the lower C-H bonds (2922.11cm^{-1}, 30.123% T) present in the sample as compared to other blends. TBHQ addition in biodiesel increase the oxidation stability due to the low impact of frees radicals on oxidation. The reason for increased stability in biodiesel by means of additive is the presence of C-H bonds in the sample. Due to the consumption of oxygen molecules present in the sample by means of carbon atoms extents the degradation of sample [16]. TBHQ is the phenolic (longer carbon chain) group, it forms a strong hydrogen bond cluster (C-H) between antioxidant and biodiesel. The antioxidant forming the C-H bonds which surround the O-H bond of biodiesel. The less oxygen present in the hydrophobic entities decreased the free radical attack. By means of this process, the time taken by the free radicals to breach the formed cluster is increased. The more time required for breaking the cluster leads to higher stability. The stability of biodiesel is observed upto 1000 ppm correlates to the presence of C-H molecules present in the sample. The percentage of 29.56 and 27.6 of transmittance was noted for the B100A1, B100A2 blends at the wave number of 2923.2 cm^{-1} and 2921.4 cm^{-1} respectively. That means the number of C-H molecules in the respective samples are increased by the addition of TBHQ. B100A3 (1000 ppm) displays highest stability of 5487 hours which have the lowest transmittance percentage of 7.05% at the wave number of 2922.1 cm^{-1}. B100A4 has the lower stability when compared to B100A4 blend. The deterioration of formed hydrophilic and hydrophobic cluster which is exposed to oxygen in the atmosphere is the main reason for decreased oxidation stability for the fuel blend above 1000 ppm. This contact between the oxygen molecules and biodiesel resulted in lower stability of blend B100A4 as compared to bend B100A3. B100A4 blend (1125 ppm of TBHQ) has the increased transmittance percentage of 9.65 in the wave number of 2925.2 cm^{-1}, as compared to B100A3 blend. That decreased number of C-H molecules can be correlated to the lower stability of that blend.

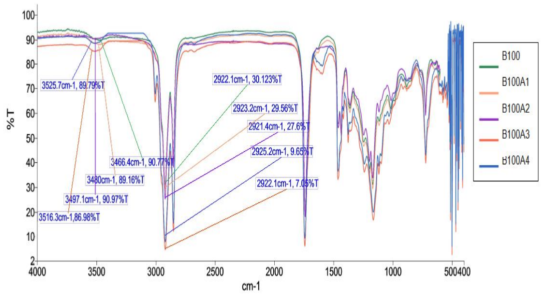

Fig 5.FTIR spectrum for all samples.

IV. MAIN FINDINGS

Results of the investigation show that:

1. The result shows that the TBHQ plays a major role in improving the oxidation stability of orange oil biodiesel.
2. The induction period of orange oil methyl ester (B100) will improve from 1.53 h to 6.69 h by the addition of TBHQ (750 ppm) which fulfills the limit provided by EN 14112.
3. B100A2 , B100A3, B100A4 meet the limitation of induction period provided by EN 14112.
4. B100A1 blend with induction time of 5.86 meets the standard ASTM 6751 for induction time.
5. As per EN 14112 standard pure biodiesel is not stable, so it is required for anti-oxidant to maintaining its stability.
6. Rancimat software extrapolates the induction period at 30°C. B100A3 (1000 ppm) resulted in higher induction period of 5487 hours at normal storage temperature (30°C).
7. TBHQ concentration in biodiesel above 1000 ppm degrades the oxidation stability due to the deterioration of hydrophilic and hydrophobic cluster between anti-oxidant and biodiesel molecular compounds.

VI. CONCLUSION

Oxidation stability is one of the main problems while using biodiesel. Orange oil biodiesel has poor oxidation stability that leads to slush and gum formation that degrades desired properties of biodiesel. From the investigated results it can be see that the biodiesel cannot be stored without any antioxidant additive. Antioxidant TBHQ improves the oxidation stability of orange oil methyl ester significantly. B100A3 blend gives the highest storage time among the other blends. Stability of biodiesel increases up to the 1000 ppm of TBHQ concentrations, after that it starts to decreases. The minimum amount of TBHQ needed for maintain the stability as per EN 14112 is 750 ppm and the optimum amount of antioxidant is 1000 ppm concentration.

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