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Long-term storage oxidation stability of Karanja biodiesel with the use of antioxidants

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ABSTRACT

Vegetable oils and their esters (biodiesel) undergo oxidation and degenerate more quickly than mineral diesel. The unsaturated fatty acids present in vegetable oils are susceptible to oxidation. One of the main criteria used for the quality assessment of biodiesel is 'storage oxidation stability'. Oxidation of the esters during the long-term storage can lead to problems in the utilization of biodiesel in the engine and can lead to rough engine operation. Contact with ambient air, exposure to sunlight, metals, and exposure to high temperature conditions accelerate the oxidation reactions leading to lower oxidation stability of biodiesel. The EU biodiesel standard (EN14214) specifies a minimum value of 6 h for biodiesel induction period at 110 °C, measured using Rancimat instrument. In order to ensure the oxidation stability specification limit 6 h for biodiesel at the filling station, the initial oxidation stability at the time of production should be definitely higher than 6 h. Addition of synthetic antioxidants is an efficient way to increase the initial oxidation stability of biodiesel. Reduction in oxidation stability can be minimized during long-term storage, if biodiesel is stored in suitable conditions because some conditions lead to quick reduction in oxidation stability.

Present experimental study investigates the effectiveness of 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) on the long-term storage oxidation stability of Karanja oil methyl esters (KOME), which is produced from a very popular highly unsaturated, non-edible oil feedstock for biodiesel production in Indian sub-continent. All the samples were stored in dark room and in air-tight bottles. The aim of this study is to find the most effective antioxidant and the minimum concentration of antioxidant required to meet the storage oxidation stability specifications. KOME samples were stored in different storage conditions (viz. in dark/sunlight exposure, with air/without air exposure, with metal/without metal exposure) at ambient temperature with an aim to assess the effect of storage conditions on the oxidation stability and the most appropriate conditions for biodiesel storage.

1. Introduction

Unsaturated fatty acids present in the molecule of vegetable oils are the major cause of poor oxidation stability. When these vegetable oils are transesterified to biodiesel, the composition and degree of unsaturation of fatty acids do not change. Hence biodiesel is prone to oxidation. During the later stages of long-term storage, oxidation of the esters can cause the biodiesel to become acidic leading to formation of insoluble gums and deposits, which lead to problems such as fuel-filter plugging and can create problems in smooth operation of the engine. Studies have reported that contact with air, metals, and exposure to sunlight, and high temperature conditions accelerate the oxidation reactions resulting in lower oxidation stability [1–7].

Some of the antioxidants such as tocopherols occur naturally in vegetable oils, which prevent the oxidation reactions to some extent. The amount of natural antioxidants in biodiesel is variable and depends upon the feedstock and production process used for biodiesel production. If the vegetable oil contains high FFA, the distillation of end product during the production of biodiesel can lead to removal of some of the natural antioxidants. This is the reason why used frying oils have poor oxidation stability [1]. Natural antioxidants give initial oxidation stability to biodiesel however most of the biodiesels produced do not meet the oxidation stability specifications (6 h). Many researchers have reported that synthetic antioxidants like 2-tert butyl hydroquinone (TBHQ), 2-tert butyl-4-methoxy phenol (BHA), 2,6-di-tert butyl-4-methyl phenol (BHT), 1,2,3 tri-hydroxy benzene (PY), and 3,4,5-tri hydroxy benzoic acid (PG) are more efficient than natural antioxidants [8–14]. Many studies report that oxidation stability decreases when biodiesel is stored for longer periods of time. The oxidation of biodiesel during storage leads to increased viscosity, increased peroxide value, increased acid number, and decreased induction period.

Oxidation of biodiesel is an auto-oxidation reaction (Fig. 1), which occurs in a set of reactions categorized as initiation, propagation, and termination.

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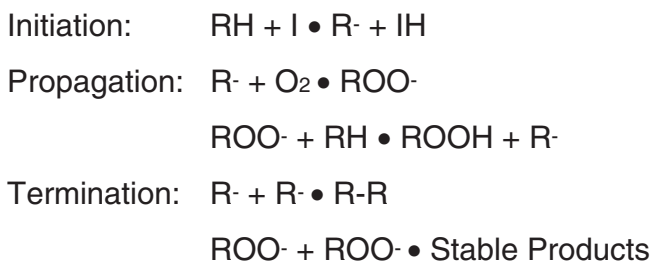

Fig. 1. Typical oxidation reactions of biodiesel.

During the initiation step, hydrogen is removed from the carbon atom next to the double bond to form a carbon based free radical. This free radical is highly reactive with diatomic oxygen and forms the peroxide free radical (ROO^-). The peroxide free radical is less reactive compared to carbon free radical, but is sufficiently reactive to quickly abstract hydrogen from carbon to form another carbon radical and a hydro peroxide (ROOH). The new carbon free radical can then react with diatomic oxygen to continue the propagation cycle. The termination of chain reaction takes place when two free radicals combine to form a stable compound. Initially the ROOH concentration remains low, however after certain length of time, known as induction period, ROOH level increases rapidly indicating the onset of the overall oxidation process [15,16].

The biodiesel feedstock varies from country to country depending on the availability of vegetable oils in the local vicinity and governmental policies. Traditional raw materials for biodiesel production are soybean oil, rapeseed oil, sunflower oil, palm oil, rice bran oil etc. [17]. Since India is net importer of edible vegetable oils for food purposes, edible oils cannot be used for biodiesel production.

Loh et al. [7] studied the influence of five antioxidants on the oxidation stability of biodiesel made from used frying oil. The antioxidants used were vitamin E, BHA, BHT, TBHQ and PG. All the antioxidants were dosed at 100, 250, 500, 750, and 1000 ppm concentration in biodiesel produced from waste frying (edible) oil. More than 100 ppm concentration of each antioxidant was able to increase the oxidation stability of freshly prepared biodiesel beyond 6 h. The oxidation stability increased with increase in concentration of antioxidants. The samples were stored in dark at room temperature and in absence of air contact for 5 weeks and then evaluated for their oxidation stability, which decreased with storage. About 10–20% decrease in oxidation stability was observed with vitamin E after 5 weeks, 8–15% with BHT, 22–35% with TBHQ, 7–10% with BHA, and 3–15% decrease in oxidation stability was observed with PG. However, it was observed that above 500 ppm of vitamin E, BHT, and TBHQ sustain the oxidation stability of 6 h up to 5 weeks of storage. BHA and PG showed the highest increase in oxidation stability at higher concentrations (500–1000 ppm), followed by TBHQ, BHT, BHA, and vitamin E. At lower concentrations, the order was not the same. The order of effectiveness of antioxidants from 500–100 ppm was: vitamin E<TBHQ<BHT<BHA<PG. An antioxidant concentration of 500 ppm and above was sufficient to meet the oxidation stability specification for long-term storage. Except PG, the concentration of 100–250 ppm of all the antioxidants was not enough to provide sufficient oxidation stability to used frying oil methyl esters.

Prankl et al. [18] studied the long-term storage oxidation stability of biodiesel derived from soybean oil (edible) at indoor and outdoor storage conditions. The induction period of freshly prepared biodiesel was nearly 10 h and the oxidation stability decreased sharply over storage. All the samples stored at ambient temperature breach the oxidation stability specification limit of 6 h after 14 weeks storage. The samples stored at a low temperature (4 °C) however retain the oxidation stability specification limit even after storage for longer time. The induction period of samples stored in sunlight was nearly zero at the end of storage period. After 14 weeks, the induction period of samples stored at low temperature (4 °C) was 70% of the initial value, while that of the samples stored in dark was approximately 50%. Tests were also carried out to assess the changes in viscosity and acid number during storage. Both viscosity and acid number increased with passage of time. Highest increase in viscosity and acid number was obtained for biodiesel samples stored in sunlight. However with other storage conditions, slight increase in viscosity and acid number were observed. In the same study, biodiesel samples were stored for very long period of time (3.5 years) and at the end of the storage, none of the biodiesel samples were having induction period more than 2 h, however sample viscosities were still within the specification limits.

Tang [11] studied the long-term storage oxidation stability of biodiesel derived from soybean oil (edible) at indoor and outdoor storage conditions. The antioxidants used for the investigation were: BHA, BHT, TBHQ, DTBHQ, Ionol BF 200 (IB), PG, PY, and α-T, each 1000 ppm concentration. Indoor storage was at a constant temperature of 23 °C and the outdoor storage was at ambient temperatures in the Michigan area from December 2006 to September 2007. The freshly prepared biodiesel had an oxidation stability of 3.52 h. For Indoor storage, the oxidation stability decreased gradually by roughly 60% over 9 months i.e. from 3.52 h to 1.42 h. The highest initial oxidation stability increase was obtained with PY (11.54 h). However with PY, there was rapid reduction in oxidation stability from 11.54 h to 1.65 h after 9 months. The most effective antioxidant observed was TBHQ. The initial induction period was 11.08 h and it was very stable up to 9 months of storage. The initial values of oxidation stability of soybean biodiesel samples with 1000 ppm of DTBHQ, BHA and α-T were 6.54, 6.59 and 3.84 h respectively. After 9 months, the reduction in oxidation stability was gradual and was observed to be 23.7, 36.4 and 36.5% respectively. With 1000 ppm of PG, BHT and IB, the initial induction periods were 10.32, 6.37 and 5.94 h respectively, but there was sharp reduction in oxidation stability for 2 months and after that induction period decreased slightly up to 9 months. For outdoor storage conditions, there were sharp variations in temperature for the samples. For initial 4 months during the winter, temperatures were low while for next 5 months during summer, the temperatures were relatively higher. Accordingly, DTBHQ, BHA, PY, and PG samples showed a slower reduction in oxidation stability in the low temperature period and then rapid reduction in the summer time because of higher temperature storage. For TBHQ, BHT and IB, the effect was almost similar to that of indoor conditions. Again TBHQ was the most effective antioxidant for 9 months. The reduction in oxidation stability after 9 months for untreated biodiesel was 38.8%, while for BHT and IB; it was 47.1% and 40.1% respectively. After 9 months of outdoor storage, the minimum induction period was obtained with PY (0.4 h), which was highest initially (11.54 h).

Du Plessis et al. [6] studied storage oxidation stability of sunflower (edible) oil methyl and ethyl esters. Samples were stored at room temperature in glass containers in indirect daylight for 40 days. Freshly prepared methyl ester had an induction period of 7.33 h whereas for ethyl ester, it was 4.83 h. During first 16 days, oxidation stability for both biodiesel samples decreased sharply and afterwards, the reduction was gradual. For all observations, the oxidation stability of ethyl ester was found to be lower than methyl ester. Methyl ester sample was also stored at lower temperature (5 °C) and the induction period was determined at regular intervals. It was observed that induction period decreased by only 12.5% after 16 days, for the sample stored at lower temperature as compared to 60% reduction for the sample stored at room temperature. In the same study, the storage oxidation stability of sunflower oil methyl ester treated with 400 ppm of TBHQ was also analyzed. These samples were stored at room temperature in closed glass container. The induction period was determined at regular interval over a period of 24 days. Mittelbach et al. [1] investigated the storage oxidation stability of biodiesel samples obtained from rapeseed oil (edible) and used frying oil (edible). The samples were stored for 200 days between 20 and 22 °C

in six different storage conditions. The storage conditions were: 1. Light and open to air; 2. Dark and open to air; 3. Metal and open to air; 4. Light and without air contact; 5. Dark and in absence of air contact; and 6. Metal and in absence of air contact. The induction period of freshly prepared biodiesel was nearly 6 h for both rapeseed oil methyl ester and used frying oil methyl ester. The samples exposed to metals showed complete loss of oxidation stability i.e. zero induction period after 150 days of storage. After 200 days storage, all samples of rapeseed biodiesel were having oxidation stability lower than 2 h while that of used frying oil, was lower than 3 h. Peroxide number, acid number and viscosity gradually increased during storage, while there was a sharp increase in these parameters for the samples stored in light and open to air.

Sendzikiene et al. [19] studied the reduction in induction period of four biodiesel samples derived from rapeseed oil, linseed oil, lard and tallow (edible) that were stored for 60 days. Initial induction periods were slightly higher than 6 h, 3 h, 0.4 h and 0.3 h for rapeseed, linseed, and tallow and lard biodiesel respectively. After 30 days, the induction period of tallow and lard biodiesel reduced to zero. After 60 days, linseed oil biodiesel was having oxidation stability of 0.3 h and rapeseed oil biodiesel slightly higher than 1 h, failing oxidation stability specification of EN 14112.

Bora et al. [5] investigated the increase in peroxide value and kinematic viscosity of the Mahua oil methyl esters stored in six different storage conditions for a year without air contact. At the end of storage period, the peroxide values were high indicating poor oxidation stability of samples particularly for samples stored under 'open to air' and inside the room (27.8 mg/kg) and exposed to metal and air (28.01 mg/kg). Biodiesel samples showed marginal increase in viscosity over storage for one year, however few samples showed higher increase in viscosity e.g. samples stored in open air, inside the room (5.9 cSt) and exposed to metal and air (5.9 cSt).

Most of these studies reported in open literature have been carried out on edible oils to understand the oxidation stability behavior and very little effort has been made to understand the same for non-edible oil feed-stocks. This becomes extremely important because of the ongoing 'food vs. fuel' debate, which tends to discourage the use of edible oils for fuel production.

Karanja oil is one of the major non-edible oil feedstock species for producing biodiesel in India on a large scale. Karanja oil has 84% unsaturated acids compared to 56.6% in palm oil, 78.9% in Jatropha oil, 84.5% in soybean oil, and 88.4% in Sunflower oil [20]. Very limited scientific studies are carried out on the oxidation stability behavior of Karanja biodiesel so far. This comprehensive experimental study aims to fill this gap. Biodiesel produced from Karanja oil has been investigated for storage stability under various storage conditions in the present investigations for over 70 days. The effect of various anti-oxidants added in different concentration to Karanja biodiesel on the storage stability has also been experimentally assessed for over 4 months in this investigation.

2. Materials and methods

Karanja oil methyl ester (KOME) i.e. biodiesel was produced by transesterification of Karanja oil. Alkali catalyst NaOH (1 wt.% of oil) was mixed with high grade methanol and added to the reactor containing vegetable oil (alcohol to oil molar ratio 6:1). The transesterification reaction was carried out at 55 °C at a stirring speed of 800 rpm for 1 h according to optimum conditions reported in literature [21]. Biodiesel yield obtained was approximately 90% suggesting that the reaction was nearly complete. After completion of the reaction, the reaction products were transferred to a separating funnel, where upper phase i.e. biodiesel was separated from the lower phase i.e. glycerol, followed by subsequent washing (by distilled water) and moisture removal processes for biodiesel.

Oxidation stability of biodiesel samples with varying dosage of antioxidants was studied using Rancimat instrument (Metrohm, Switzerland; 873). This is a computer controlled measurement instrument for determining the oxidation stability of biodiesel according to EN 14112, which is included in the EU biodiesel standard EN 14214. The main parts of Rancimat include reaction vessel, measuring vessel and electrode for measuring conductivity. Biodiesel samples are kept at a constant temperature of 110 °C and air at a flow rate of 10 l/h bubbles through each sample. Each measuring vessel contains distilled water (60 ml). The products of biodiesel oxidation are transferred into measuring vessel with the air bubbling through the distilled water. The conductivity of distilled water is continuously monitored by the electrodes. The oxidation of biodiesel is recognized by the sharp increase in conductivity of water due to absorption of oxidized organic acids (formed due to oxidation of biodiesel) into the distilled water.

The antioxidant 2,6-di-tert butyl-4-methyl phenol (BHT; purity grade > 99%) was supplied by Merck Ltd, Mumbai, India and 1,2,3 tri-hydroxy benzene (PY; purity grade > 99%) and 2-tert butyl-4-methoxy phenol (BHA; purity grade > 98%) were supplied by Merck Specialties Pvt. Ltd., Mumbai, India. The antioxidants 3,4,5-tri hydroxy benzoic acid (PG; purity grade > 98%) and 2-tert butyl hydroquinone (TBHQ; purity grade > 98%) were supplied by Loba Chemie Pvt. Ltd., Mumbai, India. The antioxidants were dosed at concentrations of 300, 500, 700 and 1000 ppm in KOME (biodiesel). All the antioxidants were found to dissolve completely in the biodiesel at all concentrations. The chemical structures of these antioxidants are given in Fig. 2.

The initial increase in induction periods due to addition of antioxidants was assessed with Rancimat. After this, these 20 biodiesel samples were stored for 6 months in a closed room in translucent plastic bottles, without air contact and their induction periods were monitored on a monthly basis. Further in this study, 8 biodiesel samples were stored in different storage conditions for 70 days. The induction periods of these eight biodiesel samples were measured at regular interval, after every 10 days. The reported values of Induction period are average of 3 determinations. Variability of induction periods was found experimentally to be within ±4%. These eight samples were stored in two set of storage conditions. Four samples were stored indoors (in dark/no exposure to sunlight) and the other four samples were stored outdoors (exposure to direct sunlight), all in translucent plastic bottles with without air contact/open to air and with metal/without metal exposure. Thus following set of storage conditions were experimented with:

1. Dark, open to air, with metal	1.Sunlight, open to air, with metal
2. Dark, without air contact, with metal	2.Sunlight, without air contact, with metal
3. Dark, open to air, without metal	3.Sunlight, open to air, without metal
4. Dark, without air contact, without metal	4.Sunlight, without air contact, without metal

3. Results and discussion

KOME has very high level of unsaturated fatty acids [linoleic acid (18:2) −12%, oleic acid (18:1) −72%], due to which the initial oxidation stability of KOME was observed to be only 1.82 h. This was very close to average induction period (1.9 h) reported for biodiesel samples by McCormick et al. [22]. EN 14214 recommends a minimum induction period of 6 h at filling station. It is natural to expect that the end use of biodiesel may take up to 3–6 months in storage and transportation from the date of production. To ensure an induction period of 6 h at the filling station, the initial oxidation stability of biodiesel must be reasonably higher than 6 h. Further, the decrease in oxidation stability with time may be different for different antioxidants. Hence it becomes important to find out the effectiveness of antioxidants during storage. The aim of this study is to find the most

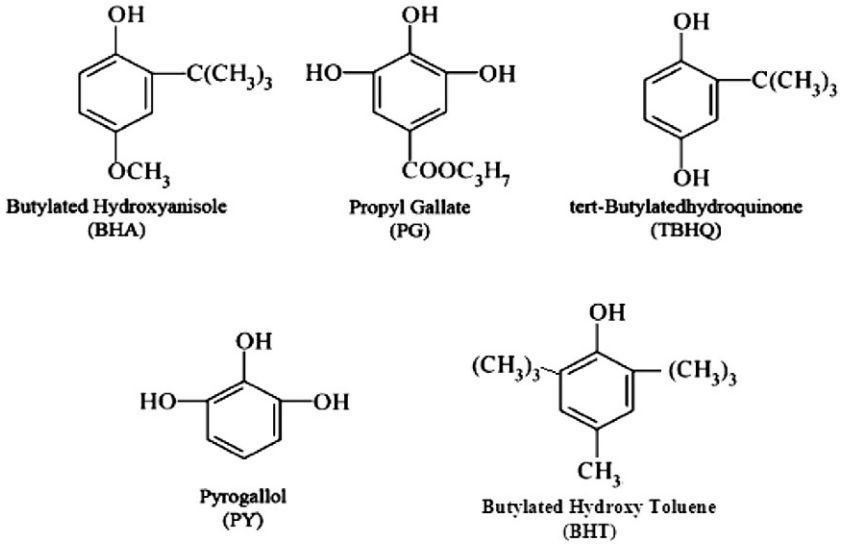

Fig. 2. Chemical structure of various antioxidants used.

effective antioxidant and minimum concentration of antioxidant required to meet the specifications, when biodiesel is stored for longer time.

3.1. Long-term storage oxidation stability of KOME with antioxidants

To make Karanja oil methyl esters (biodiesel from non-edible oil) competitive to the world market, it became necessary to add synthetic antioxidants to the biodiesel, immediately after the manufacturing. The increase in induction periods was observed to be different for different antioxidants as given in Table 1.

All these twenty biodiesel samples were stored in dark-room in translucent bottles with no exposure to air/metals/sunlight. The induction period of each of the sample was measured every month using Rancimat. It was observed that oxidation stability gradually decreased with time for all antioxidants. The results are summarized in the graphs (Fig. 3) for all antioxidants.

As seen from this figure, the highest increase in oxidation stability was observed with PY at all concentrations followed by PG and BHA. BHT and TBHQ do not attain the induction period of 6 h even with 1000 ppm antioxidant concentration. PY was also reported to be the most effective anti-oxidant for soybean oil methyl ester followed by PG, TBHQ and BHA [11].

With PY 300 ppm concentration, initially the biodiesel was able to achieve oxidation stability of 6 h, and after 1 month, the oxidation stability reduced to less than 6 h. However biodiesel samples with PY 500, 700 and 1000 ppm were able to meet the oxidation stability specifications even after 4 months. The induction period of PY 500 ppm reduced from 14.65 to 8.80 h after 4 months storage. The induction period of PY 700 and 1000 reduced from 17.19 to 11.26 h and 22.49 to 20.02 h respectively after 4 months.

Table 1
Initial induction period of KOME.

Antioxidant concentration	TBHQ	PY	PG	BHT	BHA
(ppm)	Induction period (h)				
300	3.49	6.17	4.87	3.64	3.63
500	3.60	14.65	7.71	3.87	6.32
700	3.96	17.19	10.26	4.55	6.54
1000	4.94	22.49	13.19	5.9	8.29

The non-edible oil derived biodiesel samples with 700 and 1000 ppm concentration of PG were able to meet the oxidation stability specification even after 4 months of storage. The 500 ppm samples were able to retain the oxidation stability only for 2 months and then the induction period breached 6 h. None of the biodiesel samples dosed with BHA, BHT and TBHQ were able to retain the oxidation stability for longer periods of time.

The decreasing induction period tendency of BHA was found to be quite different from other antioxidants. BHA showed an abrupt decrease in induction period after 1 month of storage and thereafter, the oxidation stability decreased slowly and gradually. The initial oxidation stability at BHA 500, 700, and 1000 ppm was 6.32, 6.54 and 8.29 h respectively, which decreased to 2.66, 3.02 and 4.18 h respectively after 1 month. None of the BHA biodiesel samples were able to meet the oxidation stability specifications after 1 month of storage. However, after 1 month, the reduction in induction period was marginal for subsequent months.

3.2. Long-term storage oxidation stability of KOME under various storage conditions

The decrease in oxidation stability is highly dependent on the storage conditions. Air contact, exposure to sunlight, metal and high temperature conditions have catalytic effects and expedite the oxidation reactions resulting in lower oxidation stability.

In present experimental study, eight Karanja biodiesel samples were stored in different storage conditions. During water washing and subsequent moisture removal process, some of the natural antioxidants are removed. Thus the initial oxidation stability of water washed biodiesel is observed to be relatively lower. Dry washing with magnesol helps retain the natural antioxidants and hence the oxidation stability of freshly prepared biodiesel is comparatively higher. Therefore Karanja biodiesel was made from dry washing technique using magnesol instead of water washing in this research. It was observed that the induction period of dry washed, freshly prepared Karanja biodiesel was 2.74 h, which is higher than water washed Karanja biodiesel (1.82 h) reported earlier in this study. A 500 ppm PY was added to enhance the initial oxidation stability of biodiesel. This increases the oxidation stability from 2.74 to 21.12 h. The samples with an initial oxidation stability of 21.12 h were then stored in two sets of storage conditions as per the experimental plan discussed in the earlier section.

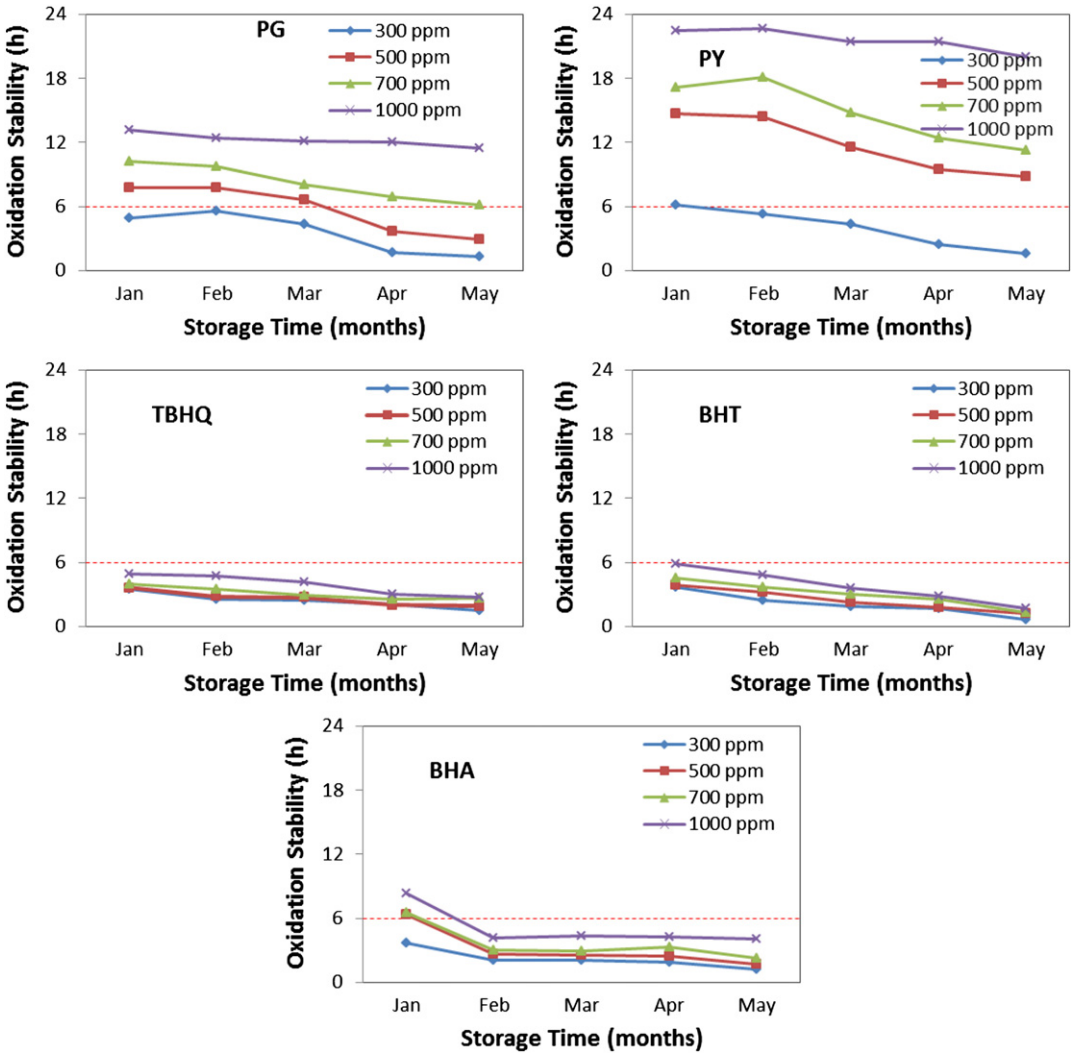

Fig. 3. Storage oxidation stability of KOME with antioxidants.

3.3. Outdoor storage of KOME

Outdoor samples were stored in such a way that sunlight fall directly on the samples for few hours. These four samples were evaluated for oxidation stability using Rancimat and the results are reported in Fig. 4.

Non-edible oil derived biodiesel samples (indoor and outdoor storage) were stored from 11th March to 20th May for approximately 70 days. The average temperature of March is approximately 28–32 °C during the sunshine. Nights are relatively cooler compared to day. Temperature falls to 15–20 °C at night. April was comparatively hotter. Average maximum and minimum temperature of April ranged from 35 to 38 °C and 20 to 22 °C respectively. May was extremely hot. Average maximum temperature of May crossed 40 °C. Due to very high temperatures prevailing in May, a higher loss in oxidation stability of biodiesel can be expected. Similar results were also observed from the present experimental research. A larger reduction in induction period was observed in the month of May compared to March and April for the samples stored in dark. The samples stored in direct sunlight were already having very low oxidation stability till May. Therefore it can be noted from the results presented above that the exposure to sunlight and air are the two most adverse conditions for storing biodiesel. In the first 10 days, the induction period reduced drastically from 21.12 to 2.25 h and 3.42 h for the sample stored at sunlight-open air-metal and sunlight-open air- w/o metal. The most stable sample was the one stored without air contact and without metal exposure. None of the biodiesel samples were able to retain the oxidation stability specifications of 6 h for more than 40 days. After 60 days, the oxidation stability of samples open to air-metal and open to air- w/o metal were almost zero. These results are in conformity with the observations made by Knothe that presence of air, sunlight, metals (effect of storing container) and elevated temperatures facilitates rapid oxidation of methyl esters [23].

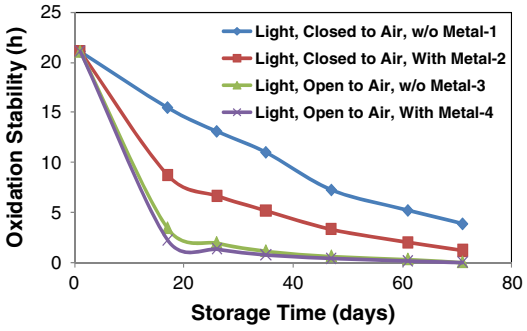

Fig. 4. Oxidation stability of biodiesel stored outdoors (exposed to sunlight).

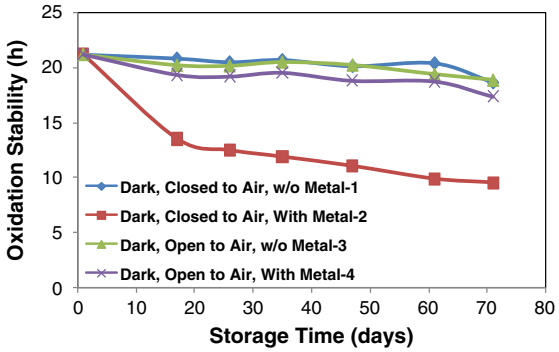

Fig. 5. Oxidation stability of biodiesel stored indoors (no exposure to sunlight).

3.4. Indoor storage of KOME

Four biodiesel samples were stored in dark without exposure to sunlight under different storage conditions as mentioned earlier. These four samples were assessed for oxidation stability using Rancimat and the results are reported in Fig. 5.

It can be seen from the Fig. 5 that all biodiesel samples retain the oxidation stability specifications of 6 h even after 60 days storage. Samples with metal exposure degrade faster than the ones without exposure to metal. Surprisingly, induction period of samples without air contact, with metal exposure was lower than open to air, with metal exposure. McCormick et al. correlated metal concentration in the biodiesel with reduction in oxidation stability [22]. They also observed that biodiesel samples having individual or total metal concentrations higher than 6 ppm exhibit very short induction period.

It was observed that by mistake, a metal piece of copper was added in this sample along with mild-steel pieces. It indicated that copper has significantly higher catalytic effect compared to mild steel on biodiesel degradation. This observation of strong catalyzing effect of copper was also reported by Knothe et al. [24]. After 60 days, the decrease in oxidation stabilities for samples 1, 2, 3 and 4 were observed to have reduced to 18.64, 9.53, 18.81 and 17.36 h respectively from the initial value of 21.12 h.

4. Conclusions

Long storage oxidation stability of KOME biodiesel samples prepared from non-edible Karanja oil were evaluated for different antioxidants in different concentrations (300, 500, 700 and 1000 ppm). PY was observed to retain the oxidation stability specification limit of 6 h for longer period of time followed by PG. The biodiesel samples with 500, 700 and 1000 ppm of PY were able to retain the oxidation stability even after 4 months. Biodiesel samples with 700 and 1000 ppm concentration of PG were also able to retain the oxidation stability after 4 months storage. However, the 500 ppm sample was able to retain the oxidation stability only for 2 months and then the induction period reduced below 6 h. For 300 ppm, the oxidation stability is below 6 h from the very start and reduced to 1.30 h after 4 months. None of the biodiesel samples dosed with TBHQ, BHT and BHA were able to retain the oxidation stability for longer periods of time.

Exposure to sunlight and air were the most adverse condition for storing biodiesel. In the first 10 days, the induction period reduced drastically from 21.12 to 2.25 and 3.42 h respectively for the sample stored in sunlight/open air/metal contact and sunlight/open air/without metal contact. Indoor samples were stored in dark without any exposure to sunlight. All the samples stored indoors retained the oxidation stability specification limit of 6 h after 60 days storage. Samples with exposure to metal degraded faster than the ones without exposure to metal. Higher catalytic effect of copper compared to mild steel was also observed. In Summary, it is recommended to store the Karanja biodiesel with PY under dark storage condition without exposure to air and metallic surfaces. The biodiesel derived from non-edible Karanja oil was able to meet the biodiesel specification requirements for oxidation stability with appropriate choice of anti-oxidants and therefore it is expected to perform as good as biodiesel derived from edible oil feedstocks.

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