Research Article

Comparative Studies of Oxidative Stability Properties of Biodiesel Produced from *Azadirachta indica* and *Hevea brasiliensis* seeds.

C. S. Ezeanyanaso[1]*, V. I. Ajibola[2], E. B. Agbaji[2], E.M. Okonkwo[1], O. J. Okunola[1] and Y. Alhassan[1]

[1]National Research Institute for Chemical Technology, P. M. B. 1052, Basawa, Zaria, Nigeria.
[2]Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

*Corresponding Author's Email: chikaeze2@gmail.com

ABSTRACT

The aim of the study was to establish the stability of biodiesel due to oxidation. Two non-edible seed oils were used; *Azadirachta indica* and *Hevea brasiliensis* were used to produce biodiesel and first rapid oxidative stability of the biodiesel were assessed then their properties with and without additives compared thereof over a range of one year storage period. The results of stability of the biodiesels for rapid induction and long term period with and without additives revealed that physico-chemical properties of the biodiesel produced from *Azadirachta indica* and *Hevea brasiliensis* seeds oil changed with the time. For the rapid test, none of the biodiesel samples could pass the 6 hrs oxidation test with neem biodiesel exhibiting the best oxidation stability and the rubber seed the worst. Both the additives, namely 0.5% *tert*-butyl hydroquinone (TBHQ) and 0.1% Ecotive increased the oxidation stability of all the three biodiesel samples to more than 6hrs. The one year storage stability study revealed that per-oxide value, density, viscosity and acid number increased for all the methyl esters with time. However, the calorific value was found to be decreasing for all the samples. The rate of change of different physico-chemical properties was found to be less in case of all the biodiesel with an additive. However, Ecotive appeared to be a better additive as compared to TBHQ for increasing the shelf life of biodiesel.

Keywords: Oxidative Stability, Biodiesel, *Azadirachta indica, Hevea brasiliensis,* TBHQ, Ecotive

INTRODUCTION

The development of a sustainable alternative source of renewable energy has been the greatest global challenge of the century, hence recently, biodiesel is considered as an important alternative biofuel due to its environmental benefits and simple industrial production from renewable resources. Biodiesel has the added advantage of higher lubricity compared to petro-diesel (Jain and Sharma, 2011). However, biodiesel being a mixture of methyl esters of vegetable oil fatty acids is more susceptible to oxidation than petro-diesel. A previous study on the storage stability of methyl esters found that there was deterioration during storage, and suggested the addition of antioxidants to ensure storage stability (Thompson *et al*., 1998). Another study found that there was no measurable deterioration of rapeseed, sunflower and camelina methyl esters stored in closed drums for 18 months (Fröhlich, 1999). The biodiesel has the same fatty acids compositions similar to the parent oils or fatties with considerable amount of unsaturated fatty acids. Its oxidative stability, therefore, becomes crucial quality issue during long term storage (Jain and Sharma, 2010a; Dunn, 2006). A number of research groups are working to find out the substances that inhibit this oxidation process and maintain the quality of biodiesel (Jain and Sharma, 2010b; Jain and Sharma, 2010b).

Knothe (2007) reviewed the susceptibility of biodiesel to oxidation. Oxidative degradation during transport and storage causes deterioration of the physical properties of the biodiesel making it unstable and unusable (Bouaid *et al*., 2007; Dunn, 2005; Dinkov *et al*., 2009). The reaction with atmospheric oxygen is accelerated by elevated temperatures, contact with metal surfaces (Mittelbach and Remschmidt, 2004), exposure to sunlight and air (Prankl and Schindlbauer, 1998; Knothe, 2006) and by the presence of metal compound impurities (Sarin *et al*., 2010).

During oxidation process, the fatty acid methyl ester usually forms a radical next to the double bond. This radical quickly binds with the oxygen of the air, which is itself a bi-radical and forms peroxide radical. The rapid radical destruction cycle begins thereafter. This peroxide radical immediately creates a new radical from the fatty acid methyl ester, which in turn binds with oxygen of the air and in this way, the destructive radical auto-oxidation cycle starts. During this process, up to 100new free radicals are created quickly from one single radical meaning thereby, that decomposition occurs at an exponentially rapid rate resulting in the formation of a series of by-products (Hui, 1996). These species so formed cause the fuel to eventually deteriorate. Finally, the oil spoils and become rancid very quickly. As shown in Fig. 1, oxidative rancidity begins with an initial chain reaction followed by propagation reaction that involves unstable peroxides and hydro peroxides followed by the termination reactions resulting in the formation of aldehydes, alcohols and carbonic acids.

Initiation: $RH + I \rightarrow R\cdot + IH$

Propagation: $R\cdot + O_2 \rightarrow ROO\cdot$

$ROO\cdot + RH \rightarrow ROOH + R\cdot$

Termination: $R\cdot + R\cdot \rightarrow R\text{-}R$

$ROO\cdot + ROO\cdot \rightarrow$ Stable Products

Fig. 1 Primary Oxidation Reaction *(Adapted from Jain and Sharma, 2011).*

Although there are numerous literatures on the storage, thermal and oxidation stability of biodiesel and effect of antioxidants on the stability of biodiesel synthesized from non-edible oils, but little work is available on oxidation stability and effect of antioxidant on biodiesel from *Azadirachta indica* and *Hevea brasiliensis* oil seeds. Hence this study is aimed at determining the effect of some additives on the oxidative stability of biodiesel produced from *Azadirachta indica* and *Hevea brasiliensis* oil seeds.

MATERIALS AND METHODS

Sample Collections and Oil Extraction

Dried *Azadirachta indica* seeds were obtained from the National Research Institute for Chemical Technology, Zaria (Nigeria), while the dried *Hevea brasiliensis* seeds were obtained from the Rubber Research Institute Benin (Nigeria). The seeds were cleaned by removing debris using hand picking method, dried to constant mass in an oven at 50 ℃ for 72 h, dehauled to remove the seed coat (with little or no oil), and the seeds dried at 50 ℃ for another 48 h. The oil was extracted by oil expeller. The seeds were fed to a series of expellers to receive a mild pressing on continuous basis, as each screw press gradually increased the pressure on the incoming material through the interior of a closed barrel. The extracted oil were drained out through a small gap between positioned hardened steel bar in the barrel cage. The oils were dark colour, with neem oil being more viscose and denser. The oils were filtered using muslin cloth to remove dirt and other inert materials. The oils were heated in flasks up to near boiling point to remove water contaminant, allowed to cool to room temperature (27℃) and taken for biodiesel production.

Esterification of Seed Oil

The Free fatty acid (FFA) content of the biodiesel was determined using ASTM standard methods, by initially determination of acid value by neutralization reaction using 0.1M KOH, hence the FFA is evaluated by dividing the acid value by 2. The neem oil had 0.78 % Free Fatty Acid (FFA) content and was found suitable for direct transesterification. The rubber seed oil had high FFA content of 16.58 % and was refined, as the yield of esterification process decreases considerably where FFA value > 2 % (Ramadhas *et al*., 2005). The FFA of rubber seed oil was reduced below 2 % using paratoluene sulphonilic acid as catalyst prior to transesterification. A round bottom flask was used as laboratory scale reactor vessel, and a hot plate with magnetic stirrer was used for the heating. The reaction/heating time, agitation speed and temperature, were measured for the test runs of combination of reactants and process conditions.

Determination of Rapid Oxidative Stability of Biodiesel

The method used for the determination of this property was described by American Oil Chemist's Society (1997) Cd 12b92. The oxidative stability of the biodiesel samples was evaluated by means of the Rancimat equipment model 617, under temperatures of 100 and 105^{0}C and air flow of 20 Lh^{-1}. A small test flame is directed in to the cup at regular intervals with simultaneous interruption of stirring. The flash point is taken as the lowest temperature at which the application of the test flame, causes the vapor above the sample to ignite momentarily. Samples of 5g were utilized, weighed in the Rancimat flask. The oxidation was then induced by the passage of the air flow through the sample, kept under constant temperature. The volatile products of the reaction, which were blown with the air, were collected as distilled water and measured by the change in electric conductivity of the water. They were expressed through a curve from which the induction period can be calculated by the interception of two lines: a tangent to the inclination and another tangent to the curve level part. All determinations for each oil sample were carried out in triplicate and expressed as means.

Long Storage Stability of Biodiesel

Three biodiesel samples (1 kg each of biodiesel from *Azadirachta indica* and *Hevea brasiliensis* seed oil) were stored for 12 months at room temperature under argon in a closed glass bottle exposed to daylight. One of the samples without any treatment was used as a reference. While the two other samples were supplemented with 0.5% *tert*-butyl hydroquinone (TBHQ) and 0.1% Ecotive (a commercial antioxidant). Supplementation was carried out by dissolving the 5g of TBHQ and 1g of Ecotive separately in each of the biodiesel under study. This solution was stirred for 30 min at ambient temperature; both TBHQ and Ecotive are readily soluble under these conditions. During the entire stirring period, a gentle flux of inert gas (argon) was bubbled inside the sample. Nitrogen was used only during preparation of the concentrated solution to protect the antioxidant from damage. Homogenization inside the storage vessel was achieved by rolling in two opposite directions for 15 min before storage. During storage, samples were taken out periodically and different quality parameters such as peroxide value, density, kinematic viscosity, acid number, calorific value and flash point were determined according to standard methods (AOAC, 1990; ASTM).

RESULTS AND DISCUSSION

Rapid Oxidative Stability of Biodiesel

Rapid Induction Period (RIP) tests (plot of conductivity against time) of biodiesel samples without and with additives are shown on Figs. 1 – 6. The data from the Rancimat tests were widely varied ranging from 0.0 – 6h NME and 0.0 – 0.9h for RME, while for 0.5% TBHQ and 0.1% Ecotive the test were varied between 0.00 – 6.5h and 0.0 – 7.5h respectively. The stability of biodiesel is likely poorer than fossil diesel and blending of biodiesel in fossil diesel affects the stability of fuel significantly. Chemically, biodiesel is an ester molecule and more prone to be hydrolyzed to alcohol and acid in the presence of air or oxygen. Presence of alcohol will lead to reduction in flash point and presence of acid will increase acid number. In either of the cases, the product will become off specification. A comprehensive storage stability study of biodiesel was carried out to assess the degradation of biodiesel during storage and evaluate the effect of additive to improve the storage stability.

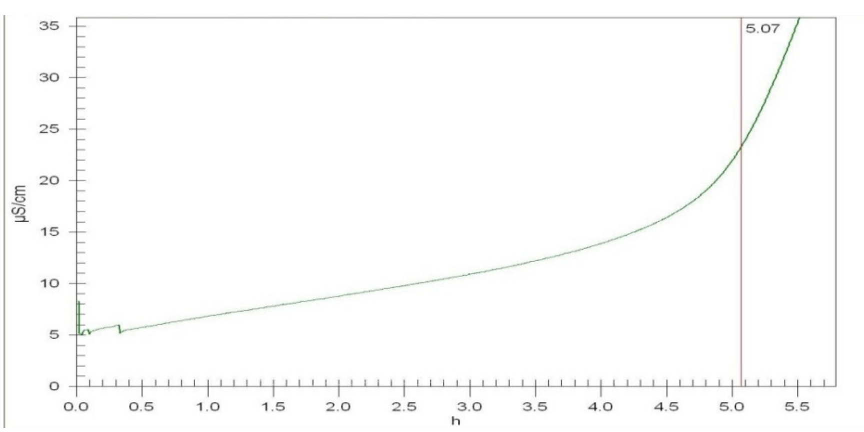

Figure 1: Rapid induction period of NME

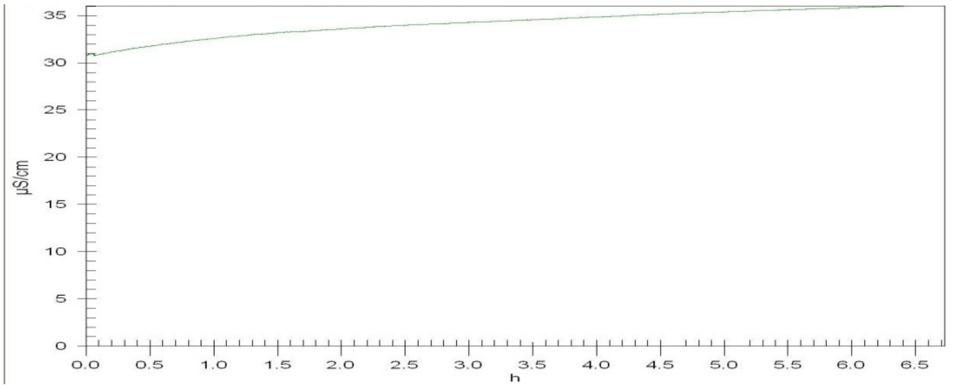

Figure 2: Rapid induction period of NME with 0.5% TBHQ

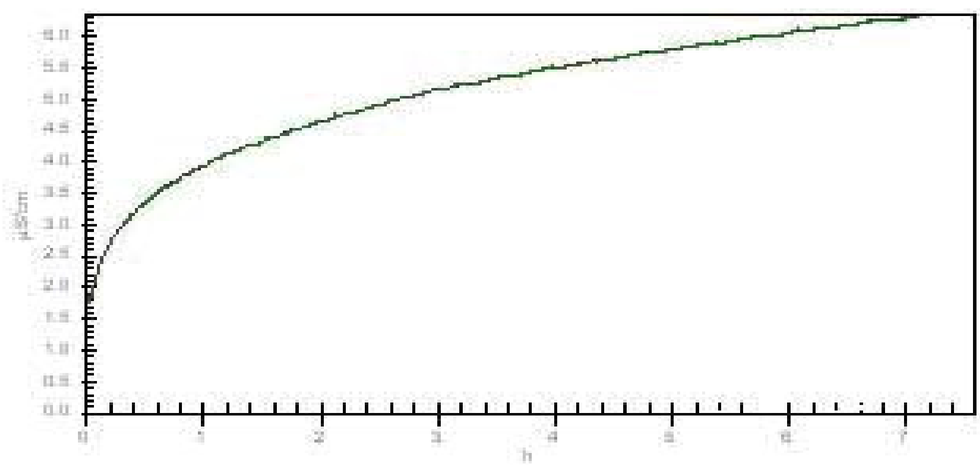

Figure 3: Rapid induction period of NME with 0.1% Ecotive

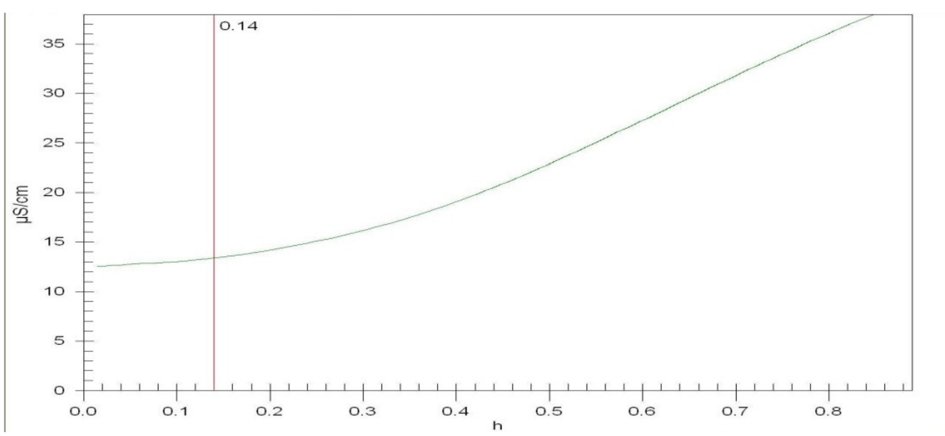

Figure 4: Rapid induction period of RME

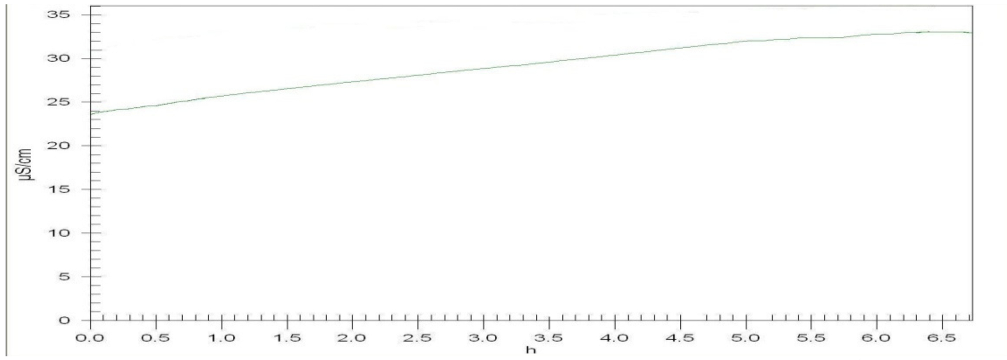

Figure 5: Rapid induction period of RME with 0.5% TBHQ

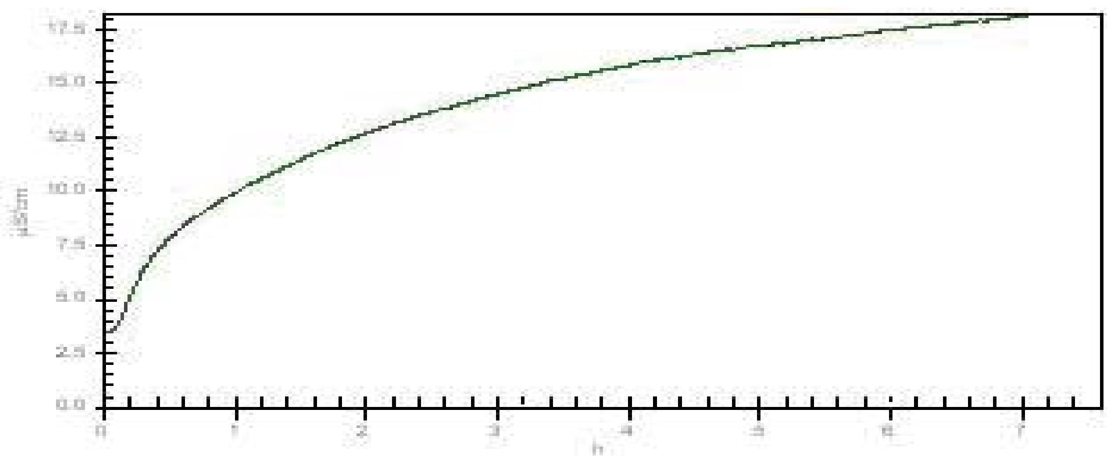

Figure 6: Rapid induction period of RME with 0.1% Ecotive

In the case of storage stability due to aerial oxidation, the changes in the several physico-chemical properties such as peroxide value, density, calorific value, flash point, acid number and viscosity can be expected. In order to introduce biodiesel on a large scale, it is necessary to describe its storage stability requirements because changes arising during oxidation and subsequent degradation can seriously impair the quality and performance of such products.

Long Term Storage Stability Testing

In order to study the long term storage stability of biodiesel, samples of NME, and RME were tested for peroxide value, density, acid number, viscosity and calorific value for a storage period of one year with and without additive. All these parameters were periodically evaluated on monthly basis.

Peroxide Value

Figs. 7 - 8 showed the variation of peroxide values of NME and RME with and without additive over a storage period of 12 months. The peroxide values were found to increase with storage period for all the three fuels. The rate of increase was been found in the order RME > NME. The two additives; Ecotive and TBHQ doped in the two biodiesel fuels slowed down the change in peroxide values of all the biodiesel fuels. The peroxide value in case of NME (16.8meq/kg), more than doubled in the fourth month, thus increased by 7.9 times at the end of the test. The value of peroxide value was 20.1 at the beginning of test and more than nine fold increase was recorded for RME.

Since peroxide value is an index of oxidation of vegetable oil or its derivative, it is obvious that oxidation of biodiesel takes place at a rapid rate due to inbuilt oxygen and unsaturated fatty acids. From the results, it is observed that the additive Ecotive has exhibited better results than TBHQ and retarded oxidation of all the two biodiesel fuels at a higher rate as compared to TBHQ. The increase in peroxide value was lowered by 1.76 and 2.01 times at the end of test for NME and RME fuels respectively with the addition of Ecotive. This implies that the fuels are more stable with additive of the antioxidants.

Density

Figures 9 – 10 represents the variation of density of NME and RME with and without additive over a storage period of 12 months. The densities were found to increase with storage period for all the three fuels. The increase was found to be highest for RME. The density in case of NME and RME at the beginning was 0.8824 and 0.8881 g/cc and increased to 0.8869 and 0.894 g/cc at end of the test. A similar trend of increase in density for all the fuels with the two additives was also observed. However, the effect of increase in density of both the biodiesel was slowed down by using the additive and with Ecotive, the increase of density was lower as compared to TBHQ.

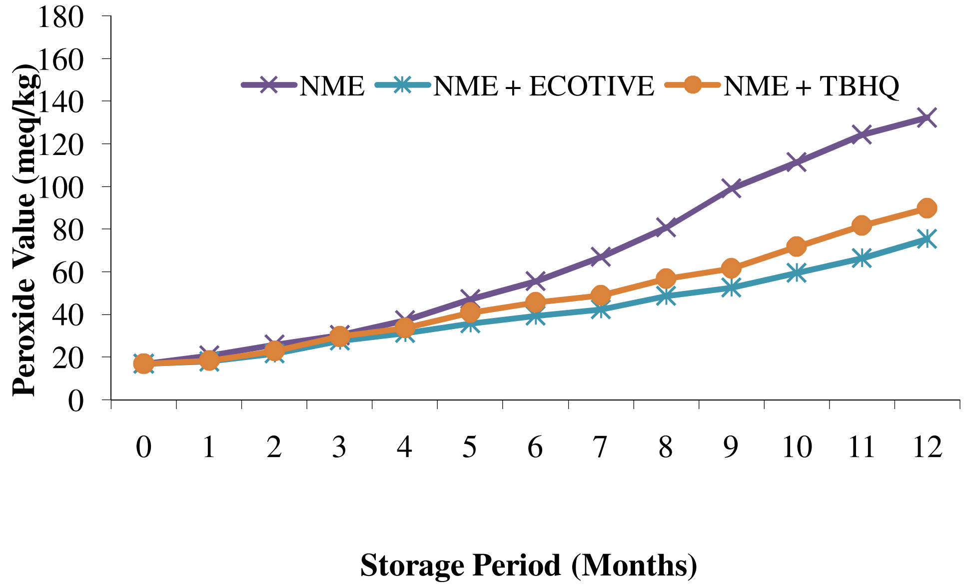

Figure 7 Effect of storage on peroxide value of NME

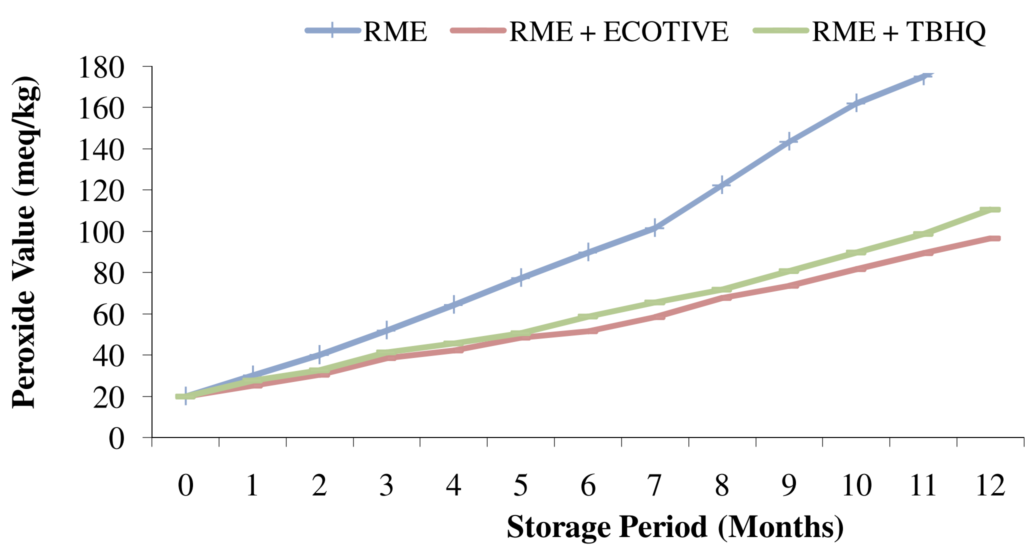

Figure 8 Effect of storage on peroxide value of RME

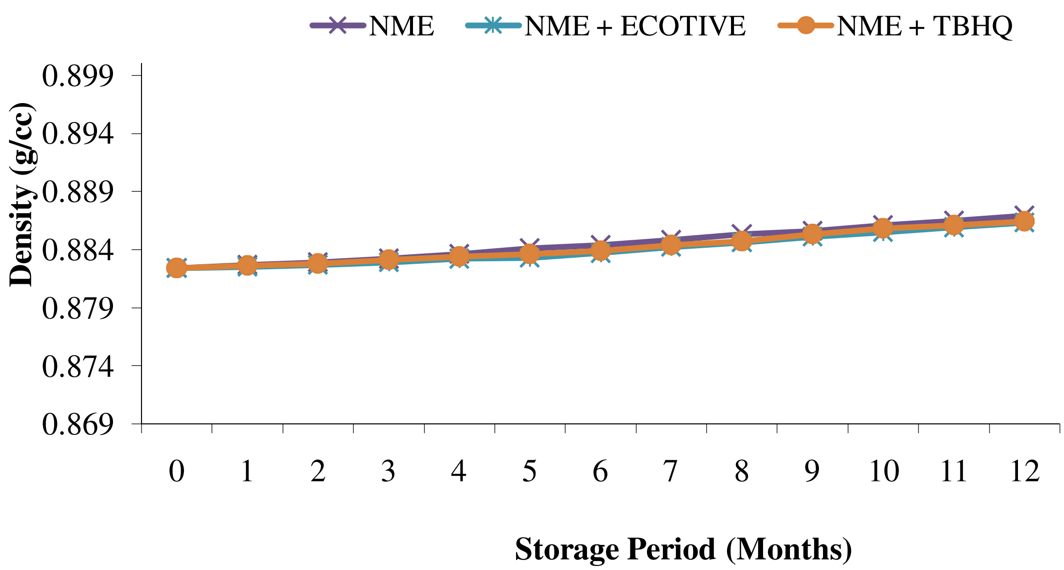

Figure 9 Effect of storage on Density of NME

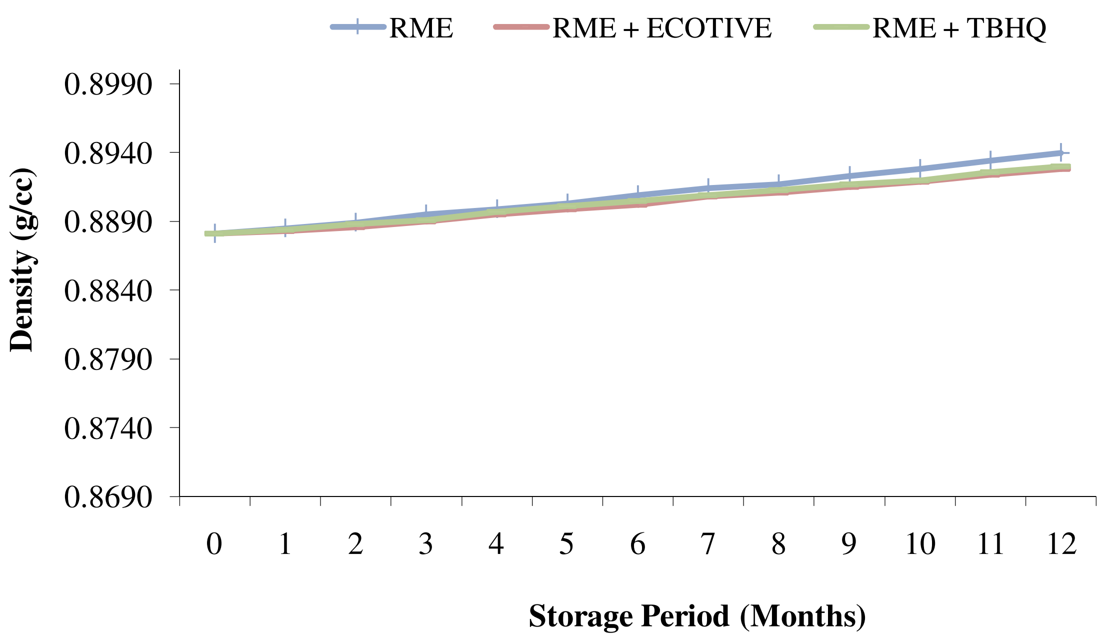

Figure 10 Effect of storage on Density of RME

Flash Point

Figs. 11 – 12 represent the variation of flash point of NME and RME with and without additive over a storage period of 12 months. The values of flash point were found to decrease with storage period for all the fuels. The flash point in case of NME and RME were 183 and 197°C respectively. The flash point of NME was 128°C in 7th month which is off ASTM specification. Similarly, the flash point of RME was 129°C in 4th month which is off ASTM specification. The additives Ecotive and TBHQ slowed down the decrease in flash point of all the biodiesel. Neem was off ASTM specification in 10th months and RME in 7th months. The results with TBHQ were inferior to the results with Ecotive.

Acid Number

Figure 13 – 14 represents the variation of acid number (AN) of NME and RME with and without additive over a storage period of 12 months. The Acid numbers were found to be increasing significantly with storage period for all the three biodiesel fuels. The Acid numbers in case of NME and RME 0.16 and 0.13 respectively. The NME reached to the AN value of 0.56 in 8th month was off ASTM specification. The RME was off ASTM specification in the third value having AN of 0.52. At end of the test, AN for NME and RME were 0.88 and 1.41 respectively giving 5 and 10 fold increase over the initial values. Both the additive, namely Ecotive and TBHQ has reduced the increase in AN for all the biodiesel samples.

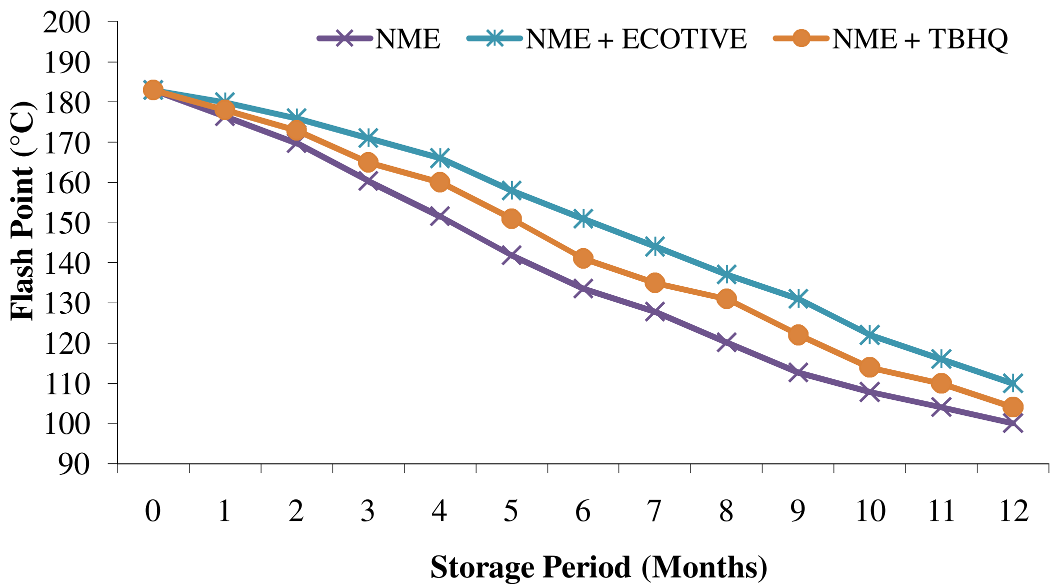

Figure 11 Effect of storage on Flash Point of NME

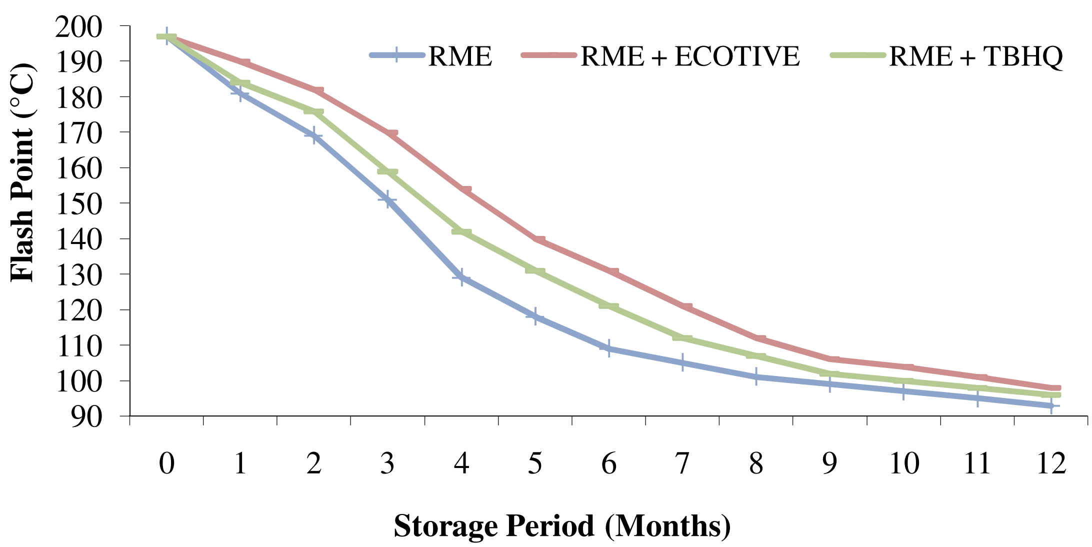

Figure 12 Effect of storage on Flash Point of RME

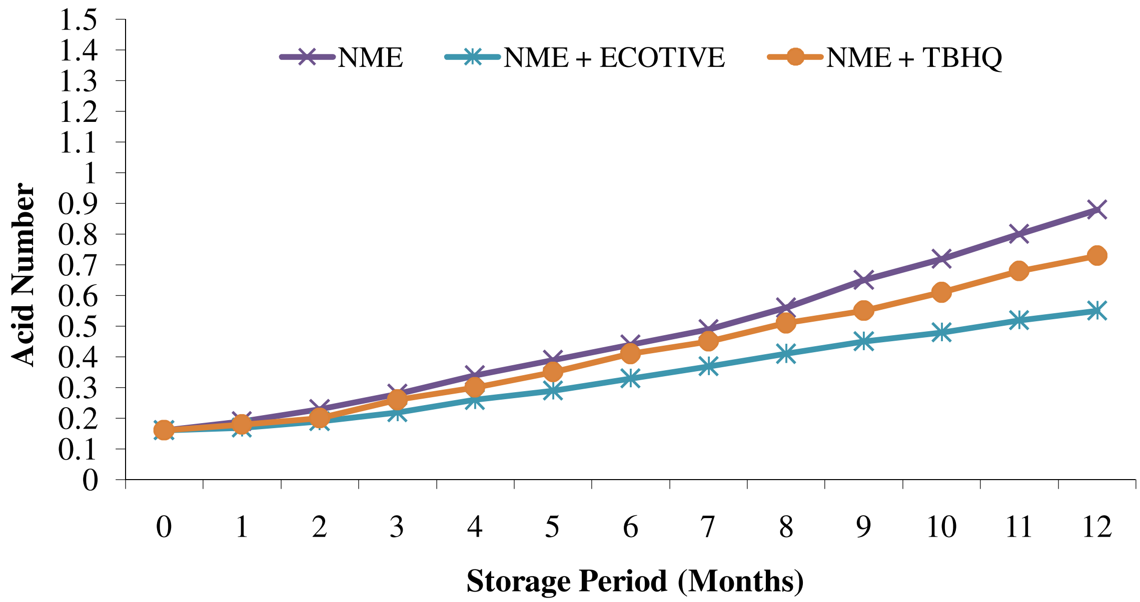

Figure 13 Effect of storage on Acid Number of NME

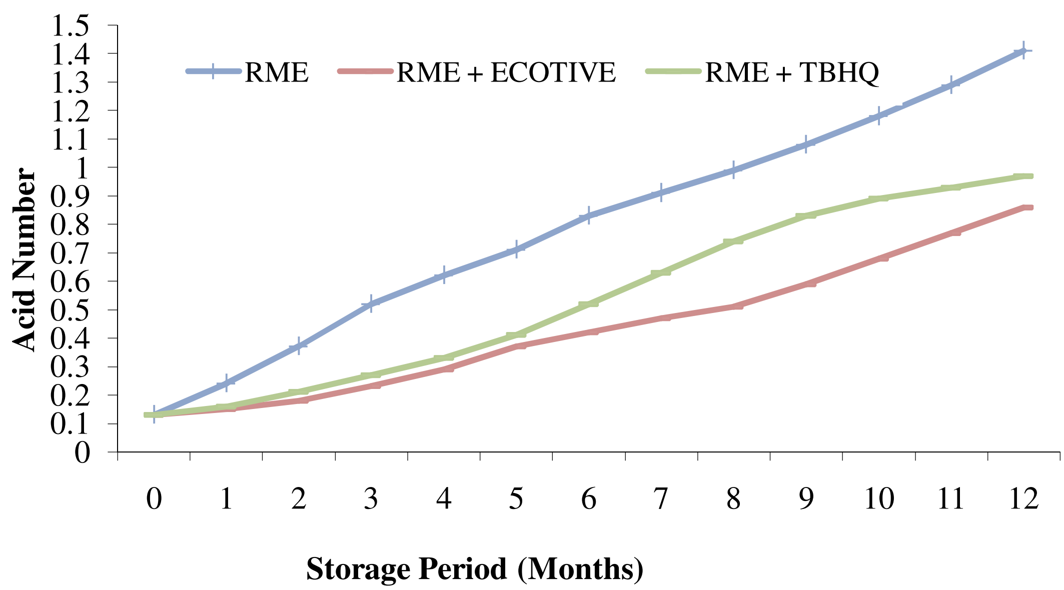

Figure 14 Effect of storage on Acid Number of RME

In fact with the use of additives, the duration at which biodiesel became off specification was advanced than without additive with Ecotive yielding better results.

Kinematic Viscosity The

Variation of kinematic viscosity of all the three fuels with and without additive over a storage period of 12 months is represented in Figures 13 - 14. The value of viscosity was found to be increasing with storage period for all the fuels. The increase was found to be highest for RME. The viscosities in case of NME and RME at beginning were 5.27 and 5.27cSt respectively. The NME reached to the value of 6.12 in 9th month and became off specification. The viscosity for RME was 6.03 in 3rd month and the fuel was off ASTM specification. At end of the test, the viscosities for NME and RME were 6.4 and 7.16cSt. Respectively indicating an increase of around 21 and 36% from the beginning. The additives Ecotive and TBHQ, slowed down the increase in viscosity for all the biodiesel with Ecotive exhibiting better results than TBHQ.

Calorific Value

The variation of calorific value of JME, NME and RME fuels with and without additives over a period of 12 months is represented in Figures 15 – 16. The calorific values were found to be decreasing with storage period both for JME, NME and RME fuels. The rate of decrease was found to be more for RME than for NME and JME. The calorific values in case of JME, NME and RME at 0 months were 40.43, 40.178 and 39.65 MJ/kg respectively.

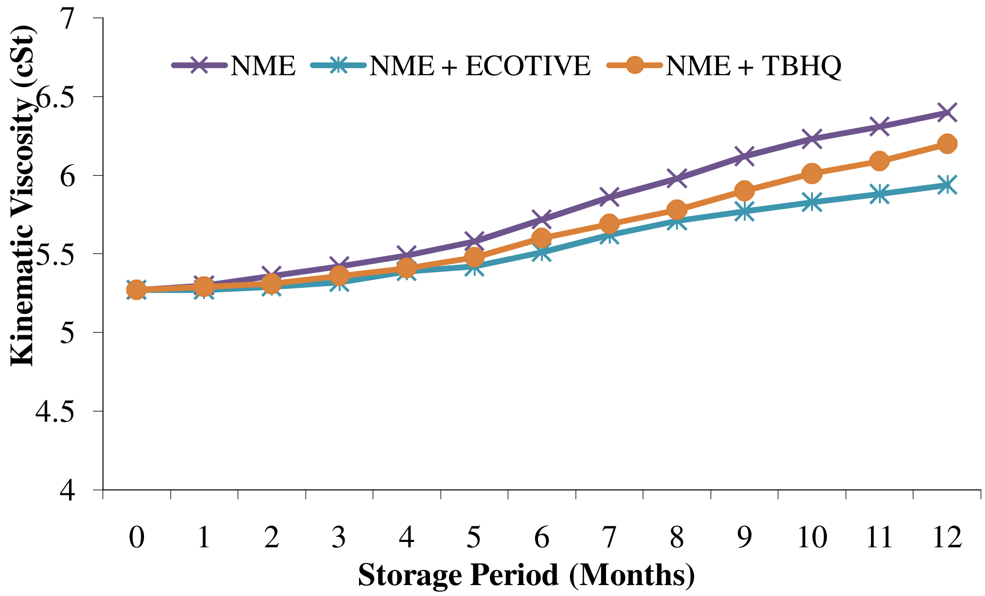

Figure 13 Effect of storage on Kinematic Viscosity of NME

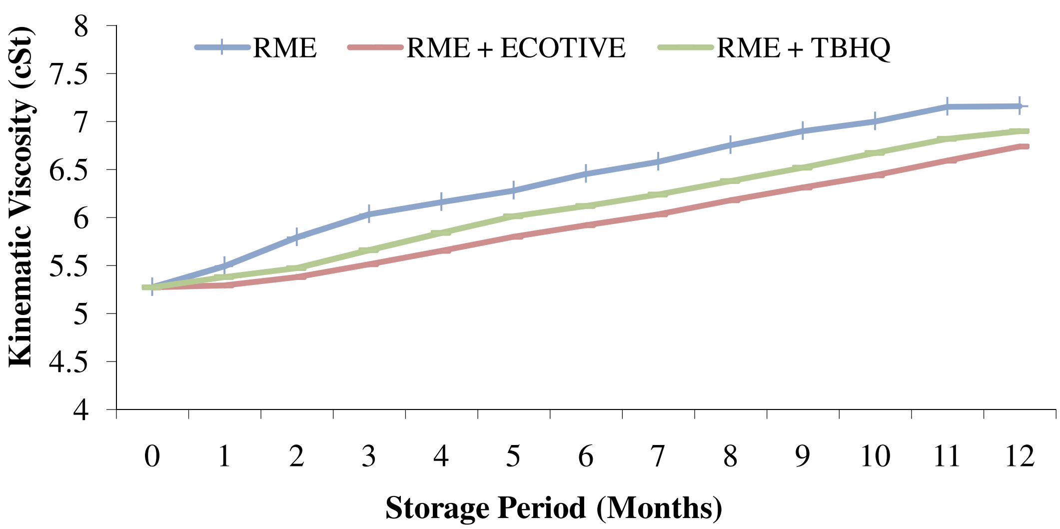

Figure 14: Effect of storage on Kinematic Viscosity of RME

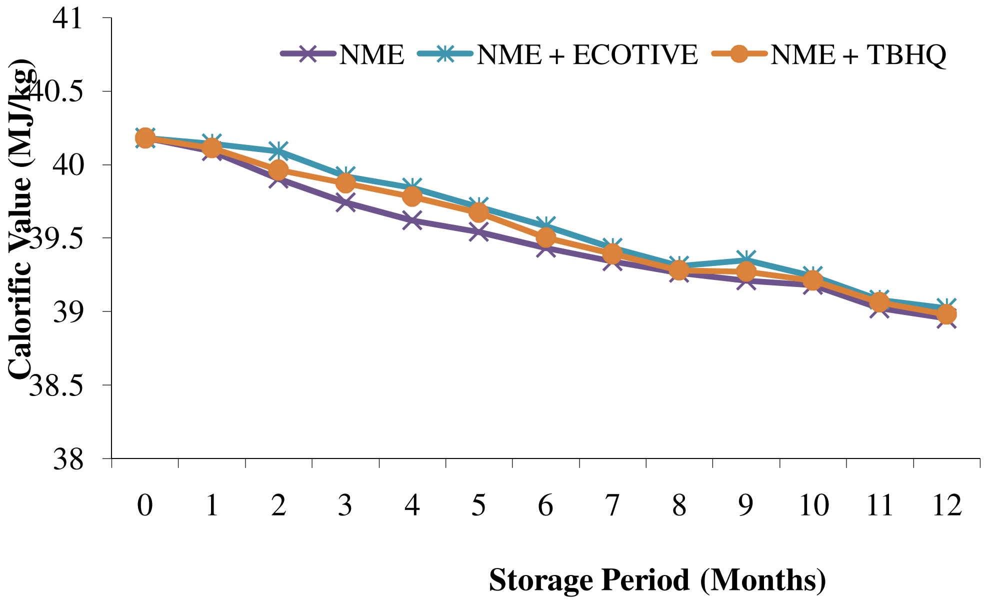

Figure 15 Effect of storage on Calorific Value of NME

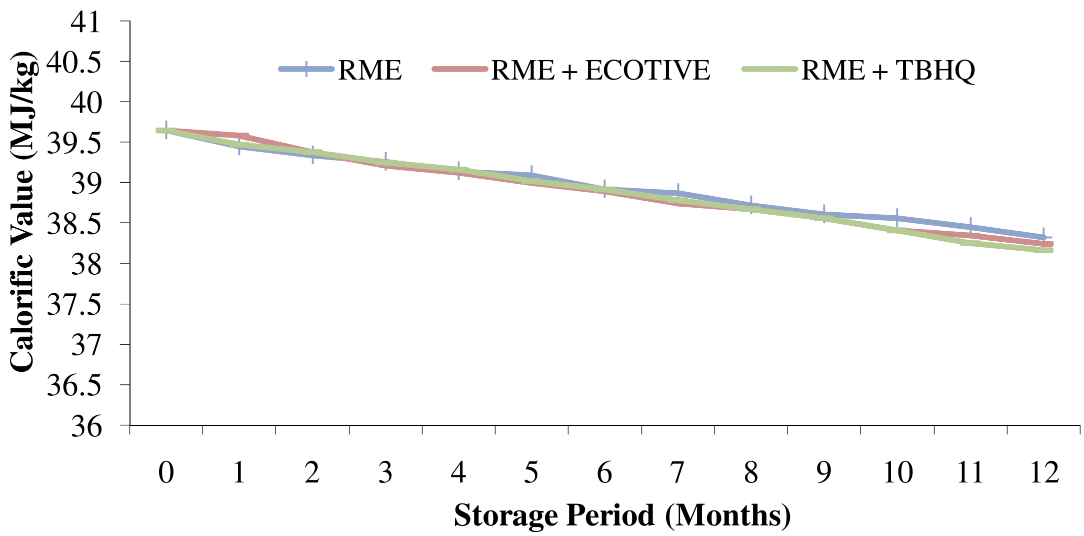

Figure 16 Effect of storage on Calorific Value of RME

At the end of the test, calorific values for JME, NME and RME were 39.24, 38.95 and 38.32 MJ/kg respectively. The additives Ecotive and TBHQ, slowed down the decrease in calorific value for the biodiesel fuels.

CONCLUSION

From the studies, there was no biodiesel sample that could pass the 6 hrs oxidation test with neem biodiesel exhibiting the best oxidation stability. Both additives, namely 0.5% TBHQ and 0.1% Ecotive, increased the oxidation stability of all the two biodiesel samples to more than 6hrs. The one year storage stability study revealed that peroxide value, density, viscosity and acid number increased for all the methyl esters with time. However, the calorific value was found to be decreasing for all the samples. The rate of change of different physico-chemical properties was found to be less for all the biodiesel samples blended with an additive. However, Ecotive appeared to be a better additive as compared to TBHQ for increasing the shelf life of biodiesel.

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