Int J Energy Environ Eng (2016) 7:85–91
DOI 10.1007/s40095-015-0191-z

ORIGINAL RESEARCH

Effects of antioxidants on oxidation and storage stability of *Croton megalocarpus* biodiesel

W. O. Osawa[1] · P. K. Sahoo[3] · J. M. Onyari[1] · F. J. Mulaa[2]

Received: 11 February 2015 / Accepted: 9 September 2015 / Published online: 5 November 2015

Abstract The effects of antioxidants and storage on oxidation stability of croton biodiesel and its blends with petro-diesel were determined using PetroOxy equipment. The biodiesel and blends were kept in Pyrex reagent bottles and stored in a metallic locker at room temperature for 8 weeks, a condition that imitated ordinary storage environment in tanks before use. The oxidation stability indices of the biodiesel and blends were determined by measuring Rancimat induction periods for 8 weeks at intervals of 2 weeks. Although the Rancimat induction period for freshly prepared biodiesel of 4 h was higher than the commonly used American standard (ASTM D6751) limit of 3 h, it was lower than the European standard (EN 14214) of 6 h. The induction periods of B50 and lower blends were, however, equal to or greater than 6 h. The Rancimat induction periods for biodiesel with 100 ppm antioxidants were 5.6, 6.8 and 7.8 h for Butylated hydroxyanisol (BHA), Propyl gallate (PRG) and Pyrogallol (PYG), respectively, while the Rancimat induction periods for biodiesel with 1000 ppm antioxidants were 6.8, 8.2 and 10 h for BHA, PRG and PYG, respectively. The oxidation stability index for neat biodiesel decreased by 45 % while that for biodiesel with 1000 ppm antioxidants depreciated by 16, 12.2 and 20.59 % for PYG, PRG and BHA, respectively, during the 8-week storage period. A more rapid decline in oxidation stability was observed in the biodiesel and blends without antioxidants than those with antioxidants. The results from this study showed that the use of appropriate concentrations of suitable antioxidants can greatly improve the oxidation stability of biodiesel and blends which can therefore be stored over longer periods of time before use without undergoing extensive and deleterious oxidative deterioration.

Keywords Croton biodiesel · Oxidation stability · Antioxidants · Storage stability

Abbreviations

ASTM	American Society for Testing and Materials
B5	5 % biodiesel, 95 % diesel blend
B10	10 % biodiesel, 90 % diesel blend
B15	15 % biodiesel, 85 % diesel blend
B20	20 % biodiesel, 80 % diesel blend
B50	50 % biodiesel, 50 % diesel blend
B100	100 % biodiesel
BHA	Butylhydroxyanisole
BHT	Butylated hydroxytoluene
EN	European Standard
IP	Induction period
OSI	Oxidation stability index
PRG	Propyl gallate
ppm	Parts per million
PYG	Pyrogallol
TBHQ	*tert*-Butylhydroquinone

✉ W. O. Osawa
ottaosawa@yahoo.com

[1] Department of Chemistry, College of Biological and Physical Sciences, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya

[2] Department of Biochemistry, College of Medical and Health Sciences, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya

[3] Department of Mechanical Engineering, University of Petroleum and Energy Studies, Dehradun, Uttarakhand 248007, India

Introduction

The concept of using biofuels in internal combustion engines was established by the inventor of diesel engine, Rudolf Diesel who showed that peanut oil could be effectively used in a diesel engine at an exhibition in Paris in 1900. However, due to adequate supply and lower cost of petro-diesel at that time, no substantial research activities were conducted on biofuels [1]. The ever-escalating fossil fuel costs and strict world guidelines on exhaust emissions have enhanced the need for substitution of fossil fuels with less polluting and readily available renewable fuels for internal combustion engines [2]. Since the world's energy requirement is constantly increasing, sustainable alternative and environmental friendly sources of fuels that can satisfy the rising demand should be identified [3].

Biodiesel has become very crucial owing to higher demand on existing petroleum reserves and lower hazardous emissions as compared to petroleum diesel-fuelled engines [4]. Biodiesel prepared from low-cost non-edible oils, restaurant waste and animal fats can provide substitute fuel that is technically and environmentally acceptable and economically competitive [5]. Although biodiesel-fuelled engines are less polluting than petro-diesel, biodiesel readily undergoes oxidation. The oxidation leads to increased acidity and formation of insoluble gums and sediments that can plug fuel filters [6]. Biodiesel prepared from many feedstocks is generally more prone to oxidation than petro-diesel unless modified or treated with antioxidants. Biodiesel dealers are therefore concerned that it may form sediment during storage while equipment operators fear that sediment and gum may form during use and cause engine damage [7].

The vulnerability of biodiesel to oxidation during storage is due to diverse levels of unsaturation in its structure [8]. The rate of oxidation of biodiesel depends both on the number of double bonds and their positions within the molecule [9]. Oxygen readily gets attached to the bis-allylic site and initiates autoxidation chain reaction sequence. Thus, the oxidation stability of lipids such as biodiesel mainly depends on the number of bis-allylic sites in the unsaturated compound [10]. The overall oxidation stability of biodiesel is also affected by conformational *cis–trans* isomerization. Although the *trans*-unsaturation is more stable than the *cis*-unsaturation, conjugated *trans*-unsaturations are more sensitive to oxidation than *cis*-unsaturations [11].

Biodiesel oxidation is initiated by the formation of radicals at bis-allylic sites which readily isomerize to form stable intermediate compounds that reacts with oxygen to form peroxide [12]. The biodiesel (esters) is then destroyed and the secondary oxidation products formed include aldehydes, ketones, low molecular weight acids and volatile organic compounds. The oxidation products finally polymerize to form sludge which makes the biofuel unsuitable for use and may cause damage to the engine [13]. The rate of oxidation of biodiesel depends on factors such as temperature, light, radiation intensity and presence of natural antioxidants. Antioxidants bind free radicals thereby stabilizing fatty peroxyradicals and stopping oxidation chain reactions [10, 13]. The oxidation of lipids such as biodiesel decreases their fuel quality due to the formation of hazardous secondary products during storage [14]. The duration over which lipid containing compounds such as biodiesel can be stored before use depends on their stability. However, lipids can also be protected from oxidation by addition of antioxidants immediately after preparation [15].

Terry et al. [16] reported that at advanced levels of oxidation, biodiesel blends can separate into two phases which can cause fuel pump and injector problems. Sarin et al. [17] reported that synthetic antioxidants were more effective at improving the oxidation stability of Jatropha methyl ester than natural antioxidants. Hess et al. [18] reported that apart from improving the oxidation stability of biodiesel, addition of certain commercial antioxidants led to reduction in nitrogen oxides engine emissions. Karavalakis et al. [19] reported a sharp decrease in fuel stability of a commercial biodiesel over a 10-week storage period. They observed that addition of antioxidants greatly improved the stability. Kivevele et al. [20] reported that although addition of antioxidants greatly improved the oxidative stability of croton biodiesel, it had little effects on engine exhaust emissions.

The most commonly used synthetic antioxidants in cooking oils to prevent oxidation are essentially phenols such as Butylated hydroxyanisol, *tert*-Butyl hydroquinone, Butylated hydroxytoluene, Propyl gallate and Pyrogallol [21]. The synthetic phenols disrupt free-radical oxidation chain reactions by contributing hydrogen from the phenolic hydroxyl groups thereby forming stable free radicals which do not promote oxidation of lipids. It is therefore important to add the phenolic antioxidants either immediately after preparation of the product or during the manufacturing process since they neither have the ability to reverse oxidation of the oils nor to suppress hydrolytic oxidation which involve enzymatically catalysed hydrolysis of fats [22].

Many studies have shown that croton biodiesel and blends can be effectively used as an alternative to petro-diesel. Aliyu et al. [23] reported that the performance of croton biodiesel was comparable to pure diesel fuel although the biodiesel produced less smoke and nitrogen oxides. Osawa et al. [24] reported that croton biodiesel blends of up to 50 % with petro-diesel can be effectively used as an alternative fuel without compromising the engine performance. Since the oxidation and storage

stability determine the duration that a particular fuel can be stored or used without causing any hazardous effects in internal combustion engines, it is important that comprehensive studies are performed under different conditions in order to identify the most suitable storage conditions. Improvement of oxidation and storage stability can enable the biodiesel to be kept over a longer duration of time without fear of formation of oxidation products which can either damage engine or lower its fuel qualities. In this study, the effects of five commercial antioxidants on oxidation and storage stability of croton biodiesel and its blends with petro-diesel were investigated over a period of 8 weeks under ordinary storage conditions.

Materials and methods

Materials and reagents

Croton biodiesel was freshly prepared through a two-stage process from croton oil as described by Osawa et al. [25]. Five common and widely used synthetic antioxidants were initially employed in the preliminary tests during this study. The analytical grade commercial antioxidants, Pyrogallol (PYG), Propyl gallate (PRG), Butylated hydroxyanisol (BHA), Butylated hydroxytoluene (BHT) and *tert*-Butylhydroquinone (TBHQ) from Merck Chemicals used in this study were supplied by HV Technologies. The petro-diesel used for blending was purchased from an Indian Oil petrol station in Dehradun City in Uttarakhand State, India.

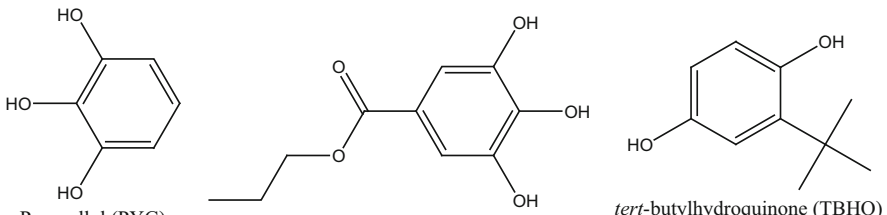
Sample preparation

Samples of biodiesel blends were made by mixing petro-diesel with freshly prepared dry croton biodiesel in various proportions. The samples were separately mixed with accurately weighed antioxidants to form different concentrations of the antioxidant solution in parts per million (ppm). Control samples without antioxidants were also prepared.

Experimental procedure

The effects of commercial antioxidants on oxidation stability of croton biodiesel was initially tested by preparing 1000 ppm solutions of the five commonly used commercial antioxidants in different portions of freshly prepared biodiesel samples [15, 17, 22]. The samples with antioxidants and control sample were separately subjected to oxidative stability test in PetroOxy equipment.

Exactly 5 ml of each sample was mixed with oxygen in a sealed test chamber at a pressure of 700 kPa and temperature of 140 °C in a PetroOxy equipment. These conditions initiated a very fast artificial aging process, which was measured by a pressure drop within the chamber. The oxidation stability was determined by measuring the time between start of the test and the time at which a pressure drop of 10 % below the maximum pressure was detected (induction period). The three antioxidants that gave the best results were selected for further studies on storage stability of the biodiesel and its blends. The molecular structures of the five synthetic antioxidants that were used for this study are shown below:



The biodiesel and blends were kept in a metallic locker at room temperature for 8 weeks. The storage conditions reflected ordinary environment under which biodiesel could be kept in metallic or plastic tanks before use. The effects of storage and addition of antioxidants on the oxidation stability were determined at regular intervals of 2 weeks. Figure 1 shows the PetroOxy

Fig. 1 PetroOxy equipment

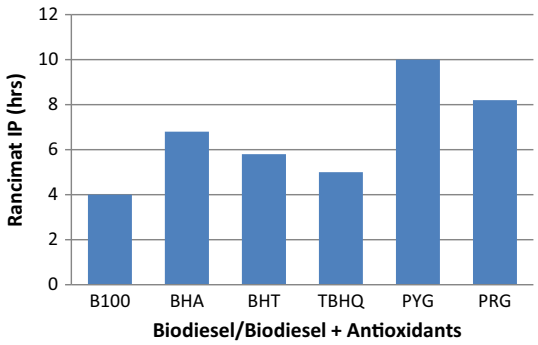


Fig. 2 Rancimat induction periods for Croton biodiesel with various antioxidants

equipment that was used for the determination of oxidative stability.

Results and discussion

Effect of antioxidants on the oxidative stability of croton biodiesel

Figure 2 shows the effects of the five selected commercial antioxidants on oxidation stability of croton biodiesel (B100). It was noted that although the oxidation stability index (OSI) of croton biodiesel satisfied the ASTM-6751 limit of 3 h, it did not meet the EN-14112/IS-15607 standard of 6 h. The low oxidation stability of croton biodiesel can be explained by the high proportion of polyunsaturated fatty acid methyl ester of about 78 % which makes it quite susceptible to oxidation [8, 26].

All the antioxidants employed in this study boosted the oxidation stability of croton biodiesel as shown by the higher Rancimat induction periods (IPs) for croton biodiesel with antioxidants as compared to those without antioxidants. Among the five antioxidants employed in this study, Pyrogallol (PYG) resulted in the highest increase in IP followed by Propyl gallate (PRG), Butylated hydroxyanisol (BHA), Butylated hydroxytoluene (BHT) and *tert*-Butylhydroquinone (TBHQ) respectively. Karavalakis et al. [27] reported a similar trend for Pyrogallol and Propyl gallate.

Liang et al. [28] reported that the antioxidant abilities of phenolic antioxidants depends on the number of –OH groups occupying 1, 2 or 1, 4 positions in the aromatic ring as well as the capacity and electronic characteristics of the ring substituent present. They explained that the active –OH groups provide protons which prevents formation of free radicals or interferes with propagation of free radical and hence reduce the speed of oxidation.

The lower antioxidant ability of BHA as compared to PYR and PRG can be explained by the fact that BHA has only one –OH group directly bonded to the aromatic ring while both PYR and PRG have three –OH groups each, two of which are on 1, 2 positions on the aromatic ring. The presence of more –OH directly attached to the aromatic ring in PYG and PRG provides more sites for reaction with free radical to form stable molecules and hence prevent the oxidation of the methyl ester chain of biodiesel [13, 22, 29].

Although TBHQ also has –OH groups bonded to the aromatic ring on the 1, 4 positions, its lower antioxidant activity as compared to BHA can be explained by undesirable prooxidant interaction with biodiesel and blends, which in some cases can result to a reduction in the oxidation stability of biodiesel [26]. The Rancimat IPs for croton biodiesel with either *tert*-butylhydroquinone (TBHQ) or Butylated hydroxytoluene were both lower than the European (EN-14112/IS-15607) recommended value of 6 h for biodiesel.

Effect of 1000 and 100 ppm antioxidants on storage stability of biodiesel

The initial Rancimat IPs for biodiesel with 100 ppm antioxidants were 5.6, 6.8 and 7.8 h for BHA, PRG and PYG, respectively, while that for the biodiesel with 1000 ppm antioxidants were 6.8, 8.2 and 10 h for BHA, PRG and PYG, respectively. Thus an increase in concentration of antioxidants resulted in improved oxidation stability, with PYG providing the highest percentage increase of 28 %.

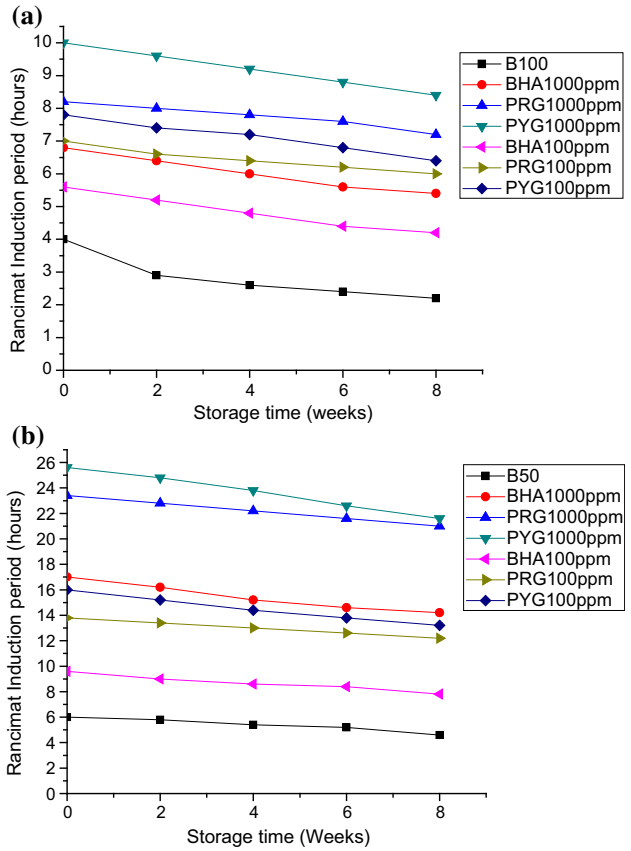


Fig. 3 **a** Effect of 1000 and 100 ppm antioxidants on storage stability of biodiesel, B100. **b** Effect of 1000 and 100 ppm antioxidants on storage stability of B50 blend

The oxidation stabilities of the biodiesel and blend samples decreased with increase in storage period. The greatest percentage decrease in Rancimat IP of 45 % during the 8 weeks storage period was recorded on the neat biodiesel without antioxidants. The Rancimat IPs for the biodiesel with 1000 ppm antioxidants depreciated by 16, 12.2 and 20.59 % while that with 100 ppm antioxidants depreciated by 17.95, 14.28 and 25 %, for PYG, PRG and BHA, respectively. Thus a more rapid decline in the oxidation stability was observed in the biodiesel without antioxidants than that with antioxidants. A similar trend in oxidation stability of commercial biodiesel was reported by Karavalakis et al. [19] over a 10-week storage period. Figure 3a shows the effects of storage and addition of 100 and 1000 ppm antioxidants on the oxidation stabilities of biodiesel, B100.

Effect of 1000 and 100 ppm antioxidants on storage stability of B50 blend

The B50 blend which originally had a Rancimat IP of 6 h depreciated by 23.33 % to a Rancimat IP of 4.6 h during the 8-week storage period. The Rancimat IPs for the B50 blends with 100 ppm antioxidants depreciated from 9.6 to 8, 13.8–13 and 16–13.8 h for BHA, PRG and PYG, respectively, while the blends with 1000 ppm antioxidants depreciated from 17 to 14, 23.4–20.2 and 25.6–19.6 h for BHA, PRG and PYG, respectively, during the 8-week storage period. Both the 100 and 1000 ppm solutions of the three antioxidants provided effective stability for the B50 blend since the final oxidation stability index (OSI) was greater than the minimum recommended value of 6 h at the end of the 8-week storage period. Figure 3b shows the effects of storage and addition of 100 and 1000 ppm antioxidants on the oxidation stability of biodiesel blend, B50.

Effect of 100 ppm antioxidants on storage stability of B20, B15 and B10 blends

All the biodiesel blends displayed a general decrease in oxidation stability with increase in storage period. The Rancimat IP for biodiesel blends B20, B15 and B10 without antioxidants depreciated by 17.24, 15.49 and 14.43 %, respectively, during the 8-week storage period. The percentage decrease in oxidation stability however decreased with increase in concentration of petro-diesel in the blends due to increased stability of petro-diesel. A more rapid decline in oxidation stability was observed in biodiesel blends without antioxidants than those with antioxidants. These results were consistent with those reported by Karavalakis et al. [19].

Although Pyrogallol provided the maximum initial improvement in oxidation stability, the rate of depreciation of biodiesel blends with Pyrogallol was slightly faster than those with Propyl gallate. It was also observed that the biodiesel blends with Pyrogallol slightly turned dark on storage. This could be probably due to formation of more stable radicals of Propyl gallate with the biodiesel molecules than Pyrogallol. Figure 4a–c shows the effect of antioxidants and storage on the oxidative stabilities of B20, B15 and B10 blends, respectively. The petro-diesel used for blending in this study had Rancimat IP of 37.6 h. Thus both 100 ppm Pyrogallol and Propyl gallate effectively maintained the oxidation stability of B10 biodiesel blend above that of petro-diesel during the 8-week storage period.

Conclusions

Although the oxidation stability of croton biodiesel satisfied the ASTM D6751 limit of 3 h, it did not satisfy the EN-14112/IS-15607 Rancimat induction period standard of 6 h. The oxidation stability of freshly prepared neat biodiesel also reduced at a very fast rate of 45 % during the 8-week storage period to an oxidation stability index of

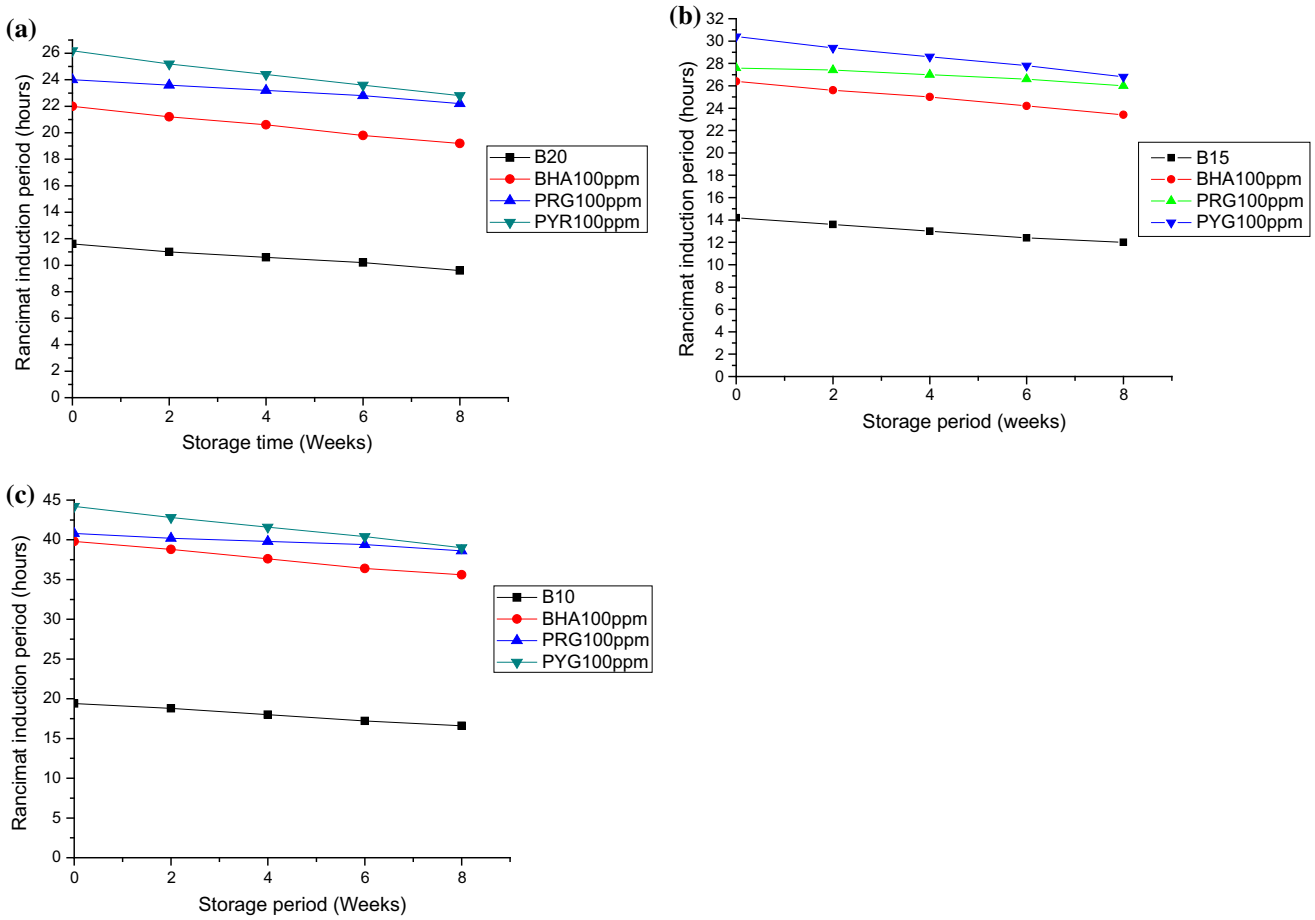


Fig. 4 **a** Effect of 100 ppm antioxidants on storage stability of B20 blend. **b** Effect of 100 ppm antioxidants on storage stability of B15 blend. **c** Effect of 100 ppm antioxidants on storage stability of B10 blend

2.2 h. A more rapid decline in oxidation stability occurred in the croton biodiesel and its blends without antioxidants than those with antioxidants implying that presence of antioxidants greatly enhanced the stability of biodiesel and its blends. The lower oxidation stability and rapid deterioration of croton biodiesel over the 8-week storage period showed that it required some improvement through addition of adequate amount of antioxidants. Although the B50 and lower blends of the biodiesel had Rancimat IP values equal to or greater than the minimum recommended value of 6 h, the IP for the B50 blend reduced from 6 to 4.6 h over the 8-week storage period.

Among the three antioxidants investigated in this study, Pyrogallol was the most effective in improving the oxidation stability of the biodiesel and blends since it resulted in the highest increase in oxidation stability followed by Propyl gallate and Butylhydroxyanisole respectively. However, the oxidation stability of the biodiesel and blends with Pyrogallol depreciated slightly much faster than those with Propyl gallate during the 8-week storage period, suggesting that Propyl gallate provided the best storage stability as shown by the lowest percentage decrease in induction periods during the 8-week storage period. The B10 blend could however, be effectively protected by either 100 ppm PYG or PRG since the Rancimat IPs of the blend with either antioxidant at the end of the 8-week storage period were both higher than that of the petrodiesel used for blending.

The results from this study showed that use of appropriate concentrations of suitable antioxidants can greatly help in improving the oxidation and storage stability of croton biodiesel and its blends under ordinary storage conditions. The addition of antioxidants can therefore be employed to enable croton biodiesel and blends to be stored over longer duration of time before use without undergoing extensive and deleterious oxidative deterioration. Since the speed of oxidation of biodiesel depends on factors such as temperature, light and radiation intensity, studies should be undertaken to identify suitable concentrations of antioxidants that can effectively provide long-term storage stability of croton biodiesel and blends under different conditions. Since previous studies have shown that croton biodiesel blends can be used as an effective alternative to biodiesel and addition of antioxidants does

not result in any hazardous emissions, the determination of suitable antioxidants can immensely contribute in increasing the commercial production and use of the biodiesel blends. In addition to improving the rural economies, commercial production and widespread use of croton biodiesel blends can greatly reduce the pollution effects of fossil fuels by providing readily available renewable fuel and hence reduce the ever increasing demand on existing petroleum reserves.

Acknowledgments The authors wish to express their appreciation to National Council of Science, Technology and innovation (NACOSTI), Kenya and the Government of India for the award of research grant and CV Raman Fellowship respectively. The authors also wish to express their gratitude to the management and staff, University of Petroleum and Energy Studies, India, for their hospitality in hosting the corresponding author during the Fellowship. Finally, the authors wish to thank all staff in biodiesel and chemistry laboratories for all assistance offered during the fellowship and permission to use the PetroOxy equipment for analysis of oxidation and storage stability.

References

1. Agarwal, A.K., Das, L.M.: Biodiesel development and characterization for use as a fuel in compression ignition engines. ASME Gas Turbines Power. **123**, 440–447 (2000)
2. Sahoo, P.K., Das, L.M.: Process optimization for biodiesel production from Jatropha, Karanja and Polanga oils. Fuel **88**, 1588–1594 (2009)
3. Taher, H., Al-Zuhair, S., Al-Marzouqi, H. A., Haik, Y., Farid, M. M.: A review of enzymatic transesterification of microalgal oil—based bioldiesel using supercritical technology. *Enzyme Res*. 1–18 (2011)
4. Park, J.-Y., Kim, D.-K., Lee, J.-P., Park, S.-C., Kim, Y.-J., Lee, J.-S.: Blending effects of biodiesels on oxidation stability and low temperature flow properties. Bioresour. Technol. **99**, 1196–1203 (2008)
5. Modi, M.K., Reddy, J.R.C., Rao, B.V.S.K., Prasad, R.B.N.: Lipase-mediated conversion of vegetable oils into biodiesel using ethyl acetate as acyl acceptor. Bioresour. Technol. **98**, 1260–1264 (2007)
6. Monyem, A., Van Gerpen, J.H.: The effect of biodiesel oxidation on engine performance and emissions. Biomass Bioenergy **20**(4), 317 (2001)
7. McCormick, R.L., Ratcliff, M., Moens, L., Lawrence, R.: Several factors affecting the stability of biodiesel in standard accelerated tests. Fuel Process. Technol. **88**, 651–657 (2007)
8. Karavalakis, G., Stournas, S., Karonis, D.: Evaluation of the oxidation stability of diesel/biodiesel blends. Fuel **89**, 2483–2489 (2010)
9. Abderrahim, B., Mercedes, M., Jose, A.: Long storage stability of biodiesel from vegetable and used frying oils. Fuel **86**, 2596–2602 (2007)
10. Shah, R., Mahajan, D., Patel, S., Ball, J., Colantuoni, V., Maraj, R.: Oxidation stability in biodiesel: a brief review of current technology. Biodiesel Mag. (2009)
11. Fang, H.L., McCormick, R.L.: Spectroscopic study of biodiesel degradation pathways. SAE Technical Paper 2006-01-3300
12. Devinder, R.S.M., Patel, S., Ball, J., Colantuoni, V., Maraj, R.: Oxidation stability in biodiesel: a brief review of current technology. Biodiesel Mag. 2009
13. Sendzikiene, E., Makareviciene, V., Janulis, P.: Oxidation stability of biodiesel fuel produced from fatty wastes. Polish J. Environ. Stud. **14** (2005)
14. Frankel, E.N.: Lipid oxidation. Prog. Lipid Res. **19**, 1–22 (1980)
15. Mbatia, B., Adlercreutz, P., Mulaa, F., Mattiasson, B.: Enzymatic enrichment of n-3 polyunsaturated fatty acids in Nile perch (*Lates niloticus*) viscera oil. Euro. J. Lipid Sci. Technol. **112**(9), 977–984 (2010)
16. Terry, B., McCormick, R.L., Natarajan, M.: Impact of biodiesel blends on fuel system component durability. SAE Technical Paper No. (2006)-01-3279
17. Sarin, A., Singh, N.P., Sarin, R., Malhotra, R.K.: Natural and synthetic antioxidants: influence on the oxidative stability of biodiesel synthesized from non-edible oil. Energy **35**, 4645–4648 (2010)
18. Hess, M.A., Haas, M.J., Foglia, T.A., Marmer, W.N.: Effect of antioxidant addition on NOx emissions from biodiesel. Energy Fuels **19**(4), 1749–1754 (2005)
19. Karavalakis, G., Karonis, D., Stournas, S.: Evaluation of the oxidation stability of diesel/biodiesel blends. Fuel **89**, 2483–2489 (2010)
20. Kivevele, T.T., Kristóf, L., Bereczky, A., Mbarawa, M.M.: Engine performance, exhaust emissions and combustion characteristics of a CI engine fuelled with *Croton megalocarpus* methyl ester with antioxidant. Fuel **90**, 2782–2789 (2011)
21. Marie-Elisabeth, C., Hubert, R., Claudette, B.: Comparison of the antioxidative activity of some acid-phenols: structure-activity relationship. Biosci. Biotech. Biochem. **56**(2), 324–325 (1992)
22. Anderson, K.D., Emir, B.S., Wellington, W.D.V., Helena, M.W., Luiz, P.R.: The influence of BHA, BHT and TBHQ on the oxidation stability of soybean oil ethyl esters (biodiesel). J. Braz. Chem. Soc. (2007)
23. Aliyu, B., Shitanda, D., Walker, S., Agnew, B., Masheiti, S., Atan, R.: Performance and exhaust emissions of dieselengine fuelled with *Croton megalocarpus* (musine) methyls ester. Appl. Thermal Eng. **31**(1), 36–41 (2015)
24. Osawa, W.O., Onyari, J.M., Sahoo, P.K., Mulaa, F.J.: Experimental investigation on performance, emission and combustion characteristics of *Croton megalocarpus* biodiesel blends in a direct injection diesel engine. Int. J. Sci. Technol. **4**(1), 26–33 (2015)
25. Osawa, W.O., Onyari, J.M., Sahoo, P.K., Mulaa, F.J.: Process optimization for production of biodiesel from croton oil using two-stage process. IOSR J. Environ. Sci. Toxicol. Food Technol. **8**(11), 49–54 (2014)
26. Kivevele, T.T., Mbarawa, M.M., Bereczky, A., Laza, T., Madarasz, J.: Impact of antioxidant additives on the oxidation stability of biodiesel produced from *Croton Megalocarpus* oil. Fuel Process. Technol. **92**, 1244–1248 (2011)
27. Karavalakis, G., Hilari, D., Givalou, L., Karonis, D., Stournas, S.: Storage stability and ageing effect of biodiesel blends treated with different antioxidants. Energy **36**, 369–374 (2011)
28. Liang, Y.C., May, C.Y., Foon, C.S., Ngan, M., Hock, C.C., Basiron, Y.: The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel. Fuel **85**, 867–870 (2006)
29. DeGuzman, R., Tang, H., Salley, S., Simon, N.K.Y.: Synergistic effect of antioxidants on the oxidative stability of soybean oil and poultry fat-based biodiesel. J. Am. Oil Chem. Soc. **86**, 459–467 (2009)