Journal of Scientific & Industrial Research
Vol. 68, February 2009, pp.149-152

Storage stability of mahua oil methyl ester

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Received 22 January 2008; revised 04 December 2008; accepted 02 January 2009

Fatty acid methyl esters (FAME), used as biodiesel, degrade over time, mainly influenced by temperature, presence of light, metal, nature of the container and oxygen. Peroxide value and viscosity increases with increasing storage time of FAME samples. Use of antioxidants [3-tert-butyl-4-hydroxyanisole (BHA), 2, 6-di-tert-butyl-4-methyl-phenol (BHT) and propyl gallate (PrG)] could significantly improve stability of FAME. Storage (1 y) period can be regarded as a more than realistic time span for commercial life of biodiesel.

Keywords: Antioxidants, Mahua oil methyl esters, Storage stability

Introduction

Biodiesel ages more quickly than petro diesel due to chemical structure of fatty acid esters present in biodiesel. In advanced stages, oxidation can cause the fuel to become acidic and to form insoluble gums and sediments that can plug fuel filters. Biodiesel (containing 10% oxygen by wt) may be hydrolyzed to alcohol that leads to reduction in flash point, and acid that increases total acid number. Therefore, presence of alcohol and acid make biodiesel comparatively unstable on storage, and doping of biodiesel in petrodiesel will affect stability of fuel significantly[1]. Autoxidation of unsaturated fatty acids proceeds with different rates depending on the number and position of double bonds, which may lead to gum formation.

During oxidation process, fatty acid methyl ester (FAME) usually forms a radical next to the double bond. This radical quickly binds with oxygen in air, which is a biradical. This forms peroxide radical, which immediately creates a new radical from FAME, which in turn binds with oxygen in the air. Then, destructive radical auto-oxidation cycle starts. During this process, up to 100 new radicals are created quickly from one single radical, meaning that decomposition occurs at an exponentially rapid rate and results in formation of a series of by-products[1]. Finally, oil spoils and become rancid. Oxidative rancidity begins with an initial chain reaction as

$$RH \rightarrow R^*$$

This is followed by a reaction that involves unstable peroxides and hydroperoxides

$$R^* + O \rightarrow ROO^*$$
$$ROO^* + RH \rightarrow R\text{–}OOH + R^*$$

This is followed by termination reactions giving aldehydes, alcohols and carbonic acids

$$R^* + R^* \rightarrow R\text{–}R$$
$$ROO^* \rightarrow R^* + R\text{–}OO\text{–}R$$

Synthetic antioxidants are reported more efficient than natural antioxidants[2]. Some stability studies were also carried out on methyl and ethyl fatty acid esters under different storage conditions[3]. Effect of storage conditions on stability of biodiesel[4-6] has been studied. Stability evaluation of biodiesel from sunflower oil methyl esters[7,8], soybean oil methyl esters[9,10], tallow fats methyl esters and used frying oil methyl esters[7,8,11] has been carried out using antioxidants [TBHQ, propyl gallate (PG), pyrogallol (PY), butylated hydroxyanisole (BHA), 2,6-di-*tert*-butyl-4-methyl-phenol (BHT)], and a-tocopherol

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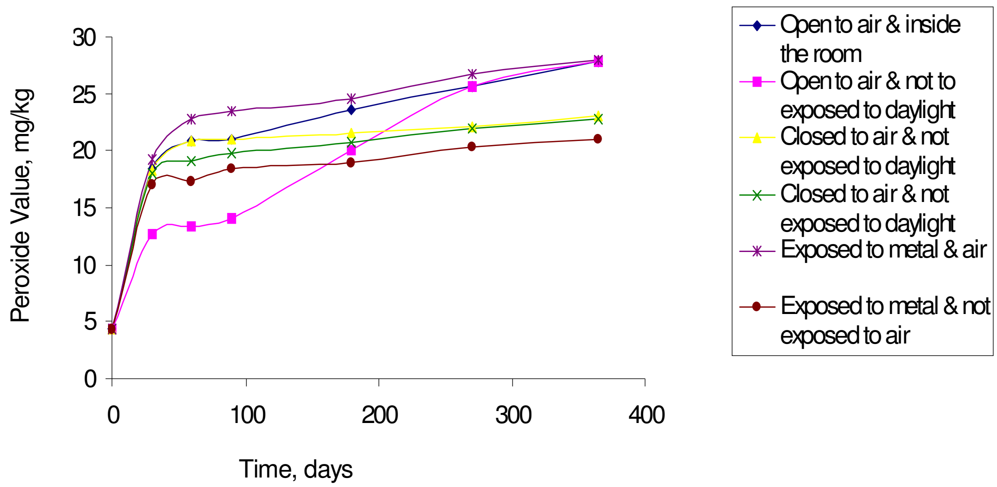

Fig. 1—Peroxide values of MOME during storage

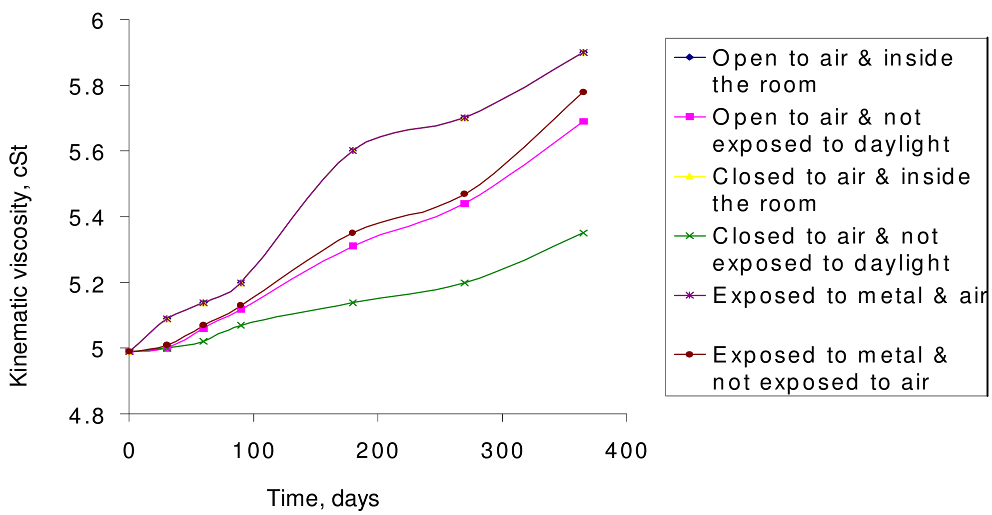

Fig. 2—Viscosity of MOME during storage

as oxidation retardant. PY and PG have shown beneficial effects on biodiesel oxidative stability.

In this work, storage stability of biodiesel made from mahua (*Madhuca indica*) oil as mahua oil methyl ester (MOME) was studied for degree of physical and chemical deterioration of MOME over a storage time of 12-months under different storage conditions, and to find out most effective antioxidant for biodiesel derived from mahua oil.

Materials and Methods

Materials

Samples of MOME were prepared *via* transesterification of mahua oil, which was collected from local Delhi market. Antioxidants (BHA, BHT and PrG) were purchased from Merck. Hydrochloric acid (HCl, sp gr 1.19), glacial acetic acid, potassium iodide, sodium thiosulfate, arrowroot starch, potassium hydroxide were purchased from Merck. All chemicals

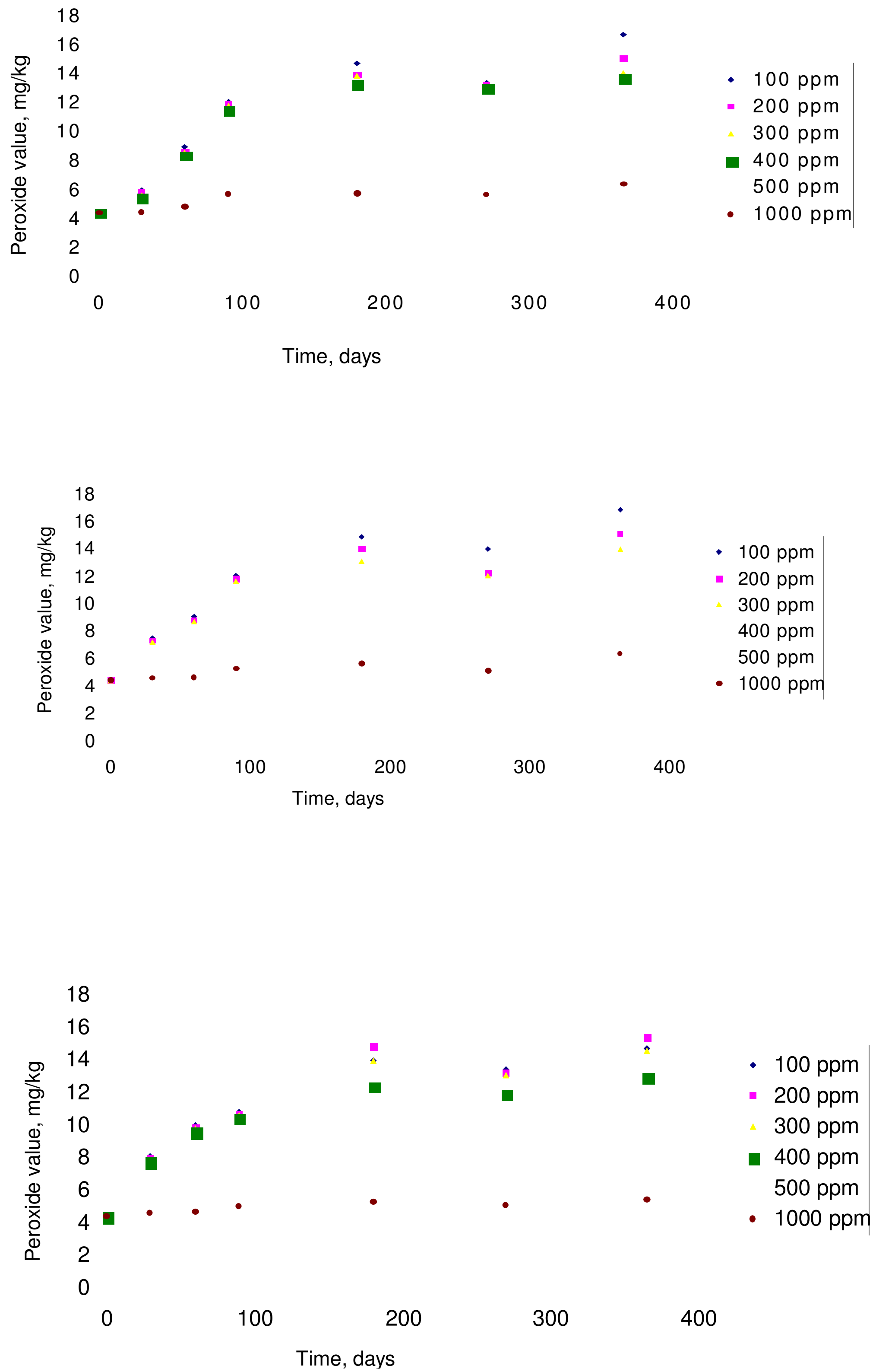

Fig. 3—PV of MOME at different concentrations for one year using following antioxidants: a) BHA; b) BHT; c) PrG

used were analytical reagent grade. Biofuel samples were supplemented with 100, 200, 300, 400, 500, and 1000 ppm of each antioxidant, respectively, and corresponding Peroxide value (PV) and viscosity were measured immediately (week zero). PV was measured according to ASTM D 3703-99 method. Kinematic viscosity was measured according to ASTM D 445 method.

Procedure

Biodiesel sample, dissolved in 1, 1, 2-trichloro- 1, 2, 2- trifluoroethane, was contacted with aqueous potassium iodide solution to reduce peroxides. Different storage conditions, under which biodiesel sample (1 l each) were stored for 365 days between 18° and 40°C, were: i) Open to air and inside the room; ii) Open to air and not exposed to daylight; iii) Closed to air and inside room; iv) Closed to air and not exposed to daylight; v)Exposed to metal (tin) and air; vi) Exposed to metal (tin) and without exposed to air; vii) Closed to air, inside room and BHA (100-500 ppm); viii) Closed to air, inside room and BHT (100-500 ppm); ix) Closed to air, inside room and PrG (100-500 ppm); x) Closed to air , inside room and BHA (1000 ppm); xi) Closed to air, inside room and BHT (1000 ppm); and xii) Closed to air , inside room and PrG (1000 ppm).

Results

Fatty acid composition of mahua oil was found as follows: palmitic, 16.0-28.2; stearic, 20.0-25.1; arachidic, 0.0-3.3; oleic, 41.0-51.0; and linoleic, 8.9-13.7%. Analysis of MOME gave following physico-chemical properties: Kinematic viscosity$^{40°C}$, 4.99 cSt; relative density$^{15°C}$, 0.875; flash point, 147°C; cloud point, 5°C; pour point, - 2°C; copper strip corrosion$^{100°C}$ for 3 h, No. 1a; calorific value, 35.173 MJ/kg; acid value, 0.5 mg KOH/g; carbon residue, 0.0292 % wt.

Peroxide Value (PV)

PV increased (Fig. 1) with storage time (1 year), particularly for samples stored under open to air and inside room (27.8 mg/kg) and exposed to metal and air (28.01 mg/kg).

Viscosity

During storage, viscosity of MOME increases by formation of more polar, oxygen containing molecules and also by formation of oxidized polymeric compounds. Biodiesel samples showed a slight increase in viscosity after being stored for 12-months (Fig. 2), particularly for samples stored under open to air and inside room (5.9 cSt) and exposed to metal and air (5.9 cSt).

Effect of Antioxidants on PV

Storage stability of MOME was investigated using antioxidants (BHA, BHT, PrG) at different concentrations (100-1000 ppm). Addition of antioxidant reduced hydroperoxide formation at 1000 ppm concentration (Fig. 3).

Conclusions

For storage (1 year) of MOME, for all biodiesel samples, PV and viscosity increase over time. Fuels exposed to daylight degrade at faster rate than others fuels. Antioxidant strongly influenced oxidative stability of MOME as: BHT < BHA < PG. Air contact and presence of metal affect degradation of biodiesel. To achieve a highly stable biodiesel and to avoid oxidation, it is necessary to limit access to oxygen and exposure to light.

References

1 Dunn R O & Knothe G, Oxidative stability of biodiesel in blends with jet fuel by analysis of oil stability index, *J Am Oil Chem Soc*, **80** (2003) 1047-1048.

2 Liang Y C, May C Y, Foon C S, Ngan M A, Hock C C & Basiron Y, The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel, *Fuel*, **85** (2006) 867-870.

3 Du Plessis L M, De Villiers J B M & Van der Walt W H, Stability studies on methyl and ethyl fatty acid esters of sunflower oil, *J Am Oil Chem Soc*, **62** (1985) 748-752.

4 Bondioli P, Gasparoli A, Della B L, Tagliabue S & Toso G, Biodiesel stability under commercial storage conditions over one year, *Eur J Lipid Sci Tech*, **105** (2003) 735-741.

5 Prankl H, High biodiesel quality required by European standards, *Eur J Lipid Sci Tech,* **104** (2002) 371-375.

6 McCormick R L, Alleman T L, Ratcliff M & Moens L, Survey of quality and stability of biodiesel and biodiesel blends in the United States in 2004, *National Renewable Energy Laboratory Technical Report No. NREL/TP-540-38836*, October 2005.

7 Lacoste F & Lagardere L, Quality parameters evolution during biodiesel oxidation using rancimat test, *Eur J Lipid Sci Technol*, **105** (2003) 149-155.

8 Mittelbach M & Schober S, The influence of antioxidants on the oxidation stability of biodiesel, *J Am Oil Chem Soc*, **80** (2003) 817-823.

9 Dunn R O, Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel), *Fuel Process Technol*, **86** (2005) 1071-1085.

10 Dunn R O, Effect of oxidation under accelerated conditions on fuel properties of methyl soyate (biodiesel), *J Am Oil Chem Soc,* **79** (2002) 915-920.

11 Schober S & Mittelbach M, The impact of antioxidants on biodiesel oxidation stability, *Eur J Lipid Sci Technol*, **106** (2004) 382-389.