Springer

KSME

Journal of Mechanical Science and Technology 31 (7) (2017) 3611~3617
www.springerlink.com/content/1738-494x(Print)/1976-3824(Online)
DOI 10.1007/s12206-017-0648-5

FTIR evaluation on the fuel stability of calophyllum inophyllum biodiesel: Influence of tert-butyl hydroquinone (TBHQ) antioxidant[†]

Mohamed Shameer P.[*] and Ramesh K.

Department of Mechanical Engineering, Faculty of Engineering, Government College of Technology, Coimbatore 641013, India

(Manuscript Received January 14, 2017; Revised March 4, 2017; Accepted March 13, 2017)

Abstract

'Storage oxidation stability' is one of the most significant criteria for appraising the biodiesel quality. Poor oxidation stability is the chief technical blockage related with the commercialization of biodiesel. The present paper investigates the effects of Tert- butyl hydroquinone (TBHQ) antioxidant additive concentrations on the long-term storage stability, thermal stability and accelerated oxidation stability of Calophyllum inophyllum biodiesel. Fourier transform infra-red (FTIR) spectroscopy was used to characterize the biodiesel oxidation variability, following the regions of C-H and O-H bonds in FTIR spectrum for different concentrations of TBHQ. Addition of TBHQ at 1000 ppm concentration (B100A3) with pure biodiesel enhances the oxidation stability by 94.67 %, storage stability by 14.47 % and thermal stability by 69.55 %; whereas further concentration of antioxidant deteriorates the formation of hydrophobic and hydrophilic clusters between biodiesel/antioxidant compounds, which is characterized by FTIR spectrum data. It is concluded that the Calophyllum inophyllum biodiesel could be accumulated for an extensive period by dosing 1000 ppm of TBHQ antioxidant.

Keywords: Calophyllum inophyllum; TBHQ; Oxidation stability; Storage stability; Thermal stability; FTIR

1. Introduction

India and US recorded 7.1 % and 1.2 % higher fossil fuel consumption than 2013 levels respectively. In the year 2014, the global usage of fossil fuel has been escalated by 0.8 million barrels per day. To surmount this fossil fuel usage augmentation, the biofuel implementation got its attention. Biofuel production has been increased by 7.4 % globally in the year 2014, among which India displayed the biodiesel production of about 0.320 million tones which is 29.1 % higher level than previous year [1]. The increment in energy utilization in Asia will be escalated about 1.5 % by the year 2030 [2]. The major global energy crisis leads to implementation of biofuel in transportation sector [3]. Degradation of biodiesel due to oxidation products leads to spoil the fuel properties, quality and its performance while fueling in diesel engines. This deprived oxidation stability of biodiesel curbs its commercialization, as it is less resistant to oxidation reaction. Hence fuel stability is an important issue that must be focused in biodiesel research.

1.1 Significance of biodiesel fuel stability

Generally biodiesel is less resistant to oxidation process than that of diesel. Vital factor for the acceptance of biodiesel in global market is fuel quality assurance. Biofuel companies that produce, store and transport biodiesel are more concerned with sediment and gums formation during storage attributed to oxidation products. A precise fuel quality standard is mandatory for any biodiesel manufacturer to employ warranty coverage during commercialization. Even though biodiesel displays the drawback of degradation due to oxidation instability, it should be commercialized in-order to surmount the energy crisis and environmental pollution issues. 'Fuel stability' is the term deals with the resistance to degradation process of a fuel. The degradation may be due to various factors like oxidation, thermal-oxidative decomposition, hydrolysis and foreign particles contamination. Fuel stability is conversed individually into three properties as storage stability, thermal stability and oxidation stability [4]. Antioxidants interact with the peroxide (oxidation product) radicals and lead to the formation of antioxidant free radical which stabilize the oxidation reaction and thereby inhibit the oxidation process of biodiesel [4, 5].

Calophyllum inophyllum (C.I) biodiesel has been proposed as a superior source due to its higher oil yield and heating value than other biodiesel sources like karanja, neem and jatropha [6]. Also in our previous work it was found that C.I biodiesel possess higher Oxidation stability (OS) with Induc-

[*]Corresponding author. Tel.: +91 9487766456, Fax.: +91 422 2455230
E-mail address: pmohamedshameer@gmail.com
[†]Recommended by Associate Editor Jeong Park

Table 1. Properties of fuel blends.

Properties/ samples	Kinematic viscosity @ 40 °C	Density @ 15 °C	Cetane index	Flash point	Cloud point	Pour point	Calorific value	Oxidation stability @ 110 °C
Units	cSt	kg/m^3	CCI	°C	°C	°C	MJ/kg	h
Diesel	3.9	833	54	63	6.5	-3	43.35	-
B100	4.78	873	55.8	140	13.2	4.3	38.33	8.47
B100A1	4.78	873	55.8	140	13.2	4.3	38.33	23.84
B100A2	4.78	873	55.8	141	13.2	4.3	38.33	23.90
B100A3	4.79	874	55.9	142	13.5	4.3	38.39	27.98
B100A4	4.79	876	56.1	142	13.5	4.5	38.67	26.92
B100A5	4.81	876	56.3	144	13.5	4.5	38.75	26.45

tion period (I.P) of 8.47 hours at 110 °C than other biodiesel, which is depicted by using Rancimat instrument [7]. C.I biodiesel shows 44.57 % higher OS when 20 % biodiesel added with 10 % penatnol in our previous oxidation stability analysis [7]. C.I biodiesel has been investigated and found to have improvement in oxidation stability by adding Butylated hydroxytolune (BHT) and 4-methyl-6-tert-butyphenol (MBEBP) with 30 % biodiesel/diesel blend [8]. By adding 15 % antioxidant extracted from pongamia leaf with 20 % C.I biodiesel, I.P was found to increase form 5 hours to 14 hours at 110 °C [9]. C.I biodiesel was studied for oxidation stability variation with three different additives like 2-ethylhexyl nitrate (EHN), N-phenyl-1, 4-phenylenediamine (NPPD) and N,N-diphenyl-1, 4-phenylenediamine (DPPD) at 1000 ppm concentration and found that DPPD was effective among the other additives [10].

Previous studies concluded that the synthetic antioxidant Tert-butyl hydroquinone (TBHQ) at 300 to 1000 ppm concentration is very effective in improving the oxidation stability of biodiesel extracted from soybean oil [11, 12], palm oil [13], cottonseed oil [14, 15], karanja oil [16], Terminalia belerica [17], linseed oil [18] and used cooking oil [19]. Also TBHQ has been proposed as the best additive for superior results in storage stability of biodiesel derived from soybean oil [20], jatropha oil [21], palm oil [22] and karanja oil [16]. Storage stability and thermal stability of Calophyllum inophyllum biodiesel with antioxidant have not been reached by previous researchers. Due to superior results of TBHQ and fewer studies on fuel stability of C.I biodiesel, this paper focuses its light over oxidation, storage and thermal stability variation on addition of TBHQ with Calophyllum inophyllum biodiesel.

Fourier transform infra-red (FTIR) spectroscopy has been proposed as a quick, reliable and efficient method for evaluating the fuel stability and also an efficient correlating tool for the analyzed results from Rancimat [23]. Oxidation-induced breakage of waste cooking oil methyl ester (biodiesel) linkages was explained using FTIR spectrum results [24]. FTIR has been used in our previous work of oxidation stability analysis of C.I biodiesel with pentanol addition [7]. Similarly FTIR is used in this study to characterize the effects of TBHQ at various concentrations.

2. Materials and methodology

2.1 Test fuels

General process for production of biodiesel is transesterification process (alcoholysis) [1-3, 25]. Calophyllum inophyllum oil yields about 85 % biodiesel. High grade methanol (25 % v/vol oil) was added with raw oil in the presence of an alkali catalyst sodium hydroxide (0.9 % w/w oil). Reactants were maintained at 66 °C and were stirred at 350 rpm. After 12 hours of separation process, the glycerol was removed by gravity separation. Finally by washing with distilled water, pure C.I biodiesel was obtained [7]. Antioxidant Tert- butyl hydroquinone (TBHQ) was dosed with pure C.I biodiesel in different concentrations ranging from 375, 750, 1000, 1125, 1500 ppm. TBHQ was found to be completely soluble in C.I biodiesel at all concentrations. The following six test fuel blends were prepared and evaluated: (i) Pure biodiesel (B100), (ii) 100 % biodiesel + 375 ppm TBHQ (B100A1), (iii) 100 % biodiesel + 750 ppm TBHQ (B100A2), (iv) 100 % biodiesel + 1000 ppm TBHQ (B100A3), (v) 100 % biodiesel + 1125 ppm TBHQ (B100A4), (vi) 100 % biodiesel + 1500 ppm TBHQ (B100A5). The properties of test fuels were determined (Table 1) by using equipments provided by Thermal Laboratory, Government College of Technology, Coimbatore, India.

2.2 Rancimat instrument

Oxidation stability (OS) is the tendency of fuel to resist the degradation of its physical and chemical properties by the presence of products like peroxides and hydroperoxides due to oxidation reaction [4]. OS is determined by using 873 Biodiesel Rancimat instrument (Metrohm manufacturer) based on the test method EN14214, which is also followed by Indian standard IS15607. Oxidation stability is depicted from 'Induction period (I.P)' parameter, which was measured at temperature range from 140 °C-155 °C at an equal interval of 5 °C. As per EN14214 standard, the biodiesel should display 6 hours of I.P at 110 °C.

2.3 Aluminium containers

Storage stability (SS) addresses the relative susceptibility of a fuel to resist the oxidative degradation due to microbial growth and water contagion during long- term storage. Storage stability is evaluated using standard ASTM D4625, by which the fuel is to be stored in a closed aluminium container for a period of 100 days in an incubator at 40 °C [4, 26]. Aluminium containers are used in this study, as it resist the catalytic effect on oxidation of biodiesel [5]. Regular monitoring of kinematic viscosity and acid value was done for every 10 days.

2.4 Thermo-gravimetric analyzer

Thermal stability (TS) term used to refer the fuel resistance to degradation attributed to elevated temperature higher than atmospheric condition. Generally biodiesel exhibits higher temperature during combustion inside engine cylinder, which is also evident from higher NOx (Oxides of nitrogen) emission [27, 28]. This elevated engine cylinder temperature influences the biodiesel getting re-circulated back to the fuel tank through the fuel injection system, which may lead to degradation of fuel physio-chemical properties [4]. Hence the biodiesel should also been analyzed for its thermal stability. Thermal stability was measured by thermo-gravimetric analyzer (TGA 2050). The standard for thermal stability analysis is not yet specified in any fuel quality specifications for biodiesel, but the effect of antioxidants on TS could be evaluated by using onset temperature parameter [29].

2.5 FTIR spectroscopy

As mentioned earlier, FTIR is an effective tool for correlating the oxidation stability results by characterizing the absorption frequency (600 to 4000 cm^{-1}) of specific molecular compounds in the sample using FTIR spectrum data. In this study, the fuel blends were evaluated at wave number range 3000-3700 cm^{-1} and 2700-3000 cm^{-1}, which corresponds to the presence of O-H and C-H bonds respectively in the fuel samples.

3. Results and discussion

3.1 Oxidation stability analysis

All samples have been tested initially at 110 °C for assuring the induction period of above 6 hours (Table 1). B100A3 shows the highest I.P of about 27.98 hours at 110 °C. The deviation of induction periods for pure Calophyllum inophyllum biodiesel and the consequences of TBHQ addition were investigated by testing the fuel samples at four temperatures as 140 °C, 145 °C, 150 °C and 155 °C (Fig. 1).

The measured IP values are extrapolated by automated Rancimat software and the IP at 30 °C were estimated for respective blends in terms of years and hours (Table 2).

TBHQ antioxidant shows better improvement in oxidation stability of C.I biodiesel. TBHQ at 375, 750, 1000, 1125, 1500 ppm concentration resulted in 88.05 %, 89.74 %, 94.67 %, 93.33 % and 91.49 % higher oxidation stability respectively on an average at all testing temperatures, when compared to biodiesel without any antioxidant additive. I.P increases with increase in TBHQ concentration upto 1000 ppm (B100A3), above which the I.P decreases due to its chemical structure breakage of hydrophobic and hydrophilic clusters. The mentioned characterization of declining IP for TBHQ > 1000 ppm concentration has been clearly revealed by C-H and O-H bonds in the FTIR spectrum (Fig. 4).

Table 2. Rancimat measurement (IP @ 30 °C) of fuel blends.

Samples	Extrapolated IP at 30 °C	
	(h)	(Year)
B100	753.6	0.08
B100A1	5869.2	0.67
B100A2	6832.8	0.78
B100A3	13140	1.5
B100A4	10512	1.2
B100A5	8234.4	0.94

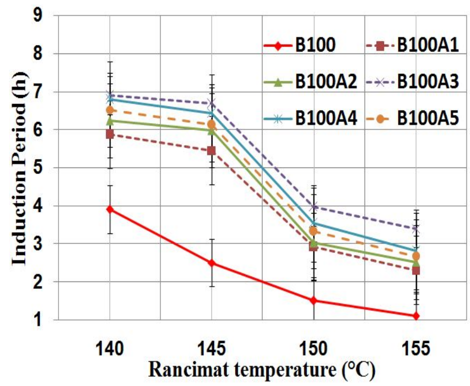

Fig. 1. Induction periods for all blends from rancimat instrument.

3.2 Thermal stability analysis

The effect of antioxidants on thermal stability of biodiesel samples have been investigated by TGA 2050 thermo-gravimetric analyzer using onset temperature (T_{ON}). The fuel samples of quantity 8 mg were purged with oxygen and were heated to 500 °C at a rate of 10 °C /min. Biodiesel without antioxidant shows onset temperature of 118.58 °C. Addition of TBHQ shows increment in onset temperature for all samples, which depicts higher thermal stability for TBHQ addition to biodiesel (Fig. 2).

B100A3 and B100A4 displayed better thermal stability, which are 69.55 % and 45.81 % higher T_{ON} than B100. Secondary oxidation products were removed due to the initiation of severe thermal oxidation at elevated temperature, which leads to sample weight loss signifying the onset temperature (T_{ON}) of thermal oxidation. Higher T_{ON} signifies better thermal stability of sample [4, 29].

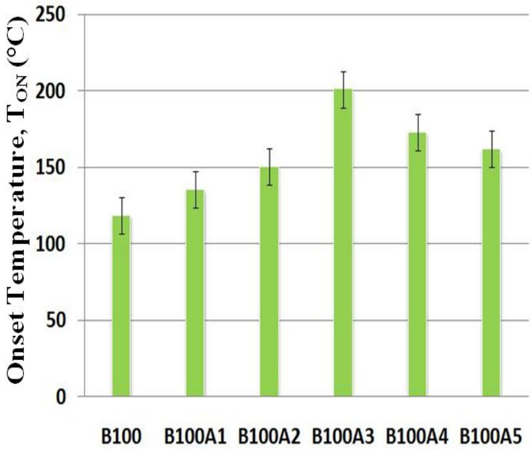

Fig. 2. Onset temperature (T_{on}) readings for fuel blends from thermo-gravimetric analyzer.

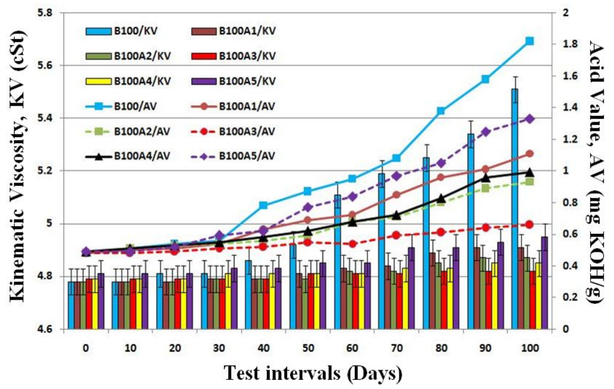

Fig. 3. Kinematic viscosity and acid value variation for fuel blends at 100 days storage stability analysis.

3.3 Storage stability analysis

Fig. 4 shows the Acid value (AV) and Kinematic viscosity (KV) change for all fuel blends over the storage period of 100 days. For an equal interval of 10 days, KV and AV were determined for all samples and were recorded. It can be seen that the AV and KV increases with storage time for all samples. Due to the formation of peroxides and oxidized polymetric compounds resulted from oxidation reaction leads to the prevalence of sediments and gums in the biodiesel samples which attributed to increase in KV [30]. Similarly the formed peroxides and hydroperoxides oxidized further into acids in the sample, which resulted in increase in acid value with increase in storage duration [30]. Pure biodiesel (B100) shows drastic augmentation in both AV and KV after 40 days of storage, whereas the additions of TBHQ shows better storage stability by lessening the increase rate of KV and AV through the resistance of oxidation process and formation rate of peroxides. TBHQ concentration upto 1000 ppm shows better resistance to increase in KV and AV. More than 1000 ppm concentration degrades the storage stability of samples due to the inferior chemical structure of B100A4 and B100A5, which

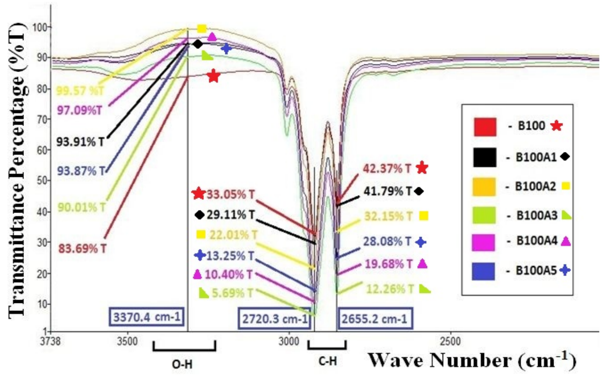

Fig. 4. FTIR spectrum for all fuel samples.

has been explained through FTIR spectrum data. TBHQ at 1000 ppm concentration (B100A3) never shows major change in KV and AV for 100 days, which insists the better long term storage stability than biodiesel sample without antioxidant additive.

3.4 FTIR assessment

FTIR spectrum data for all samples has been displayed as wave number (cm^{-1}) vs. transmittance percentage (%T) in Fig. 4 by plotting the regions of infra red spectrum which have been transmitted by specific molecular bonds presenting in the samples. Higher percentage of infra red transmittance in the graph symbolizes the lower presence of respective molecular compounds in the samples. Wave number ranges 3000-3700 cm^{-1}, 2700-3000 cm^{-1} represents O-H and C-H bonds, respectively. Oxidation reaction for a sample is chiefly organized by C-H and O-H bonds [7].

B100 sample shows lower OS, SS and TS, due to the higher oxidation rate. The reason behind the inferior fuel stability of B100 could be clearly visualized in FTIR spectrum from the strong O-H chain in 3370.4 cm^{-1} (83.69 % T), which correspond to the occurrence of more oxygen molecule. As the oxygen is more electronegative than carbon, the higher oxygen molecules seized the hydrogen group in the biodiesel. Higher content of oxygen molecules in the sample attributes to higher attraction of ambient oxygen, which leads to the formation of peroxides and hydroperoxides contributing to free radical chain reaction augmenting further oxidation of sample [7].

Addition of TBHQ additives to B100 shows increment in OS, SS and TS due to the less impact of fewer free radicals on oxidation reaction, observed from the presence of lower O-H group than B100. Due to lower oxygen molecules in antioxidant blends, the oxidation reaction is delayed. Another reason for superior results of fuel stability of antioxidant blends are the presence of higher C-H bonds displayed in FTIR spectrum.

C-H molecules consume oxygen in the sample for the formation of carbon dioxide, which leads to extent time for the sample degradation [7].

As the TBHQ antioxidant is a phenolic (longer carbon chain) group, its addition to biodiesel forms a strong cluster of

Table 3. Cost for biodiesel production and TBHQ dosage.

Description	Unit	Cost
C.I seed collection (2 kg)	Rs. per kg	5
1 liter of oil extraction from 2 kg seeds	Rs. per liter	35
Oilcake (By-product)	Rs. per kg	-10
Packing and storage of oil	Rs. per liter	4
Total cost of oil	Rs. per liter	39
Transesterification process	Rs. per liter	30
Total cost of biodiesel (B100)	Rs. per liter	69
TBHQ antioxidant additive	1000 ppm	0.00384
Biodiesel/TBHQ blend (B100A3)	Rs. per liter	69.00384

hydrogen bonds (C-H) between biodiesel and antioxidant. These compounds of clusters are very intricate to oxidize. C-H bond (hydrophobic entities) formed by antioxidant surrounds the O-H bond (hydrophilic entities) of biodiesel. The site for free radical attack is decreased by the less oxygen content of hydrophobic entities. For this reason more free radicals are necessary for breaching the formed cluster, which may take more time. This prolonged period for breaking cluster leads to elevated fuel stability [7]. Augmentation in fuel stability was observed upto 1000 ppm correlates to the increased prevalence of C-H molecules. B100A1 and B100A2 displayed 29.11 %T and 22.01 %T of C-H bonds in the wave number 2720.3 cm^{-1}, which shows increasing C-H molecules with increasing TBHQ concentration. Highest fuel stability was recorded for B100A3 (1000 ppm TBHQ) sample, which could be characterized by the peak presence of C-H bonds in 2720.3 cm^{-1} (5.69 %T) when compared to other samples. Meanwhile above 1000 ppm of TBHQ, the fuel stability has been degraded due to the deterioration of formed hydrophobic and hydrophilic clusters by overturning the orientation of cluster, exposing hydrophilic entities to oxygen content in the sample and atmosphere [7]. This contact of biodiesel molecules to the oxygen resulted in rapid oxidation of B100A4 and B100A5, when compared to B100A3. Also the lower occurrence of C-H bonds of B100A4 (10.40 %T) and B100A5 (13.25 %T) in the region 2720.3 cm^{-1}, compared to B100A3 correlates the degraded fuel stability.

3.5 Cost analysis

The cost for production of Calophyllum inophyllum biodiesel and dosage of TBHQ antioxidant additive are evaluated based on the production process existing in India in terms of rupees (Rs). The cost for production and preparation of B100A3 blend is tabularized in Table 3.

From Rancimat measurement (Table 2), it is determined that B100 and B100A3 could be stored at room temperature for 0.08 years and 1.5 years, respectively. The estimated cost comparison for storing and commercializing biodiesel with TBHQ additive (B100A3) and without additive (B100) has been depicted for 1 liter of fuel in Table 4. Nearly 800 rupees could be saved for storing 1 liter of C.I biodiesel blended with 1000 ppm TBHQ additive, which is economically more profitable. Hence the Calophyllum inophyllum biodiesel dosed with TBHQ antioxidant additive at 1000 ppm concentration could be decidedly recommended for biofuel market commercialization.

Table 4. Commercialization cost comparison.

Fuel blend	B100	B100A3
Total cost	Rs.69	Rs.69.00384
Extrapolated IP@30 °C	0.08 year	1.5 years
Total cost for storing and commercializing 1 liter of fuel per year	Rs.862.5	Rs.46.0026

4. Conclusion

In this study, Calophyllum inophyllum biodiesel treated with Tert- butyl hydroquinone (TBHQ) antioxidant at proportions of 375, 750, 1000, 1125, 1500 ppm volume to investigate the Oxidation stability (OS), Storage stability (SS) and Thermal stability (TS). The following conclusions are made based on the acquired results.

- All samples displayed induction period of above 6hours @ 110 °C, which meets the EN14214 standard obligation on oxidation stability. TBHQ at 1000 ppm concentration (B100A3) shows better results in OS, SS and TS.
- Rancimat instrument extrapolates the induction period at room temperature (30 °C), depicting the oxidation stability. B100A3 resulted in 94.67 % higher induction period than biodiesel without additive (B100).
- Onset temperature (T_{ON}) parameter signifying the thermal stability has been determined for all samples using thermo-gravimetric analyzer. TBHQ at 1000 ppm shows 69.55 % higher T_{ON} than pure biodiesel.
- Kinematic viscosity and acid value variation of the samples stored in aluminium containers for the duration of 100 days at 40 °C have been monitored to evaluate the storage stability. TBHQ above 1000 ppm volume concentration shows second-rate storage stability due to the dissolution and saturation of antioxidant with biodiesel.
- TBHQ concentration above 1000 ppm degrades the overall fuel stability, which has been characterized by analyzing the chemical structure of all samples with FTIR spectroscopy. Based on the FTIR spectrum data, it was found that B100A3 shows an average of 48.80 % higher fuel stability than biodiesel without antioxidant due to the prevalence of higher C-H bond chains (5.69 %T at 2720.3 cm^{-1}) in its molecular composition which confines the biodiesel not to get oxidized at higher rate. Meanwhile 1125 ppm, 1500 ppm concentration of TBHQ addition leads to the degradation in average fuel stability by 5.98 % and 9.71 %, respectively when compared to 1000 ppm TBHQ addition, which is due to the deterioration of formed hydrophobic and hydrophilic

clusters between biodiesel/antioxidant molecular compounds.

- Also based on its estimated efficient economy, it is concluded that Calophyllum inophyllum biodiesel dosed with 1000 ppm concentration of TBHQ antioxidant is highly recommendable for commercialization in the biodiesel market.

Acknowledgement

We thank Human Resource Development Group, Council of Scientific & Industrial Research (CSIR), Delhi, India for their support to this research.

Nomenclature

C.I : Calophyllum inophyllum
TBHQ : Tert- butyl hydroquinone
FTIR : Fourier transform infra-red
TGA : Thermogravimetric analyzer
OS : Oxidation stability
TS : Thermal stability
SS : Storage stability
IP : Induction period
T_{ON} : Onset temperature
AV : Acid value
KV : Kinematic viscosity

References

[1] P. M. Shameer, K. Ramesh, R. Sakthivel and R. Purnachandran, Effects of fuel injection parameters on emission characteristics of diesel engines operating on various biodiesel: A review, *Renewable and Sustainable Energy Reviews*, 67 (2017) 1267-1281, http://dx.doi.org/10.1016/j.rser.2016.09.117.

[2] P. M. Shameer, K. Ramesh, R. Sakthivel and R. Purnachandran, Assessment on the influence of compression ratio on the performance, emission and combustion characteristics of diesel engine fuelled with biodiesel, *Asian Journal of Research in Social Sciences and Humanities*, 6 (12) (2016) 344-372, Doi: 10.5958/2249-7315.2016. 01297.1.

[3] P. M. Shameer, K. Ramesh, R. Purnachandran and R. Sakthivel, Effects of injection timing and injection pressure on biodiesel fuelled engine performance characteristics: A review, *Asian Journal of Research in Social Sciences and Humanities*, 7 (2) (2017) 310-330, Doi: 10.5958/2249-7315.2017.00093.4.

[4] J. Pullen and K. Saeed, An overview of biodiesel oxidation stability, *Renewable and Sustainable Energy Reviews*, 16 (2012) 5924-5950, http://dx.doi.org/10.1016/j.rser.2012.06.024.

[5] Z. Yaakob, B. N. Narayanan, S. Padikkaparambil, K. S. Unni and M. Akbar, A review on the oxidation stability of biodiesel, *Renewable and Sustainable Energy Reviews*, 35 (2014) 136-153, http://dx.doi.org/10.1016/j.rser.2014.03.055.

[6] A. E. Atabani and A. da S. Cesar, Calophyllum inophyllum L. - A prospective non-edible biodiesel feedstock, Study of biodiesel production, properties, fatty acid composition, blending and engine performance, *Renew Sust Energ Rev.*, 37 (2014) 644-655, http://dx.doi.org/10.1016/j.rser.2014.05.037.

[7] P. M. Shameer, K. Ramesh, R. Sakthivel and R. Purnachandran, Experimental evaluation on oxidation stability of biodiesel/diesel blends with alcohol addition by rancimat instrument and FTIR spectroscopy, *Journal of Mechanical Science and Technology*, 31 (1) (2017) 455-463, Doi 10.1007/s12206-016-1248-5.

[8] H. K. Rashedul, H. H. Masjuki, M. A. Kalam, Y. H. Teoh, H. G. How and I. M. R. Fattah, Effect of antioxidant on the oxidation stability and combustion-performance-emission characteristics of a diesel engine fueled with diesel-biodiesel blend, *Energy Conversion and Management*, 106 (2015) 849-858, http://dx.doi.org/10.1016/j.enconman.2015.10.024.

[9] S. Ramalingam, M. Govindasamy, M. Ezhumalai and A. Kaliyaperumal, Effect of leaf extract from Pongamia pinnata on the oxidation stability, performance and emission characteristics of calophyllum biodiesel, *Fuel*, 180 (2016) 263-269, http://dx.doi.org/10.1016/j.fuel.2016.04.046.

[10] M. M. Rashed, M. A. Kalam, H. H. Masjuki, M. Habibullah, H. K. Imdadul, M. M. Shahin and M. M. Rahman, Improving oxidation stability and NOx reduction of biodiesel blends using aromatic and synthetic antioxidant in a light duty diesel engine, *Industrial Crops and Products*, 89 (2016) 273-284, http://dx.doi.org/10.1016/j.indcrop.2016.05.008.

[11] E. C. R. Maia, D. Borsato, I. Moreira, K. R. Spacino, P. R. P. Rodrigues and A. L. Gallina, Study of the biodiesel B100 oxidative stability in mixture with antioxidants, *Fuel Processing Technology*, 92 (2011) 1750-1755, http://dx.doi.org/10.1016/j.fuproc.2011.04.028.

[12] Z. Yang, B. P. Hollebone, Z. Wang, C. Yang and M. Landriault, Factors affecting oxidation stability of commercially available biodiesel products, *Fuel Processing Technology*, 106 (2013) 366-375, http://dx.doi.org/10.1016/j.fuproc.2012.09.001.

[13] Y. C. Liang, C. Y. May, C. S. Foon, M. A. Ngan, C. C. Hock and Y. Basiron, The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel, *Fuel*, 85 (2006) 867-870, http://dx.doi.org/10.1016/j.fuel.2005.09.003.

[14] D. M. Fernandes, D. S. Serqueira, F. M. Portela, R. M. N. Assuncao, R. A. A. Munoz and M. G. H. Terrones, Preparation and characterization of methylic and ethylic biodiesel from cotton seed oil and effect of tert-butyl hydroquinone on its oxidative stability, *Fuel*, 97 (2012) 658-661, http://dx.doi.org/10.1016/j.fuel.2012.01.067.

[15] H. Tang, A. Wang, S. Salley and K. Y. S. Ng, The effect of natural and synthetic antioxidants on the oxidative stability of biodiesel, *Journal of American Oil Chemistry Society*, 85 (2008) 373-382, Doi:10.1007/s11746-008-1208-z.

[16] A. Obadiah, R. Kannan, A. Ramasubbu and S. V. Kumar,

Studies on the effect of antioxidants on the long-term storage and oxidation stability of Pongamia pinnata (L.) Pierre biodiesel, *Fuel Processing Technology*, 99 (2012) 56-63, http://dx.doi.org/10.1016/j.fuproc.2012.01.032.

[17] C. Maumita and D. C. Baruah, Investigation of oxidation stability of Terminalia belerica biodiesel and its blends with petrodiesel, *Fuel Processing Technology*, 98 (2012) 51-58, http://dx.doi.org/10.1016/j.fuproc.2012.01.029.

[18] S. S. Pantoja, L. R. V. da Conceicao, C. E. F. da Costa, J. R. Zamian and G. N. da Rocha Filho, Oxidative stability of biodiesels produced from vegetable oils having different degrees of unsaturation, *Energy Conversion and Management*, 74 (2013) 293-298, http://dx.doi.org/10.1016/j.enconman.2013.05.025.

[19] M. Lapuerta, J. Rodríguez-Fernandez, A. Ramos and B. Alvarez, Effect of the test temperature and antioxidant addition on the oxidation stability of commercial biodiesel fuels, *Fuel*, 93 (2012) 391-396, http://dx.doi.org/10.1016/j.fuel.2011.09.011.

[20] D. M. Fernandes, R. H. O. Montes, E. S. Almeida, A. N. Nascimento, P. V. Oliveira and E. M. Richter, Storage stability and corrosive character of stabilized biodiesel exposed to carbon and galvanized steels, *Fuel*, 107 (2013) 609-614, http://dx.doi.org/10.1016/j.fuel.2012.11.010.

[21] S. Jain and M. P. Sharma, Effect of metal contaminants and antioxidants on the storage stability of Jatropha curcas biodiesel, *Fuel*, 109 (2013) 379-383, http://dx.doi.org/10.1016/j.fuel.2013.03.050.

[22] H. Tang, R. C. De Guzman, K. Y. S. Ng and S. O. Salley, Effect of antioxidants on the storage stability of soybean-oil-based biodiesel, *Energy Fuels*, 24 (2009) 2028-2033, Doi: 10.1021/ef9012032.

[23] R. K. Saluja, V. Kumar and R. Sham, Stability of biodiesel - A review, *Renewable and Sustainable Energy Reviews*, 62 (2016) 866-881, http://dx.doi.org/10.1016/j.rser.2016.05.001.

[24] P. Y. Furlan, P. Wetzel, S. Johnson, J. Wedin and A. Och, Investigating the oxidation of biodiesel from used vegetable oil by FTIR spectroscopy: Used vegetable oil biodiesel oxidation study by FTIR, *Spectroscopy Letters*, 43 (2010) 580-585, http://dx.doi.org/10.1080/00387010.2010.510708.

[25] P. M. Shameer and K. Ramesh, Green technology and performance consequences of an eco-friendly substance on a 4-stroke diesel engine at standard injection timing and compression ratio, *Journal of Mechanical Science and Technology,* 31 (3) (2017) 1497-1507, Doi 10.1007/s12206-017-0249-3.

[26] J. Pullen and K. Saeed, Experimental study of the factors affecting the oxidation stability of biodiesel FAME fuels, *Fuel Processing Technology*, 125 (2014) 223-235, http://dx.doi.org/10.1016/j.fuproc.2014.03.032.

[27] P. M. Shameer and K. Ramesh, Experimental evaluation on performance, combustion behavior and influence of in-cylinder temperature on NOx emission in a D.I diesel engine using thermal imager for various alternate fuel blends, *Energy*, 118 (2017) 1334-1344, http://dx.doi.org/10.1016/j.energy.2016.11.017.

[28] P. Mohamed Shameer and K. Ramesh, Study on clean technology-assisted combustion behavior and NOx emission using thermal imager for alternate fuel blends, *Int. J. Environ. Sci. Technol.* (2017) Doi:10.1007/s13762-017-1353-8.

[29] W. B. W. Nik, F. N. Ani and H. H. Masjuki, Thermal stability evaluation of palm oil as energy transport media, *Energy Conversion and Management*, 46 (2005) 2198-2215, Doi: 10.1016/j.enconman.2004.10.008.

[30] G. Karavalakis, D. Hilari, L. Givalou, D. Karonis and S. Stournas, Storage stability and ageing effect of biodiesel blends treated with different antioxidants, *Energy*, 36 (2011) 369-374, Doi: 10.1016/j.energy.2010.10.029.

Ramesh K. received his Ph.D. degree in Mechanical Engineering from Anna University Chennai, Tamil Nadu, India in 2013. He is currently working as Assistant Professor (Senior Grade) of Mechanical Engineering at Government College of Technology, Coimbatore, Tamil Nadu, India for a period of 12 years (2005-2017). He has published 30 research articles under scopus indexed journals related to his research area. He has 17 years of teaching experience. His research interests include energy, combustion, environmental pollution, vibration analysis and manufacturing processes.

Mohamed Shameer P. received his Post Graduate degree in Thermal Engineering from Anna University Chennai, Tamil Nadu, India in 2015. In 2009, he joined Mechanical Engineering and graduated as University Rank Holder in Anna University Chennai, Tamil Nadu, India. He has published 8 research articles under scopus indexed journals related to his research area. He is currently working as a Teaching Research Associate and doing his research (Ph.D. degree) in renewable energy, biodiesel, fuel stability and combustion at Government College of Technology, Coimbatore, Tamil Nadu, India.