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Short communication

Study of a novel phenolic-ester as antioxidant additive in lube, biodiesel and blended diesel

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ABSTRACT

A novel phenolic-ester denoted as **Bz-4-tBz** was synthesized by esterification reaction between the 1,2,4,5-benzenetetracarboxylic acid and 3,5-di-*tert*-butyl-4-hydroxybenyl alcohol in *N,N'*-dimethylacetamide using *N,N'*-dicyclohexylcarbodiimide as catalyst. The **Bz-4-tBz** was evaluated as antioxidant in polyol by the rotatory bomb oxidation test while the Rancimat test were also done for evaluating the antioxidant potential in the biodiesel (B100) and blended diesel (B20). The RBOT time of polyol was observed to be increased from 6.72 min to 17.42 min when blended 2000 mg/kg **Bz-4-tBz** in it. The oxidation stability of biodiesel (B100) and blended diesel (B20) was also found to be increased.

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Introduction

Apart from the other desirable properties like high viscosity index, cleanliness, lubricity, low pour point and corrosion, etc, an important characteristic for lubricants is the high oxidation stability since it is considered as principle cause of the lubricant aging leading to the blackening, formation of sludge, loss of lubrication, etc [1]. Exposure to heat and air greatly accelerates the lube degradation [2]. So even today when the high performance synthetic lubricant base oil technologies are available, at least one antioxidant is added in every lubricant formulation for enhancing performance characteristics [3]. Biodiesel is obtained generally by the transesterification reaction of vegetable oils (triglycerides) with the methanol [4]. If this triglyceride has the unsaturated fatty component, it leads the low oxidative stability of the biodiesel [5]. Although this property of low oxidative stability makes the biodiesel biodegradable but this limits its shelf life. So high oxidative stability it is a matter of great concern for biodiesel too for the sake of quality standpoints which is generally achieved by addition of a good antioxidant [6]. By now numerous classes of antioxidants are available for lubricants and fuels e.g., sulphur and

phosphorus compounds, boron compounds, aromatic amines, hindered phenols and organometallic compounds. Sterically hindered phenols are important class of antioxidants being extensively used for lubricants, greases and biodiesel since 1960s e.g., BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole) and TBHQ (tert-butylhydroquinone). High antioxidative efficiency, low toxicity and no unwanted colour contribution to the blend are some important advantages associated with these antioxidants, but their low volatility and somewhat difficult dispersibility are the main limitations leading to their evaporation in the operating conditions [3]. The recent trend in the development of the antioxidants is to design the antioxidants with high molecular weight so low volatility with easy dispersible nature and low toxicity in order to function under high-temperature oxidation conditions.

Recent literature indicates some advantages to synthesize the hindered phenolic compounds having high molecular weight too e.g., tetrakis [3-(3,5-di-*tert*-butyl-4-hydroxy phenyl)propionyl oxymethyl] methane is a widely known commercial antioxidant additive which is synthesized by the transesterification reaction between methyl-(3,5-di-*tert*-butyl-4-hydroxy phenyl)propionate ester and pentaerythritol [7,8]. A mixed ester of dipentaerythritol with 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid and isostearic acid was synthesized which was found to have the low volatility. When evaluated as antioxidant additive in synthetic

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ester lubricant by RBOT (rotator bomb oxidation test), it showed the excellent antioxidant potential [9]. Mixed ester of pentaerythritol with oleic acid, gallic acid and 3, 5-di-*tert*-butyl-4-hydroxybenzoic acid were also evaluated as multifunctional additive with antioxidant activity in N-butyl palmitate/stearate (a biolubricant reference fluid) [10]. 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione was used as a primary antioxidant additive along with other secondary antioxidants in lubricant formulation [11]. Some hindered phenolic compounds with high molecular weight like Octyl-3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl) benzene and benzene-propanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxyl-, C7-9-branched alkyl esters have been found to be highly effective for engine oils and industrial lubricants applications [3].

In the present work, we have synthesized a novel high molecular weight hindered phenolic ester **Bz-4-tBz** by the reaction between 1,2,4,5-benzenetetracarboxylic acid and 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol in order to reduce the volatility and easy dispensability due to increased aromatic content and introduced ester functionalities in comparison to BHT and BHA. The **Bz-4-tBz** was characterized by CHN analysis, FT-IR, NMR and TG analysis, etc. The performance evaluation of the synthesized additive as antioxidant was done by using rotary bomb oxidation test (RBOT) in polyol (biolubricant reference base fluid) while the Rancimat test was used to evaluate the antioxidant activity in B100 biodiesel (**Bz-4-tBz**) and diesel blended biodiesel (B20).

Experimental

Materials

1,2,4,5-benzenetetracarboxylic acid, 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol and N,N'-dicyclohexylcarbodiimide (DCC) were purchased from Sigma-Aldrich and used as received. N,N-dimethylacetamide (DMAc) was purchased from Merck Millipore. Polyol which used as reference lube base was purchased from Mohini Organics Pvt. Ltd. Mumbai, India. It is chemically pentaerythritol tetra oleate available by the brand name of "MONECOL[®]-509". It is a yellow coloured viscous oily liquid with acid value, 3.0 mg KOH/gm max.; saponification value, 190 ± 5 mg KOH/gm; moisture, 1.0% max. and solidification point, <0 °C. The biodiesel prepared from *Jatropha curcas* seed oil was obtained from the biofuels group of our institute. The specifications of the biodiesel (B100) obtained from the *Jatropha curcas* oil as per EN14214 [12] are as follows: density at 15 °C, 888.6 kg/m³; total sulphur, <1 ppm; kinematic viscosity at 40 °C, 4.55 cSt; CCR, 10% residue, 0.13% wt; copper strip corrosion (~3 h at 100 °C), 1.0; acidity total, 0.49 mg KOH/g; cetane index, 56.6; flash point, 135 °C; pour point, +3 °C; cloud point, +8 °C. Diesel fuel specifications as per EN590 [13] are as follows: sulphur, 481.7 ppm; density at 15 °C, 0.8314 g/cc; kinematic viscosity at 40 °C, 3.18 cSt; IBP, 145.5, FBP, 382.5; distillate, 99.0; residue, 0.5% vol; cetane index, 54.19; copper corrosion, one; calorific value, 9466.37 cal/gm; water, 59 ppm, pour point, -3 °C; WSD, 374.5 μm and average friction coefficient, 0.169. All other chemicals were of the highest available grade and were used without further purification.

Synthesis of Bz-4-tBz

The antioxidant additive **Bz-4-tBz** was synthesized by reacting 1.27 g (5 mmol) 1,2,4,5-benzenetetracarboxylic acid and 4.72 g (20 mmol) 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol in the presence of the 0.52 g (2.50 mmol) of N,N'-dicyclohexylcarbodiimide (DCC) in 20 mL N,N-dimethylacetamide (DMAc) taken into a

250 mL three-necked round bottomed flask equipped with a magnetic stirrer, thermometer and a condenser. The mixture was refluxed at 120 °C for about 48 h. The reaction was stopped by pouring the whole content into the cooled water and then the precipitate was filtered. The dark yellow product obtained was dried at 60 °C overnight. The yield obtained of the final product was 3.80 g.

Characterization

Perkin Elmer Series II CHNS/O 2400 analyzer was used for the CHNS analysis of the **Bz-4-tBz**. Fourier transform infrared (FT-IR) spectrum was recorded on a Thermo-Nicolet 8700 research spectrophotometer with a 4 cm⁻¹ resolution (KBr pellets). A Bruker Avance 500 spectrometer in the proton noise-decoupling mode with a standard 5 mm probe was used for NMR characterization of the synthesized additive while thermogravimetry curves were recorded with a PerkinElmer EXSTAR TG/DTA 6300 using aluminium pans. The experiments were carried out under continuous nitrogen flow of 200 mL min⁻¹, and the temperature ramp was set at 10 °C min⁻¹. The mass loss was recorded from 30 to 800 °C.

Performance evaluation as antioxidant additive

Rotating bomb oxidation test (RBOT) test

Performance evaluation of the synthesized additive **Bz-4-tBz** as antioxidant additive for lube was done as per ASTM method D2272-11 [14] on a RBOT (rotating bomb oxidation test) apparatus manufactured by Stan-hope Seta, UK. Blends of additive in polyol (reference lube base oil) in different concentrations were prepared. In a typical experiment, 50.0 g sample was measured in the pressure vessel and added 5 mL of water in to it. A copper wire to be used as catalyst was taken and folded in to a spring-coil shape having an outside diameter of 44–48 mm, weight of 55.6 g, and height of 40–42 mm. The copper coil was cleaned with 220 grit silicon carbide sand paper and was used immediately. The bomb was assembled and first purged with oxygen and then charged with 90.0 ± 0.5 psi (620 kPa) of oxygen. The bomb was checked for any leakage by immersing in water. Experiments were carried out at 150 °C. The test was considered completed after the pressure dropped more than 175 kPa from the original pressure. All samples were run in duplicate, and the average RBOT time was reported.

Rancimat test

Apart from evaluating the anti oxidative potential of **Bz-4-tBz** for lubes, it was also tested in biodiesel and diesel blended biodiesel using Rancimat test which was performed on 743 Rancimat, Metrohm Ltd., Switzerland as per standardized method for determining the oxidation stability of biodiesel (B100) and diesel blended biodiesel (B20) with doped additive in different concentrations following EN 14112 with conductometric indication [15]. This is the accelerated oxidation test having the setup as shown in Fig. 1. In this typical test, 3 g sample was filled in a sealed

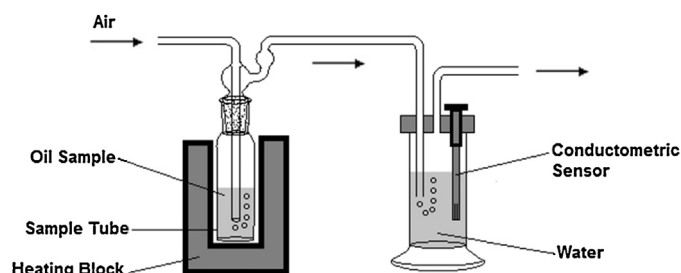


Fig. 1. Principle of Rancimat instrument.

reaction tube at a constant temperature of 120 °C while a continuous flow of air at the rate of 20 litre/h is passed through the sample. The conductivity was continuously measured of the second tube having 60 mL water until the induction time is reached. The test was run in triplicate and average results were reported.

Result and discussion

Characterization of the *Bz-4-tBz*

In order to find evidence in favour of the successful synthesis of the antioxidant having the same molecular structure of *Bz-4-tBz* which is shown in Fig. 2, various characterization techniques were used. The first direct evidence was observed by CHN analysis. According to the results, the observed values of the elemental analysis were; C, 73.63 and H, 8.44. These values were in good agreement with the calculated ones as; C, 74.57, H, 8.39.

Since the esterification is the main reaction in the synthesis of the *Bz-4-tBz* where the carboxylic and alcoholic groups couples to form new ester linkage so, FT-IR may be an effective technique to prove the successful N,N'-dicyclohexylcarbodiimide catalyzed coupling between 1,2,4,5-benzenetetracarboxylic acid and 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol. Fig. 3 shows the FT-IR

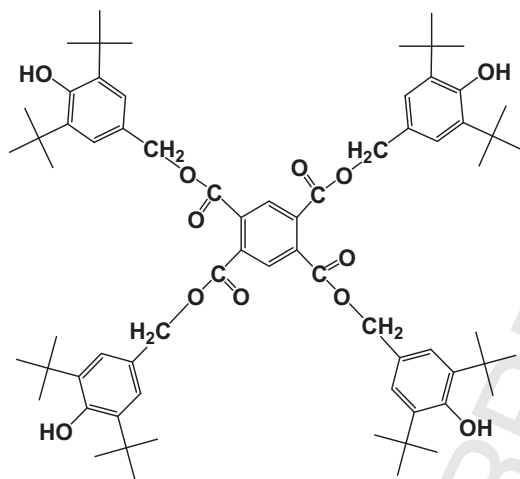


Fig. 2. Molecular structure of the synthesized *Bz-4-tBz*.

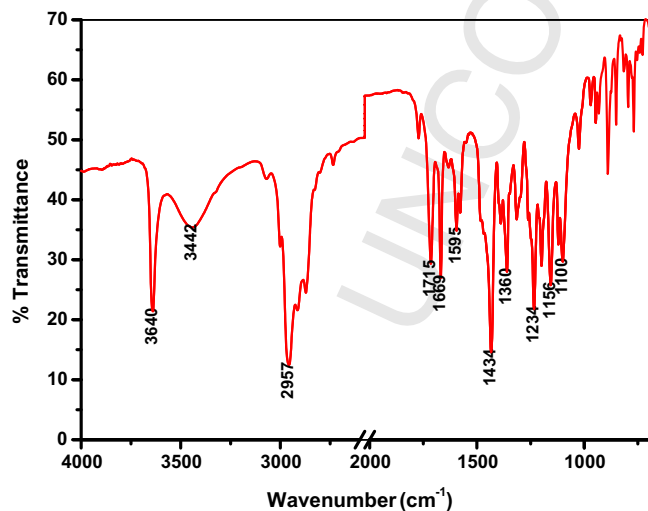


Fig. 3. FT-IR spectrum of *Bz-4-tBz*.

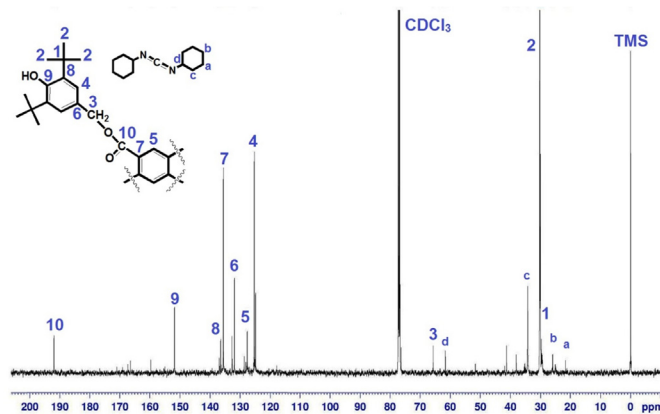


Fig. 4. ¹³C NMR of the additive *Bz-4-tBz* in CDCl₃.

spectrum of the *Bz-4-tBz* which revealed that all the characteristic peaks were observed which confirms the proposed structure of the *Bz-4-tBz* e.g., the band at 3620 cm⁻¹ corresponds to the hindered phenolic O-H stretching while the aromatic C-H stretching band appears at 3004 cm⁻¹. Asymmetric and symmetric C-H stretching (CH₃ groups) vibrations were observed at 2957 and 2870 cm⁻¹ respectively. The strong evidence in favour of the successful esterification is the appearance of strong sharp absorption band at 1715 cm⁻¹ which typically corresponds to the C=O stretching vibration of α-β unsaturated ester. Disappearance of the C=O stretching (acid) peak at 1700 cm⁻¹, and diminished O-H stretching band near 3442 cm⁻¹ corresponding to the alcoholic group of 3, 5-di-*tert*-butyl-4-hydroxybenzyl alcohol are the two other strong evidence in favour confirming the structure of *Bz-4-tBz*. Two other important peaks at 1669 and 1595 cm⁻¹ may be easily assigned to aromatic C=C stretching. Peaks at 1434 and 1360 cm⁻¹ attributed to the C-H bending (CH₃) and O-H bending (in-plane) while the C-O stretching (phenolic) and C-H wagging (CH₃) and C-O stretching (ester) peak appeared at 1230, 1156 and 1100 cm⁻¹ respectively.

Similar to the FT-IR, NMR also presents strong evidence in favour of the given structure of *Bz-4-tBz* in Fig. 2. The ¹³C NMR of the additive *Bz-4-tBz* is shown in Fig. 4. All the important signals were observed as the signals belonging to tertiary butyl groups carbons and CH₂ carbon of the 3,5-di-*tert*-butyl-4-hydroxybenzyl moiety was observed at 38 and 66 ppm respectively. Aromatic ring carbons of the 1,2,4,5-benzenetetracarboxyl and 3,5-di-*tert*-butyl-4-hydroxybenzyl moiety were observed between 125 and 155 ppm. Most important signal corresponding to >C=O (C10) appeared at 192 ppm which is a strong evidence of the successful esterification reaction between 1,2,4,5-benzenetetracarboxylic acid and 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol. Few carbons signals were also seen which corresponds to the minor impurity of N,N'-dicyclohexylcarbodiimide. Similarly ¹H-NMR spectrum of the additive *Bz-4-tBz* was found to show all characteristic signals of all protons corresponding to the hindered phenolic moiety, substituted aromatic ring and phenolic OH.

TG/DT (thermo-gravimetric/differential thermal analysis) curves of BHT and *Bz-4-tBz* were recorded in order to determine the working temperature range of this synthesized additive and also to know its thermal stability in comparison to conventional antioxidant like BHT. As per the graph shown in Fig. 5, it was observed that the *Bz-4-tBz* additive possesses higher thermal degradation temperature (268 °C) than BHT which degrades at 200 °C. Since the volatility is directly proportional to the thermal degradation, so the volatility of *Bz-4-tBz* may be considered low in comparison to BHT.

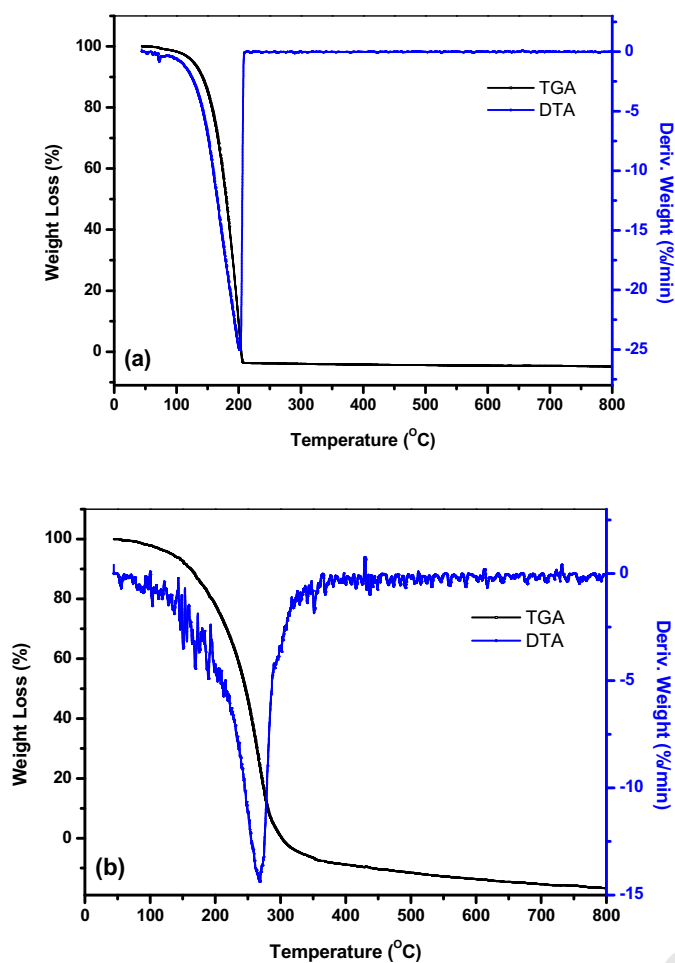


Fig. 5. TG/DT curves; (a) BHT and (b) additive *Bz-4-tBz*.

Physical properties and solubility study

The *Bz-4-tBz* obtained was turmeric yellow amorphous odourless solid in powder form and having the melting point 120 °C, packed density, 0.4554 gm/cc and lose density, 0.3145. It is soluble in the common organic solvents like acetone, methanol and toluene.

Along with the low volatility, the *Bz-4-tBz* is also supposed to have the increased solubility in lubes and fuels too in comparison to the BHT and BHA, because in the synthesized novel additive the hindered phenolic moieties are incorporated around the benzene nucleolus leading to the increased aromaticity. The generated ester functionalities may also help in salvation of this additive in polyol type lube base and the biodiesel which is also the methyl esters of the fatty acids chemically. So when solubility was tested, the *Bz-4-tBz* was found to have very good solubility in the polyol and biodiesel. Antioxidants like BHT and BHA needs the sonication at 50 °C at least for 30 min while for *Bz-4-tBz* normal stirring works well to make it soluble in the polyol and biodiesel (B100) (Fig. 6). Even in the 20% biodiesel blended diesel (B20), it is having very good solubility.

Performance evaluation as antioxidant

Rotating bomb oxidation test (RBOT) test

Four hindered phenolic moieties were incorporated around the benzene framework through the ester linkages in *Bz-4-tBz* structure. So it was supposed to possess the antioxidant activity as hindered phenols are widely used antioxidant additives for the

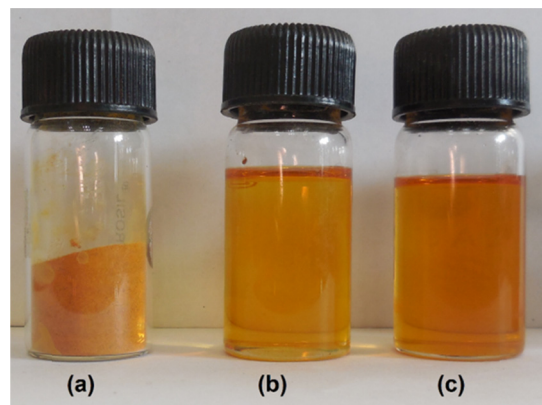


Fig. 6. (a) additive *Bz-4-tBz*; (b) additive in polyol and (c) additive in biodiesel (B100).

lubes and fuels along with the food and medicine purposes [16–18]. At first, in order to evaluate the antioxidant performance of the synthesized additive for the synthetic lubes, the different samples were prepared taking polyol as base with varying *Bz-4-tBz* concentrations as 500, 1000, 2000, 3000 and 4000 mg/kg. Rotatory bomb oxidation tests (RBOT) were conducted with these samples as per ASTM D2272 [14]. According to the expectations, the *Bz-4-tBz* was found to show the antioxidant additive character with concentration effect as the RBOT time observed for the blank polyol i.e. 6.72 min was found to be increased to a value of 12.63 min at 1000 mg/kg concentration which is further increased to 17.42 min at 2000 mg/kg concentration. No further increase in the RBOT time with increase in concentration beyond 2000 mg/kg was observed however the RBOT time was always higher in comparison to the blank. It is well known phenomenon that phenolic antioxidants like BHA have been shown to invert and act as pro-oxidant at higher loadings than optimum concentration [18–21]. So the optimum concentration of *Bz-4-tBz* is 2000 mg/kg at which the oxidative stability was found to be significantly increased to 2.59 times (Fig. 7). For comparison the RBOT test was also done with the 2000 mg/kg BHT in polyol for which the value of the RBOT time observed was 7.13 min. The higher activity may be correlated with the incorporated four phenolic moieties, increased aromatic character, increased thermal stability, low volatility and high solubility in polyol.

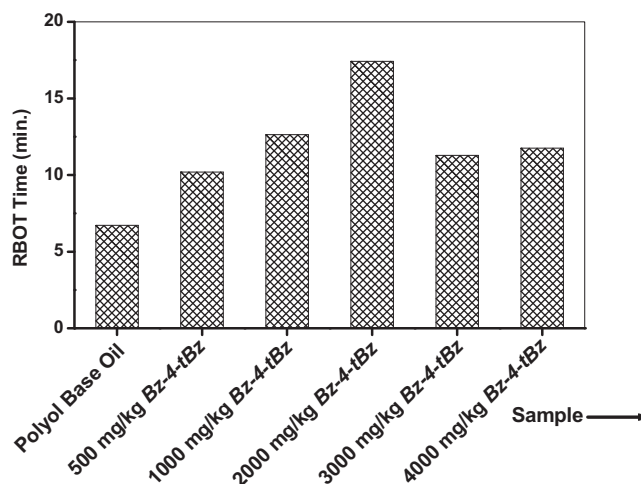


Fig. 7. RBOT time of blank polyol and its different blends with *Bz-4-tBz* additive in varying concentrations.

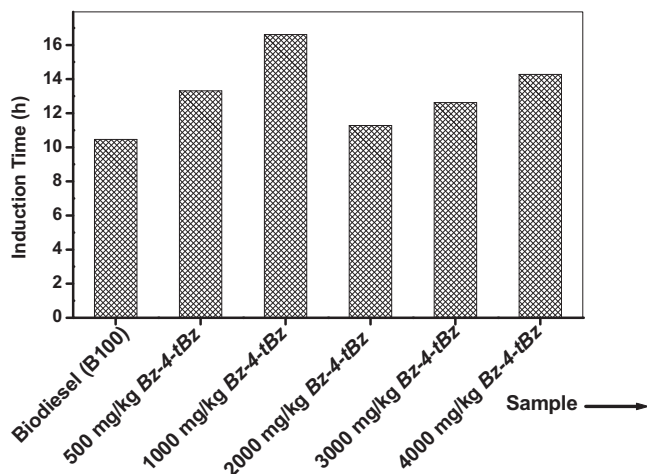


Fig. 8. Induction time by Rancimat test conducted on the biodiesel (B100) and its blends with the **Bz-4-tBz** additive at 120 °C.

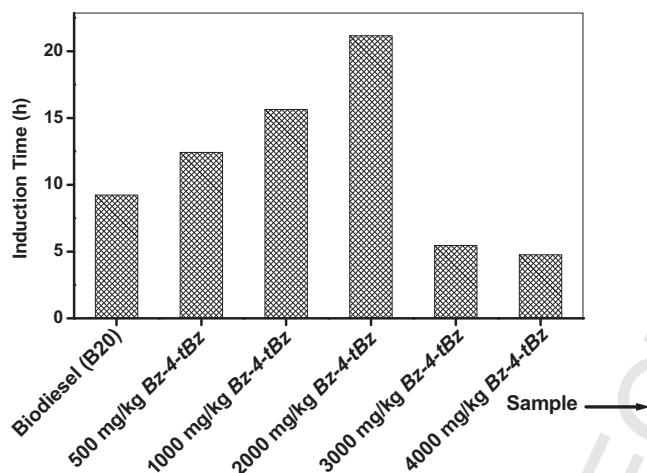


Fig. 9. Induction time by Rancimat test conducted on the biodiesel (B20) and its blends with the **Bz-4-tBz** additive at 120 °C.

Rancimat test

The synthesized additive **Bz-4-tBz** have good solubility in the biodiesel (B100) and biodiesel blended diesel (B20), so the performance evaluation was also carried out in these fuels also. Various samples were prepared varying the additive concentration (500–4000 mg/kg) in these two fuels and conducted the Rancimat test as per EN14112 standard [15]. The additive was found to be active as antioxidant in both the fuels. As far as the biodiesel in concerned, the value of the induction time for the blank biodiesel at 120 °C is 10.46 h. The additive **Bz-4-tBz** gives best performance at 1000 mg/kg concentration which increases the induction period to the 16.62 h which is a significant increase of 1.59 times (Fig. 8). On the other hand, in biodiesel blended diesel (B20), the value of the induction time for the blank sample at 120 °C is 9.23 h. The additive **Bz-4-tBz** gives best performance at 2000 mg/kg concentration which increases the induction period to the 21.6 h. This is a significant increase of 2.29 times (Fig. 9). It is worth mentioning that the induction time of the B100 sample doped with 1000 mg/kg

BHT is 14.76 h while the induction time for the sample having 2000 mg/kg BHT in B20 fuel comes out to be 17.34 h.

Conclusion

Since the conventional antioxidant additives like BHT (butylated hydroxytoluene) and BHA (butylated hydroxyanisole) have the limitation like low volatility and some time difficult solubility in lube base oil like polyol, the new molecule **Bz-4-tBz** was designed and synthesized having higher molecular weight in order to achieve the low volatility with increased solubility by incorporated higher aromatic character and ester functionalities. The chemical characterization were done using the CHN, FT-IR and NMR analysis and then the performance evaluation of the **Bz-4-tBz** as antioxidant additive in polyol (a synthetic lube base oil reference), biodiesel (B100) and blended diesel (B20) was done using the rotary bomb oxidation test (ASTM D2272) and Rancimat test (EN 14112). The **Bz-4-tBz** in 2000 mg/kg concentration in polyol enhance the RBOT time to 2.59 times while in B100 and B20 fuels the Rancimat induction time increases to 1.59 and 2.29 times at 1000 and 2000 mg/kg respectively. Further in future it would be interesting to study the performance of the **Bz-4-tBz** in presence of other type of additives like lubricity improvers, detergent dispersants, anticorrosion and viscosity modifiers, etc. which are generally added in the lubes, fuels and blended fuels along with studying its interaction with these additives at molecular level.

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References

- [1] R.M. Mortier, M.F. Fox, S.T. Orszulik (Eds.), Chemistry and Technology of Lubricants, Springer, Heidelberg, 2010.
- [2] G.H. Denison Jr., P.C. Condit, Ind. Eng. Chem. 37 (1945) 1102.
- [3] L.R. Rudnick, Lubricant Additives: Chemistry and Applications, Taylor & Francis Group, Boca Raton, 2009.
- [4] A. Demirbas, Biodiesel, 1st ed., Springer-Verlag, London, 2008.
- [5] A. Köckritz, A. Martin, Eur. J. Lipid Sci. Technol. 110 (2008) 812.
- [6] S. Schober, M. Mittelbach, Eur. J. Lipid Sci. Technol. 106 (2004) 382.
- [7] A.K. Bhatnagar, G.C. Joshi, S.C. Joshi, P.K. Sharma, A.K. Gupta, H.B. Goyal, K.G. Sharma, K. Kumar, Indian Patent No. 189476, 2004.
- [8] J.S. Hill, US Patent No. 7601862, 2009.
- [9] L. Zhang, G. Cai, W. Eli, Lubr. Sci. 25 (2013) 209.
- [10] R.K. Singh, A. Kukrety, A.K. Singh, ACS Sustain. Chem. Eng. 2 (2014) 1959.
- [11] C.A. Migdal, D.J. Sikora, US Patent No. 20050170978 A1, 2005.
- [12] EN 14214, Automotive Fuels, Fatty Acid Methyl Esters (FAME) for Diesel Engines. Requirements and Test Methods, European Committee for Standards (CEN), Belgium, 2003.
- [13] EN 590, Automotive Fuels – Diesel – Requirements and Test Methods, European Committee for Standards (CEN), Belgium, 2004.
- [14] ASTM D 2272-11, Standard test method for oxidation stability of steam turbine oils by rotating pressure vessel, in: Annual Book of ASTM Standards, 2011ASTM International West Conshohocken, PA.
- [15] EN 14112, Fat and oil derivatives, Fatty Acid Methyl Esters (FAME), in: Determination of Oxidation Stability (Accelerated Oxidation Test), European Committee for Standards (CEN), Belgium, 2003.
- [16] R.K. Singh, S. Pandey, R.C. Saxena, G.D. Thakre, N. Atray, S.S. Ray, N. J. Chem. 39 (2015) 5354.
- [17] B.K. Sharma, J.M. Perez, S.Z. Erhan, Energy Fuels 21 (2007) 2408.
- [18] R.O. Dunn, Fuel Process. Technol. 86 (2005) 1071.
- [19] G. Litwinienko, T. Kasprzyska-Guttman, M. Studzinski, Thermochim. Acta 307 (1997) 97.
- [20] B. Kowalski, Thermochim. Acta 213 (1993) 135.
- [21] B. Kowalski, Thermochim. Acta 184 (1991) 49.



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