

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

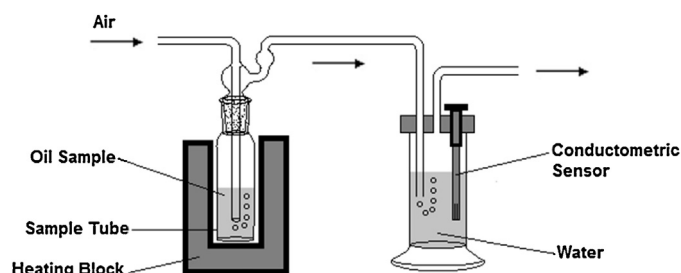


Fig. 1. Principle of Rancimat instrument.

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

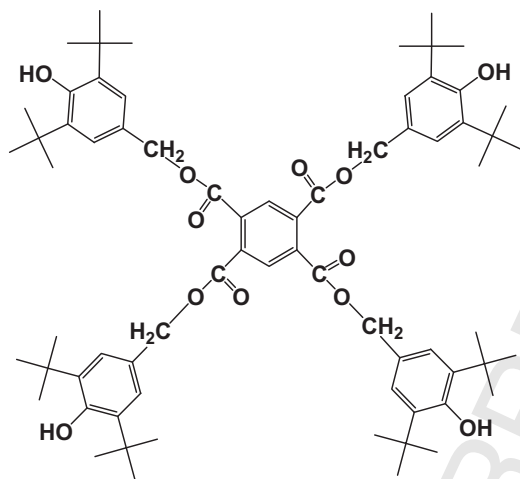


Fig. 2. Molecular structure of the synthesized *Bz-4-tBz*.

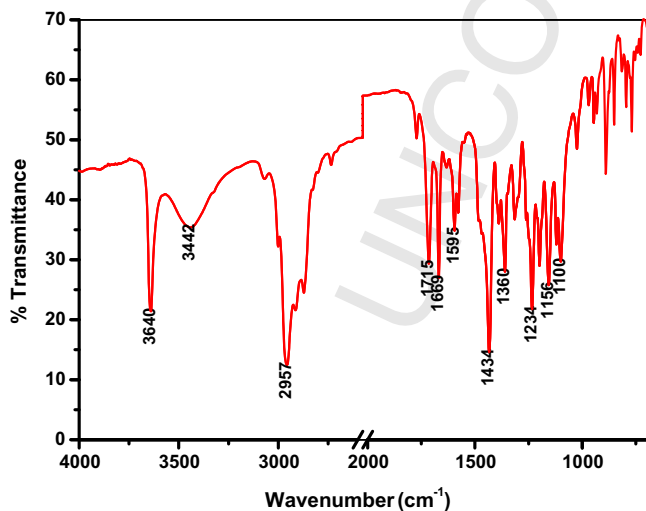


Fig. 3. FT-IR spectrum of *Bz-4-tBz*.

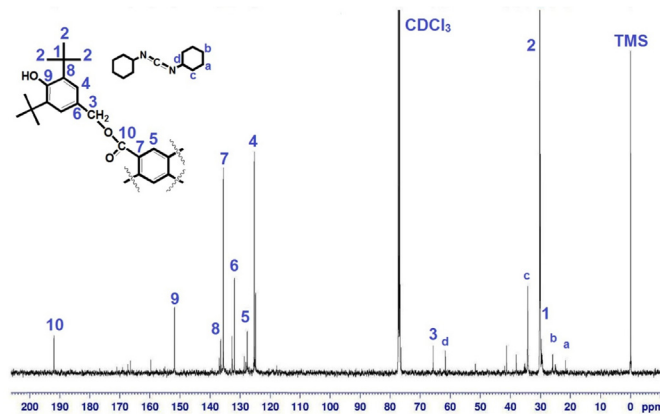


Fig. 4. ¹³C NMR of the additive *Bz-4-tBz* in CDCl₃.

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.

