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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.

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 dispersiblity 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) whiles 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/m^3; 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

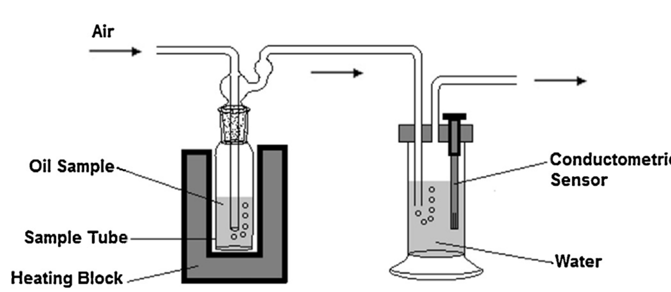

Fig. 1. Principle of Rancimat instrument.