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Synthesis of Fatty Alcohol based Sterically Hindered Esters as Potential Antioxidants for Bioadditives

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Abstract—Four hindered phenolic esters were prepared by esterification between 3-(3,5-Di-tert-butyl-hydroxyphenyl)propionic acid and fatty alcohols. The synthesized esters were characterised by NMR, IR and ESI-MS and analysed for their antioxidant properties and thermal stability. Differential scanning calorimetry (DSC) and Rancimat studies were conducted to explore the effect of synthesized compounds on oxidation stability of base oil. The results from both the studies were correlated well. Thermogravimetric analysis indicates that all the esters have significantly high thermal stability. Among all the prepared compounds myristyl alcohol ester showed better antioxidant properties whereas, stearyl alcohol ester exhibited higher thermal stability. The synthesized antioxidants can be potential bio additives for lubricant formulations.

Keywords: differential scanning calorimetry, thermal stability, oxidation induction time, rancimat, surface-volume ratio

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INTRODUCTION

Lubricating fluids are widely used in industrial and automobile applications to improve the service life of machineries by providing protection against wear and friction [1, 2]. Despite their many advantages, lubricating oils possess poor oxidation and thermal stabilities. The continuous exposure to elevated temperatures and environmental oxygen leads to the formation of free radicals [3, 4]. Additives are introduced to improve the lubricant performance and increase the shelf life by improving anti corrosion, antioxidant properties and also to enhance the tribological properties such as antiwear and antifriction [5, 6]. As per the environmental regulations low levels of sulfur, phosphate ash and metal free additives have been encouraged in lubrication applications [7–9]. In this regard, researchers synthesized some metal free additives and successfully characterised their tribological properties and their performance is comparable to conventional multifunctional additive Zinc dialkyldithiophosphates (ZDDP). Oxidative breakdown of lubricants usually results in the formation of primary and secondary oxidation products (peroxides, carboxylic acids, alcohols, aldehydes and ketones) which alter the physical and chemical properties of lubricant basestock [10]. Therefore, antioxidants are needed to delay or prevent the oxidation process of lubricant by inhibiting the formation of free radicals [11–13].

Hindered phenols and arylamines are well known antioxidant additives in lubricating oils [10, 14]. Hindered phenolic compounds act as hydrogen donors and can donate hydrogen atom to the alkoxy or alkyl peroxy free radicals to neutralize [10, 15]. Some petrochemical derived sterically hindered phenolic (SHP) compounds are well known commercial antioxidants, such as BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole) and TBHQ (*tert*-butylhydroquinone) [16, 17]. Amidation and esterification of phenolic acids and alkyl phenols are practical techniques to enhance their solubility and emulsification properties as well as oxidation inhibition performance [18, 19]. Yu et al. synthesized Schiff base bridged hindered phenolic diphenylamine antioxidants and found that the compounds have better thermal stability and antioxidant efficiency in 150SN base oil [20]. However, there has been growing interest for bio based lubricants and additives due to concerns about environmental pollution caused by mineral oil based lubricants and additives [21, 22]. Oleochemical based additives will have better biodegradability compared to traditional petroleum derived additives due to the presence of natural components and the lack of metal

ions. Singh et al. synthesized two phenolic esters of pentaerythritol monooleate and evaluated their antioxidant and tribology properties [14]. The oxidative stability of lubricant base fluid was greatly improved with each additive along with effective tribology performance. In the present study we report synthesis of sterically hindered esters with long chain fatty alcohols (C_{14}, $C_{11:1}$, C_{18}, and $C_{18:1}$), their characterization using NMR, IR and ESI-MS and their oxidation and thermal stability properties enhancement in an eco friendly base oil.

EXPERIMENTAL

Materials. 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid, myristyl alcohol, stearyl alcohol, 10-undecenol, oleyl alcohol, 1-ethyl-3(3-dimethylaminopropyl) carbodimide hydrochloride (EDC · HCl) and 4-dimethylaminopyridine (DMAP) were purchased from Sigma-Aldrich (St. Louis, USA). Silica gel (60–120 mesh) for column chromatography was purchased from M/s Acme Synthetic Chemicals (Mumbai, India) and pre-coated TLC plates (silica gel 60 F254) were purchased from M/s Merck (Darmstadt, Germany). All the solvents were purchased from M/s SD Fine Chemicals (Mumbai, India) and were of the highest grade of purity.

Characterization. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 300 and 75 MHz, respectively and TMS was used as an internal standard. Mass spectra were recorded using electron spray ionization on Waters e2695 Separators module (Waters, Milford, MA, USA) mass spectrometer. IR spectra were recorded in dichloromethane on a Perkin-Elmer Fourier Transform Infrared (FT-IR) spectrum BX instrument (model: Spectrum BX; Connecticut, USA).

General procedure for the synthesis of esters (2a-2d). A mixture of 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid (1.0 g, 3.6 mmol), fatty alcohol (5.4 mmol) and EDC · HCl (0.67 g, 4.3 mmol) were dissolved in dry DCM (20 mL), stirred at room temperature for 20 min and added DMAP (0.43 g, 3.6 mmol) to the reaction mixture and the stirring was continued for 6 h. The formation of product was monitored with TLC (hexane/ethyl acetate 90 : 10, v/v). After completion of reaction the reaction mixture was extracted in to ethyl acetate and washed with water and dried over sodium sulphate and the resulted crude product was subjected to column chromatography using hexane and ethyl acetate (90 : 10, v/v) to get pure product.

Synthesis of tetra decyl 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate (2a). Quantities of substrates taken: 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid (1.0 g, 3.6 mmol), myristyl alcohol (1.15 g, 5.4 mmol), EDC · HCl (0.67 g, 4.3 mmol) and DMAP (0.43 g, 3.6 mmol), yield obtained 93% (1.6 g) of pale yellow color solid. Mp 47–48°C; ^{1}H NMR ($CDCl_3$, ppm) δ 0.88 (t, 3H, $-CH_3$), 1.25–1.33 (m, 20H, 10*x*$-CH_2$), 1.42 (s, 18H, 6*x*$-CH_3$), 1.54–1.64 (m, 2H, $-CH_2$), 2.55–2.64 (t, 2H, $-CH_2CO$), 2.84–2.90 (t, 2H, $-CH_2-$Ar), 4.0–4.11 (t, 2H, $-OCH_2$), 6.99 (s, 1H), 7.25 (s, 2H): ^{13}C NMR ($CDCl_3$, ppm) δ 14.1, 22.7, 25, 29.3, 29.6, 31.6, 34.2, 36.5, 64.7, 124.7, 131.1, 135.9, 152.0, 173.4: IR (cm^{-1}, $CHCl_3$): 3641, 2927, 2860, 1732, 1443, 1232, 1160, 879: ESI MS: *m/z* 497 $[M + Na]^+$.

Synthesis of undec-10-ene-yl 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate (2b). Quantities of substrates taken: 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid (1.0 g, 3.6 mmol), 10-undecenol (0.92 g, 5.4 mmol) and EDC · HCl (0.67 g, 4.3 mmol) DMAP (0.43 g, 3.6 mmol), yield obtained 95% (1.48 g) of pale yellow color solid. Mp 32–33°C; ^{1}H NMR ($CDCl_3$, ppm) δ 0.88 (t, 3H, $-CH_3$), 1.24–1.34 (m, 14H, 7*x*$-CH_2$), 1.39–1.45 (s, 18H, 6*x*3$-CH_3$), 1.56–1.66 (m, 2H, $-CH_2$), 2.57–2.64 (t, 2H $-CH_2CO$), 2.86–2.94 (t, 2H, $-CH_2-$Ar), 4.08–4.12 (t, 2H, $-OCH_2$), 4.95 (m, 2H), 5.80 (m, 1H), 6.84 (s, 1H), 7.26 (s, 2H), ^{13}C NMR ($CDCl_3$, ppm) δ 14.1, 22.7, 25, 29.3, 29.6, 32.6, 34.4, 36.2, 64.8, 115.7, 123.4, 131.3, 135.6, 152.7, 173.6: IR (cm^{-1}, $CHCl_3$): 3640, 3068, 2925, 2864, 1730, 1639, 1453, 1261, 1177, 802: ESI MS: *m/z* 453 $[M + Na]^+$.

Synthesis of octa decyl 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate (2c). Quantities of substrates taken: 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid (1.0 g, 3.6 mmol), stearyl alcohol (1.45 g, 5.4 mmol) and EDC · HCl (0.67 g, 4.3 mmol) DMAP (0.45 g, 3.6 mmol), yield obtained 97% (1.84 g) of pale yellow color solid. Mp 55–56°C; ^{1}H NMR ($CDCl_3$, ppm) δ 0.88 (t, 3H, $-CH_3$), 1.25–1.33 (m, 30H, 15*x*$-CH_2$), 1.44 (s, 18H, 6*x*$-CH_3$), 1.56–1.64 (m, 2H, $-CH_2$), 2.56–2.63 (t, 2H, $-CH_2CO$), 2.83–2.90 (t, 2H, $-CH_2-$Ar), 4.0–4.11 (t, 2H, $-OCH_2$), 7.01 (s, 1H), 7.27 (s, 2H): ^{13}C NMR ($CDCl_3$, ppm) δ 14.1, 22.6, 25, 29.3, 29.6, 31.7, 34.2, 36.7, 64.6, 124.6, 131.8, 135.7, 152.0, 173.2: IR (cm^{-1}, $CHCl_3$): 3642, 2924, 2857, 1732, 1444, 1360, 1235, 1160, 874: ESI MS: *m/z* 553 $[M + Na]^+$.

Synthesis of (Z) octa dec-9-ene-yl 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate (2d). Quantities of substrates taken: 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid (1.0 g, 3.6 mmol), oleyl alcohol (1.44 g, 5.4 mmol) and EDC · HCl (0.67 g, 4.3 mmol) DMAP (0.43 g, 3.6 mmol), yield obtained 95% (1.80 g) of pale yellow color solid. Mp 38–39°C; ^{1}H NMR ($CDCl_3$, ppm) δ 0.87 (t, 3H, $-CH_3$), 1.25–1.33 (m, 22H, 11*x*$-CH_2$), 1.43 (s, 18H, 6*x*$-CH_3$), 1.56–1.63 (m, 2H, $-CH_2$), 1.99–2.04 (m, 4H, 2*x*$-CH_2$), 2.56–2.61 (t, 2H, $-CH_2CO$), 2.84–2.90 (t, 2H, $-CH_2-$Ar), 4.0–4.10 (t, 2H, $-OCH_2$), 5.36 (m, 2H, –HC=CH), 6.99 (s, 1H), 7.27 (s, 2H), ^{13}C NMR ($CDCl_3$, ppm)

δ 14.1, 22.7, 25, 29.3, 29.6, 32.8, 34.2, 36.8, 64.7, 124.8, 129.3, 131.2, 135.2, 152.2, 173.4: IR (cm^{-1}, $CHCl_3$): 3644, 2924, 2862, 1736, 1466, 1360, 1233, 1162, 876: ESI MS: *m/z* 551 $[M + Na]^+$.

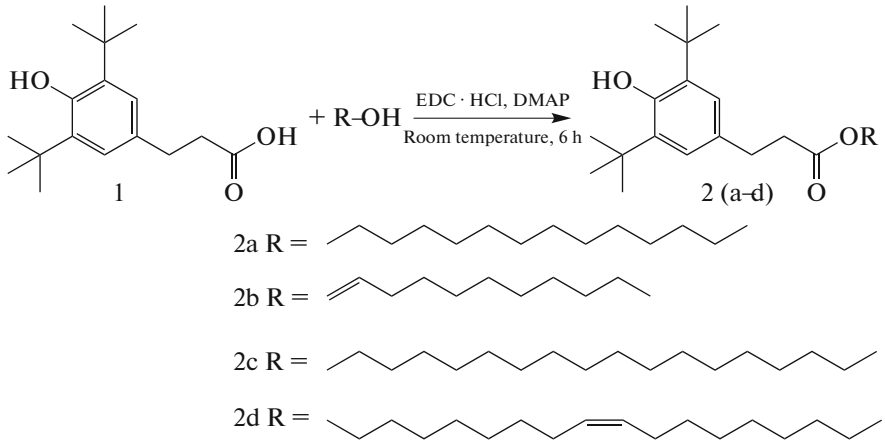
Rancimat analysis. The oxidative induction time (OIT) was investigated by a Metrohm Rancimat model 743 (Herisau/Switzerland) as per AOCS official method Cd 12b-92. The conductivity of distilled water (60 mL) was measured by continuous air flow (20 L/h) bubbled into base oil (5 g) at 110 and 140°C. The resulted volatile components were collected in water and the time taken to reach the conductivity inflection was recorded as OIT [23]. The analysis was performed in duplicate and mean value is reported.

Differential scanning calorimetry analysis. The oxidative induction time (OIT) and oxidation onset temperature (OT) were measured with differential scanning calorimeter (DSC) according to ASTM E 2009-08. DSC analyses were conducted on Q-100 thermal analyzer from TA Instruments under continuous oxygen flow at 50 mL/min in isothermal mode. Temperature was raised from 40°C to specified temperature 140°C. Typically, 5 ± 0.5 mg of tested sample was weighed in sealed aluminum pan and placed in the equipment chamber. Similarly the non isothermal tests also conducted in oxygen environment with increasing the temperature at a rate of 10°C/min up to appearance of exothermic peak. The oxidation induction time and oxidation onset temperatures were analyzed by using TA universal analysis software. The tangent was drawn by extrapolating of baseline to the maximum exothermic peak.

Thermogravimetric analysis. TA Q500 (TA Instruments, Inc., New Castle, DE, USA.) instrument was used to determine the thermal stability in non-isothermal mode by taking 4 ± 0.5 mg sample in α-Al_2O_3 crucible operated at the temperature range about 40–400°C with a heating rate of 10°C/min in continuous nitrogen gas flow of 60 mL/min.

RESULTS AND DISCUSSION

Synthesis and spectral analysis. Sterically hindered phenolic esters were synthesised with various fatty alcohols using EDC · HCl and DMAP as catalyst with 93 to 97% yield (Scheme 1). The prepared esters were characterised by ^1H NMR, ^{13}C NMR, IR and mass spectral studies. The characteristic triplet peaks appeared in ^1H NMR at 4.08–4.13 and 2.54–2.64 ppm correspond to the methylene protons of alkyl chain attached to the carbonyl oxygen and the protons α to the carbonyl carbon respectively. The peaks present at 1.24–1.32 ppm are due to fatty alkyl chain protons whereas the chemical shift values observed at 4.95–5.80 ppm indicate the presence of unsaturated protons (for the products 2b and 2d) and the signals appeared at ~7.26 ppm confirm the presence of phenyl ring. In ^{13}C NMR the prominent peak appeared at 173.2–173.6 ppm is due to carbonyl carbon and the peak observed at 64.6–64.8 ppm corresponds to the alkyl chain carbon attached to carbonyl group. The peaks observed at 22.7–34.4 ppm and 123.4–152.9 ppm corresponds to alkyl chain carbons and aromatic carbon signals respectively. In the FT-IR spectra a significant peak appeared at 3640–3644 cm^{-1} indicating the presence of phenolic OH and the characteristic peaks observed at 1732–1736 cm^{-1} and 1160–1177 cm^{-1} are attributed to ester group. The peaks appeared at ~2927 and ~2864 cm^{-1} are due to the symmetric and asymmetric stretching bands of alkyl chain. Moreover, the molecular ions *m/z* at 497, 453, 553, 551 $[M + Na]^+$ obtained by positive mode of ESI spectra further confirm the formation of target molecules. The compound octa decyl 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate (2c) is commercially known as Irganox 1076 and act as antioxidant [24, 25]. In the present study the similar class of new Irganox 1076 compounds was synthesized by varying the fatty alkyl chain and studied the effect of alkyl chain on the oxidation and thermal stabilities.



Scheme 1. Synthesis of 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionic acid, fatty alcohol esters.

Table 1. Oxidation induction time of base oil and base oil containing synthesized antioxidants evaluated by Rancimat and DSC isothermal method

Sample	Rancimat OIT values, h		DSC OIT values, h		
	Additive concentration				
	100 ppm		200 ppm		200 ppm
	110°C	140°C	110°C	140°C	140°C
Base oil	26.96 ± 0.72***	1.55 ± 0.21^{ns}	–	–	2.96 ± 0.34
B + 2a	43.24 ± 0.79***	4.63 ± 0.61^{ns}	49.23 ± 1.68***	12.36 ± 0.36***	4.33 ± 0.10
B + 2b	30.47 ± 0.56***	4.16 ± 0.39^{ns}	32.42 ± 0.88***	7.52 ± 0.60***	4.10 ± 0.48
B + 2c	42.52 ± 0.74***	4.48 ± 0.19^{ns}	46.41 ± 0.98***	11.45 ± 0.21***	4.24 ± 0.32
B + 2d	29.37 ± 0.38***	4.16 ± 0.28^{ns}	37.46 ± 0.68***	8.94 ± 0.11***	4.18 ± 0.35
B + BHT	28.46 ± 0.61***	3.26 ± 0.36^{ns}	30.24 ± 0.85***	8.56 ± 0.47***	3.96 ± 0.57

(B = base oil, 2a = tetra decyl 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate, 2b = undec-10-ene-yl 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate, 2c = octa decyl 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate, 2d = octa dec-9-ene-yl 3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate).

Antioxidant activity by Rancimat. Antioxidant activity of the base fluid and base fluid containing synthesized additives was evaluated by measuring the oxidative induction time (OIT) by conducting rancimat tests. The OIT value was obtained by plotting graph conductivity against time, a high OIT value indicates greater resistant towards oxidation [26]. The analysis was carried out by blending 100 and 200 ppm concentration of each additive in base oil and base oil without additive in the presence of atmospheric air at both 110 and 140°C temperature. The experiment was carried out in triplicate and the values are given as mean ± SD of three tests. The results found significantly ($p < 0.001$) higher OIT values in rancimat compared to DSC (One-way ANOVA test). The resulted OIT values were reported in Table 1 (***$P < 0.001$; ns: non-significant). It illustrates that at 100 ppm concentration all the additives enhanced the oxidation stability of base oil. Typically the base oil induction period of 25.96 h at 110°C and 1.55 h at 140°C were further increased to 43.24 h at 110°C and 4.63 h at 140°C in the case of base oil spiked with 2a. Further increasing the additive concentration to 200 ppm at both the temperature resulted in improvement of oxidation stability of base oil. The OIT values of base oil improved to 49.23 h at 110°C and 12.36 h at 140°C with additive 2a, it is a significant increase of more than 1.9 times comparing to 100 ppm additive dosage. All the synthesized additives exhibited improved stability however, the variation in the results is due to the nature of alkyl chain. Unsaturation in alkyl chain has significant effect on OIT values of SHP esters. Unsaturated alkyl chain containing esters showed lower oxidation inhibition ability than the saturated esters. This is due to the fact that the allylic positions to the double bonds are prone to oxidation [27, 28].

Antioxidant activity by DSC (isothermal). Isothermal differential scanning calorimetry studies were employed to determine the oxidation induction time. The time taken for the appearance of exothermic peak in the isothermal experiment is recorded as oxidation induction time [29, 30]. Antioxidant activity of synthesized compounds was examined by blending with base oil at 200 ppm concentration. Table 1 shows increase in OIT of base oil from 2.96 h to 4.33 h with additive 2a. The delay in oxidation clearly explains the efficiency of blended additive. Among all the derivatives, 2a showed superior performance followed by 2c and 2d whereas, the lower OIT observed with additive 2b may be due to the presence of terminal unsaturation. All the synthesised compounds exhibited superior performance compared to BHT. The experiment was carried out in triplicate and the values are given as mean ± SD of three tests. Figure 1a compares the OIT of Rancimat and OIT of DSC, there observed significantly ($p < 0.001$) higher OIT values for all the test samples in Rancimat than DSC according to Two-way ANOVA test (Tukey's multiple comparison test). However, comparing the results OIT of all the synthesized additives there observed significantly ($p < 0.001$) higher OIT values compared to BHT (Fig. 1b). The higher OIT value observed in Rancimat tests than DSC is mainly due to the amount of test sample, exclusively a low quantity of sample nearly 3–5 mg was used in DSC whereas, in Rancimat 5 g of sample is required. Another important factor is surface-volume ratio between tested sample and oxygen. Typically in Rancimat the surface-volume ratio of sample placed in a test tube is smaller than DSC analysis [31]. Usually the high surface-volume ratio or a small quantity of sample is more effectively react with oxygen. Moreover, the Rancimat analysis was conducted with air flow however, the DSC tests were conducted with

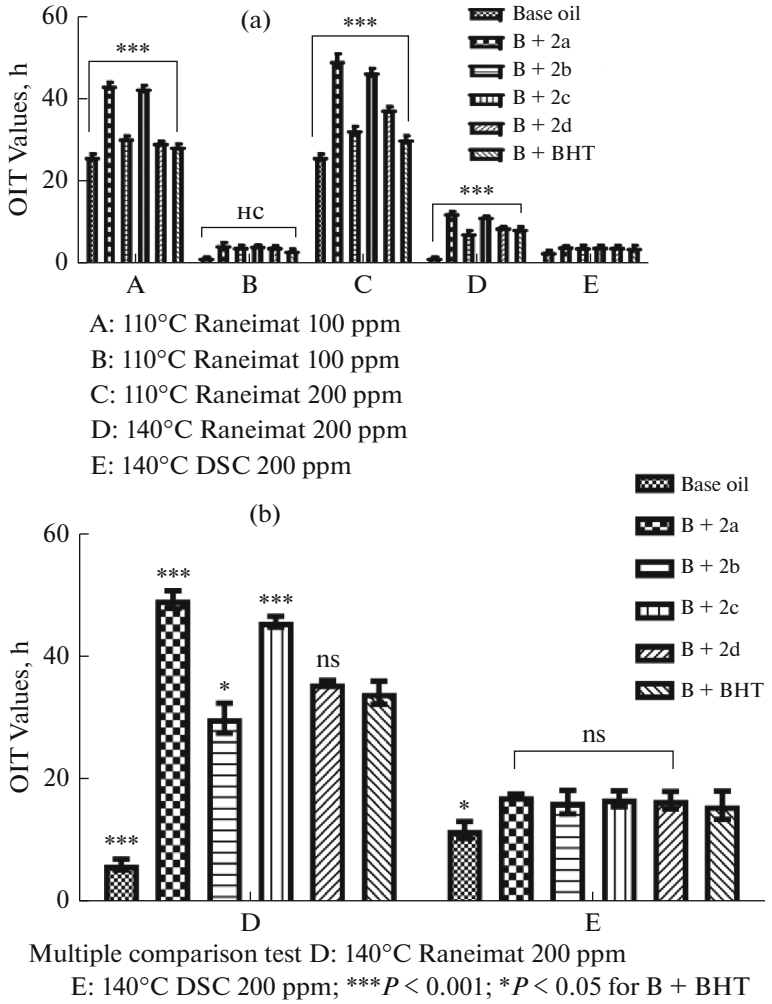


Fig. 1. (a) Antioxidant performance of synthesized compounds. (b) Comparison between DSC induction time and Rancimat induction time at 140°C and 200 ppm additive concentration.

pure oxygen hence the OIT reached by DSC is more rapid than Rancimat test [28]. A good correlation existed between DSC OIT and Rancimat OIT values as shown in Fig. 2. The correlation between DSC and Rancimat OIT is calculated from pearson correlation coefficient [26] and there exist a positive linear correlation ($R^2 = 0.875$).

Oxidation onset temperature by DSC (non isothermal). Non isothermal DSC tests were employed to determine the onset oxidation temperature (OT) and signal maximum temperature (SM) within a short time. OT values were recorded when the appearance of exothermic peak with respect to heat flow and it indicates the initiation of oxidation. The experiment was carried out in triplicate and the values are given as mean ± SD of three tests. Figure 3 illustrates the enhancement in oxidation stability of base oil blended at 200 ppm concentration of synthesized additives. Additive 2a improved the initial oxidation stability of base oil from 180 to 241°C whereas 2b, 2c and 2d improved to 231, 238, and 231°C respectively. All the additives exhibited improved oxidation stability of base oil than the commercially available antioxidant BHT (229°C). In addition to OT values SM temperature values also improved with tested additives ranging from 268 to 291°C (Table 2) compared to base oil SM value at 205°C. However, commercial additive BHT could improve the base oil SM value to 257°C only. The mean differences of oxidation stability temperatures (OT and SM) of synthesized additives (One-way ANOVA test) showed that there was statistically significant higher OT and SM values compared to BHT ($P < 0.001$). The improvements in OT and SM temperatures of additive blended base oil confirm the high antioxidant efficacy of synthesized SHP esters (***$P <$ 0.001 compared with B + BHT; ns: non-significant).

Thermogravimetric analysis. Thermal stabilities of synthesized SHP esters were examined by using thermogravimetric analysis (TGA) to describe the working temperature range of synthesized additives. Thermo-

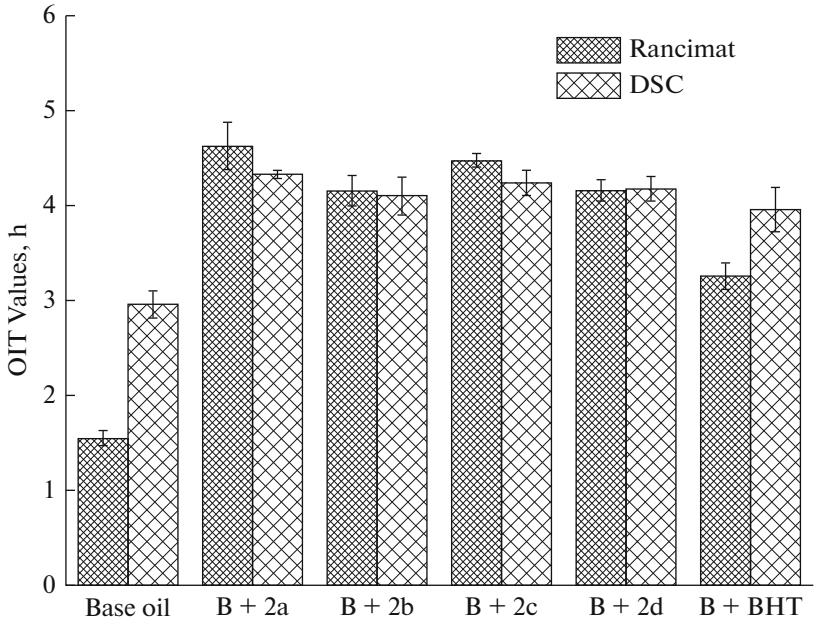


Fig. 2. Correlation between isothermal DSC induction time and Rancimat induction time.

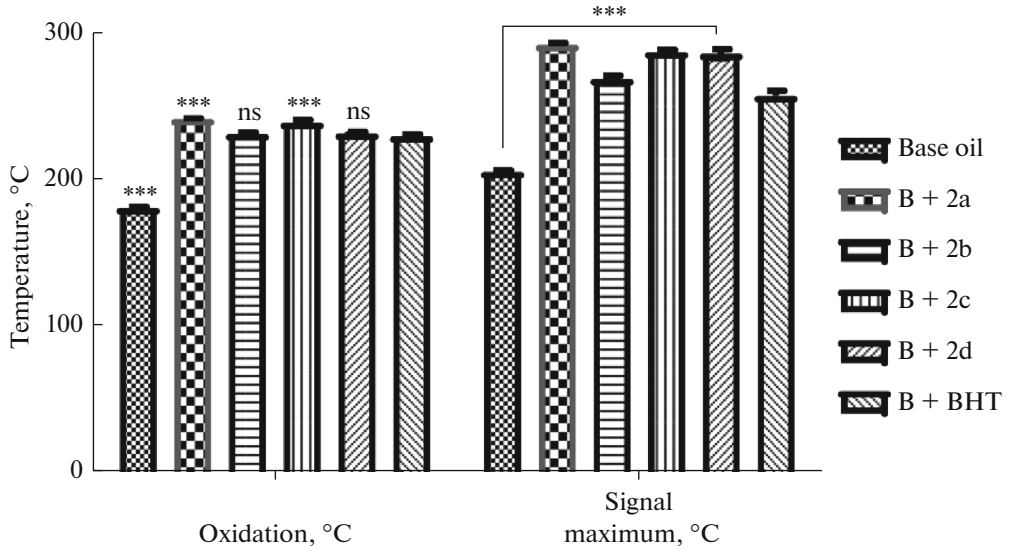


Fig. 3. Non-isothermal DSC test (onset temperature).

grams were obtained by plotting a graph temperature against weight loss (wt %) as presented in Fig. 4. The experiment was carried out in triplicate and the values are given as mean ± SD of three tests. Figure 4 and Table 3 indicates good onset decomposition temperatures (T_d) and signal maximum decomposition temperature ($T_{d\ max}$) for all the synthesized additives. The stability ranges from 243 to 290°C whereas, 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (1) shows 178°C. The mean differences of thermal degradation temperatures (T_d and $T_{d\ max}$) of synthesized additives (One-way ANOVA test) showed that there was statistically significant higher thermal degradation temperatures compared with sample 1 ($P < 0.001$) (***$P <$ 0.001). The variation in thermal stability is due to alkyl chain length and unsaturation [32].

Table 2. Antioxidant activity of SHP esters on base oil at 200 ppm concentration evaluated by DSC non-isothermal method

Sample	OIT, °C	SM, °C
Base oil	180 ± 0.81***	205 ± 0.92***
B + 2a	241 ± 0.63***	291 ± 1.25***
B + 2b	231 ± 1.13^{ns}	268 ± 2.28***
B + 2c	238 ± 1.81***	286 ± 1.40***
B + 2d	231 ± 0.81^{ns}	285 ± 3.18***
B + BHT	229 ±1.23	257 ± 3.46

Table 3. Thermal stability of SHP esters T_d and $T_{d\,max}$

Sample	T_d	$T_{d\,max}$
1	178 ± 1.58	300 ± 4.21
2a	283 ± 2.26***	355 ± 4.16***
2b	243 ± 2.50***	331 ± 2.54***
2c	290 ± 3.04***	360 ± 3.54***
2d	260 ± 0.94***	341 ± 2.48***

CONCLUSIONS

In the present study, four sterically hindered phenolic esters were synthesized and evaluated for their antioxidant efficacy in lubricant base oil using Rancimat and DSC methods. The results obtained from both methods are positively correlated with each other. The isothermal OIT and nonisothermal OT were also correlated positively and there exist nearly linear relation with each SHP esters. The thermal stability tests from TGA analysis illustrates that all the synthesized esters decomposed at higher temperatures. Compared to BHT all the synthesized esters exhibited superior antioxidant performance in the base oil in terms of enhancing the induction time and onset oxidation temperature.

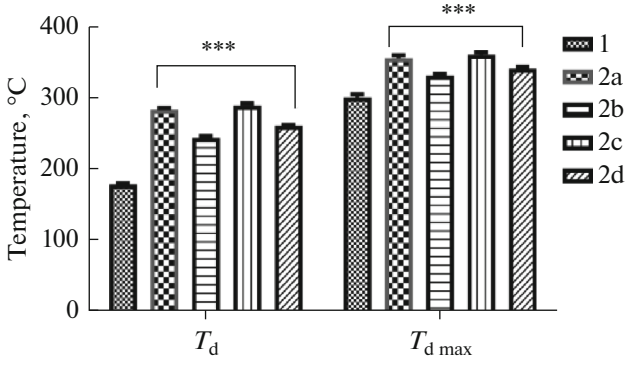


Fig. 4. Thermal stability of SHP esters.

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CONFLICT OF INTEREST

The authors declare no conflict of interest to this work.

ADDITIONAL INFORMATION

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REFERENCES

1. X. Liu, X. Shi, Y. Huang, et al., J. Alloy. Compd. **765**, 7 (2018).
2. I. Minami, H. Kamimura, and S. Mori, J. Synth. Lubr. **24**, 135 (2007).
3. S. D. Kouame and E. Liu, Tribol. Int. **72**, 58 (2014).
4. H. Omrani, A. E. Dudelzak, B. P. Hollebone, and H.-P. Loock, Anal. Chim. Acta **811**, 1 (2014).
5. F. L. G. Borda, S. J. R. de Oliveira, L. M. S. M. Lazaro, and A. J. K. Leiryz, Tribol. Int. **117**, 52 (2018).
6. P. Oulego, D. Blanco, D. Ramos, et al., J. Mol. Liq. **272**, 937 (2018).
7. C. A. Migdal, *Antioxidants, Lubricant Additives Chemistry and Applications*, Ed. by L. R. Rudnick (Marcel Dekker, New York, 2003), pp. 1–28.
8. V. Jaiswal, Kalyani, R. B. Rastogi, and R. Kumar, J. Mater. Chem. A **2**, 10424 (2014).
9. V. Jaiswal, S. R. Gupta, R. B. Rastogi, et al., J. Mater. Chem. A **3**, 5092 (2015).
10. Y. Wu, W. Li, M. Zhang, and X. Wang, Thermochim. Acta **569**, 112 (2013).
11. N. J. Fox and G. W. Stachowiak, Tribol. Int. **40**, 1035 (2007).
12. Y. Ohkatsu and T. Nishiyama, Polym. Degrad. Stab. **67**, 313 (2000).
13. K. H. Tan, H. Awala, R. R. Mukti, et al., J. Taiwan. Inst. Chem. Eng. **58**, 565 (2016).
14. R. K. Singh, A. Kukrety, and A. K. Singh, ACS. Sustain. Chem. Eng. **2**, 1959 (2014).
15. A. R. Nath, W. A. Yehye, N. W. M. Zulkifli, and M. R. Johan, Thermochim. Acta **670**, 7 (2018).
16. L. Huang, J. Ma, X. Wang, et al., Tribol. Int. **121**, 114 (2018). 12
17. S. K. Loh, S. M. Chew, and Y. M. Choo, J. Am. Oil Chem. Soc. **83**, 947 (2006).
18. A. S. Muniz-Wypych, M. M. da Costa, A. R. Oliveira, et al., Eur. J. Lipid Sci. Technol. **119**, 1700179 (2017).
19. K. Nakamura, T. Nakajima, T. Aoyama, et al., Tetrahedron **70**, 8097 (2014).
20. S. Yu, J. Feng, T. Cai, and S. Liu, Ind. Eng. Chem. Res. **56**, 4196 (2017).

21. C. H. Chan, S. W. Tang, N. K. Mohd, et al., Renew. Sust. Energ. Rev. **93**, 145 (2018).
22. P. Nagendramma, P. K. Khatri, and G. D. Thakre, J. Mol. Liq. **244**, 219 (2017).
23. *Official Methods and Recommended Practices of the AOCS*, 5th Ed., Ed. by D. Firestone (Champaign, American Oil Chemists' Society, 1997).
24. A. Xu, S. Roland, and X. Colin, Polym. Degrad. Stab. **171**, 109046 (2020).
25. L. Matisova-Rychla and J. Rychly, Polym. Degrad. Stab. **73**, 393 (2001).
26. Y. C. Liang, C. Y. May, C. S. Foon, et al., Fuel **85**, 867 (2006).
27. G. Knothe, Fuel. Process. Technol. **86**, 1059 (2005).
28. R. S. Leonardo, M. L. Murta Valle, and J. Dweck, J. Therm. Anal. Calorim. **108**, 751 (2012).
29. J. J. Pardauil, L. K. Souza, F. A. Molfetta, et al., Bioresour. Technol. **102**, 5873 (2011).
30. Z. Yaakob, B. N. Narayanan, and S. Padikkaparambil, Renew. Sust. Energ. Rev. **35**, 136 (2014).
31. C. P. Tan, Y. B. Che Man, J. Selamat, and M.S.A. Yusoff, Food Chem. **76**, 385 (2002).
32. T. C. Vagvala, S. S. Pandey, S. Krishnamurthy, and S. Hayase, Z. Anorg. Allg. Chem. **642**, 134 (2016).