



Temperature dependence of the oxidative stability of corn oil and polyalphaolefin in the presence of sulfides[☆]

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ABSTRACT

The effect of sulfide-modified corn oil (SMCO) and ditertiary dodecyl pentasulfide (PS) additives on the oxidative stability of corn oil (CO) and polyalphaolefin oil (PAO) was investigated using pressurized differential scanning calorimetry in dynamic (DDSC) and isothermal (IDSC) modes. DDSC showed a weak pro-oxidant effect of SMCO and PS in CO, and antioxidant behavior in PAO. Analysis of the IDSC data showed the existence of isokinetic temperature in both oils. Below the isokinetic temperature the sulfides behaved as antioxidants while above it they behaved as pro-oxidants. The isokinetic temperature was found to depend on the chemical structure of the oils. For the highly unsaturated CO, the isokinetic temperature was 100–135 °C, while for the fully saturated PAO it was above 200 °C. The existence of isokinetic temperature provides consistent explanation to our and literature data for oxidation behaviors of sulfide additives in oils, which appears to be contradictory (pro-oxidant vs. antioxidant) depending on experimental conditions. The isokinetic temperature suggests that accelerated oxidation test methods at elevated temperatures are poor predictors of the low-temperature performance of sulfide-containing antioxidants.

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1. Introduction

One of the properties hindering wide application of vegetable oils as lubricants is their low oxidative stability (OS) [1–4]. Because of this, a better understanding of the oxidation process of prospective bio-based lubricants and their blends with antioxidant additives is needed.

The autoxidation of organic materials occurs through a multi-step radical chain reaction [5–7]. There are two major mechanisms that the autoxidation can be slowed down with the use of additives. The first is the use of chain-terminating inhibitors. These inhibitors react with the radicals to form less reactive radicals, which do not propagate the chain reaction. The other mechanism involves the use of hydroperoxide decomposers, which react

with the hydroperoxides to form non-radical products. By removal of hydroperoxides from the system, the initiation of new radical chains is slowed down. Sulfides are considered hydroperoxide decomposers [5,7,8] since they react with hydroperoxides yielding alcohols and sulfoxides. Sulfoxides can react further and remove additional equivalents of hydroperoxides in a complicated series of reactions.

Sulfur compounds are well known to influence the OS of lubricating oils [5,9–11]. Still, their mechanism of action is not simple. There are cases where sulfur compounds act as either antioxidants or as pro-oxidants (accelerators of the autoxidation) [9,10]. Obviously, their mechanism of action depends on the test conditions and lubricant composition and warrants further investigation.

There are several methods of evaluation of the OS of oils. Some of the most popular methods include: active oxygen method [12], Rancimat [13], rotary bomb oxidation test (RBOT) [14,15], differential scanning calorimetry (DSC) [16–21], and turbine oil oxidation test (TOST) [22]. The Rancimat and active oxygen methods are designed for evaluation of vegetable oils for food applications. We do not know of cases where these methods were used for evaluation of mineral or synthetic lubricating oils. RBOT and TOST are widely

[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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Table 1
Some properties of the oils used in the study.

Oil	Peroxide value (mequiv./kg)	Kinematic viscosity at 40 °C (mm ² /s)	Kinematic viscosity at 100 °C (mm ² /s)	Moles of double bonds per molecule
CO	10.2 ± 0.3	32	7.7	4.4
PS	<0.25	n.d. ^a	n.d. ^a	0
SMCO	<0.25	124	17.7	0.45
PAO	1.7 ± 0.2	31	5.7	0

^a n.d., not determined.

accepted and used oxidation evaluation methods for lubricants. However, these two methods require large quantities of material (50 g for RBOT and 300 mL for TOST). In addition, there are no theoretical models for the interpretation of the data from these two methods. Another drawback of the TOST method is that it is very slow. The test can take over a year for some highly oxidatively stable oils [22]. On the other hand, DSC methods are fast and require small quantities of samples (several mg). In addition, there are theoretical models for analyzing data from DSC experiments.

Currently, two types of DSC experiments are most often used to investigate the OS of materials. The first is isothermal DSC (IDSC), where the sample is heated fast and held at a preset temperature. The second is dynamic DSC (DDSC), where the temperature of the sample is increased at a constant rate. Both experiments are conducted in pure oxygen, dried air or synthetic air. The gas is often pressurized to increase the oxidation rate and reduce the test time. The reaction is monitored by measuring the released heat from the sample. The onset time (t_e) and the time of the peak maximum (t_p) of the heat release are the two most often reported values in IDSC experiments. In DDSC, the onset temperature (OT) and the signal maximum temperature (SMT) are reported. The OT and SMT correspond to the temperature at which heat release begins and attains maximum values, respectively.

Literature review produced very few reports on the combined use of IDSC and DDSC for investigation of the oxidative properties of vegetable oils and lubricants. Litwinienko et al. published several papers [18–21] which showed that the autoxidation of vegetable oils is a complex process and the two methods give complementary information. The best correlation is found between the activation energies derived from t_e and OT, which correspond to the initial stages of autoxidation [19–21]. The process in DDSC is best described by a two-step reaction: first an autocatalytic formation of hydroperoxides and second decomposition of the hydroperoxides to further products. Only one autocatalytic step is observed in the IDSC data. Qiu et al. [9] conducted comparative studies of RBOT, IDSC and DDSC. The authors investigated the antioxidant property of 0.05 M sulfides in hydrotreated naphthenic base oil. The correlation between RBOT and DDSC was not very good. The best correlation was observed between SMT and RBOT time ($r^2 = 0.68$). The authors reported that they could not find a combination of temperature and pressure for IDSC that would allow them to obtain oxidative IDSC exotherm data for all blends.

Gamlin et al. [23] studied the autoxidation of refined crude oil, hydrocracked oil and polyalphaolefin (PAO) using IDSC and DDSC under pure oxygen at a pressure of 3.4 MPa. The IDSC data were used to calculate the activation energies of autoxidation. The DDSC experiments resulted in a single sharp exothermic peak, attributed to autoignition of the samples. The refined oil had higher autoignition temperature and higher activation energy than the hydrocracked oil and PAO. The authors explained the results with the presence of sulfur and nitrogen compounds in the refined oil.

We found the following studies on the antioxidant action of sulfides in lubricating oils:

Bala et al. [10] reported about the influence of different sulfides on the OS of mineral oils. Air was bubbled into a sample at a temperature of 160 °C for 192 h. The degree of oxidation was monitored by measuring the viscosity and total acid number of

the oils before and during the test. The sulfur additives improved OS of the hydrotreated oil (98% saturates and 2% aromatics), but decreased that of the solvent-refined oil (73% saturates and 26% aromatics).

Becker and Knorr [11] studied the OS of low erucic acid rapeseed oil with various antioxidant additives at 1 mol.% concentration. They measured the induction time at 130 °C of samples subjected to the modified active-oxygen method. The organic sulfides caused slight improvements in OS.

In this paper, we describe the results of a comparative oxidation stability study of two sulfur-containing compounds in PAO and in CO. IDSC and DDSC tests at high pressure of oxygen were used to evaluate OS. The effect of temperature on the antioxidant activity of sulfides was evaluated. To the best of our knowledge, this is the first study about the temperature-dependence of antioxidant activity of sulfides in lubricating oils.

2. Experimental

2.1. Materials

CO was obtained from a local (Peoria, IL) supermarket and used as supplied. Sulfide-modified corn oil (SMCO) was synthesized from CO and butanethiol using a photoinitiated thiol-ene reaction as described before [24]. The purified SMCO used in this study contained 9.7% S. Ditertiary dodecyl pentasulfide (PS) with the trade name TPS-32 was donated by Arkema Inc. (Philadelphia, PA) and used as supplied. The PS contained 30% sulfur according to the producer's specifications. PAO, with kinematic viscosity of 5.7 mm²/s at 100 °C, sold as Durasyn 166, was donated by Ineos Oligomers (League City, TX). A summary of selected properties of the oils is given in Table 1. Extra dry compressed oxygen (99.6%) was obtained from Airgas, Inc. (Radnor, PA). Barium chloride, iron(II) sulfate, hydrochloric acid, and ammonium thiocyanate were obtained from Sigma-Aldrich (Saint Louis, MO) and used as received. Indium was provided by TA Instruments (New Castle, DE).

Seven samples were used in the DSC measurements. These were: CO, PAO and SMCO without additives; blends of CO with SMCO or PS additive; and blends of PAO with SMCO or PS additive. The concentration of sulfur in the blends was 0.6 wt.% (6.19 wt.% of SMCO or 2 wt.% of PS). The blends were prepared by stirring the container manually. All blends were transparent and without precipitates, were wrapped in aluminum foil to prevent exposure to light and refrigerated between measurements.

2.2. Instrument

Differential scanning calorimetry (DSC) measurements were conducted on a TA Instruments model 2920 DSC (New Castle, DE) with a pressure cell P/N 816001.901. Hermetic alodined pans and lids from TA Instruments were used. A pinhole was punched in the lid before sealing the sample (2.7–3.3 mg) inside. The DSC instrument was calibrated before the tests using the melting point of indium (156.6 °C).

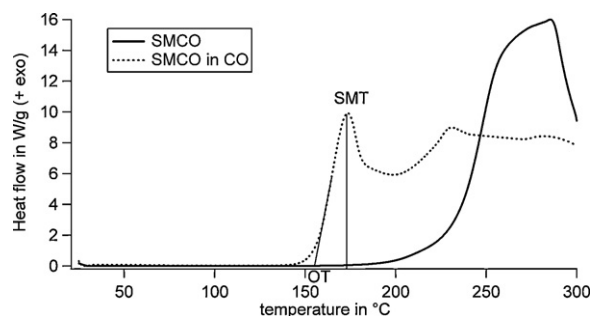


Fig. 1. Two examples of DDSC temperature scan curves. Determination of the onset temperature (OT) and the signal maximum temperature (SMT) is illustrated.

2.3. Procedure

2.3.1. Dynamic DSC (DDSC)

The pan with a 3.0 ± 0.3 mg oil sample was placed in the pressure cell chamber and purged three times with oxygen by pressurizing the cell to 620 kPa (90 psi) and opening the exit valve to release the gas. The sample was then tested at a temperature ramp of 25–300 °C, 10 °C/min heating rate, under an oxygen atmosphere at a pressure of 620 kPa and a purge rate of 100 mL/min at the outlet valve. Typical data from two DDSC experiments is illustrated in Fig. 1. OT and SMT were determined with the software supplied with the instrument. Duplicate measurements were conducted and the OT and SMT values from each measurement were averaged and used in data analysis.

2.3.2. Isothermal DSC (IDSC)

After determination of OT for autoxidation using the DDSC procedure, each sample was then run using IDSC. The procedure was as follows: the sample was heated, without oxygen flow, at an 80 °C/min rate to the test temperature. After reaching the test temperature, 4 min from the start of heating, the cell was pressurized with oxygen to 620 kPa (90 psi) with a purge rate of 100 mL/min at the outlet valve. The sample was then held at the test temperature under oxygen flow until the first exothermic peak was observed. This took anywhere between 0.5 and 1.5 h, depending on the sample being tested. The starting time of the pressurization of the sample was used as a starting time to calculate onset induction time (t_e) and peak time (t_p) in the isothermal experiment. The first test temperature, used for the IDSC experiment, was selected to be approximately 30 °C below the OT of the material determined from the DDSC experiment. The next temperatures were selected to be 5 °C higher or lower than the previous temperature, so that all experiments were carried out at conditions that yield t_p of less than 90 min. The temperature could not be very high, otherwise the initial baseline, and hence t_e could not be determined.

Below is an example how the t_e and t_p were measured for a blend of CO with PS additive. The OT of this blend from the DDSC experiment was 162 °C. The first IDSC measurement was conducted at 135 °C (Fig. 2). The intercept of the slope and the baseline was at 12.57 min. The pressurization of the sample started at the fourth min, so 4.0 was subtracted from the intercept. This yielded a t_e value equal to 8.57 min. The SMT was observed at 18.39 min; the t_p value was 14.39 min. The thermograms at 125, 120 and 115 °C had two maxima (Fig. 2). In these cases, the first peak was used to determine t_p .

2.3.3. Peroxide value determination

The peroxide value of the samples was determined according to the method of Shantha and Decker [25]. In short, the oil sample (0.01–0.30 g) was dissolved in 9.8 mL of 70 vol.% chloroform–30 vol.% methanol mixture. 50 μ L ammonium thio-

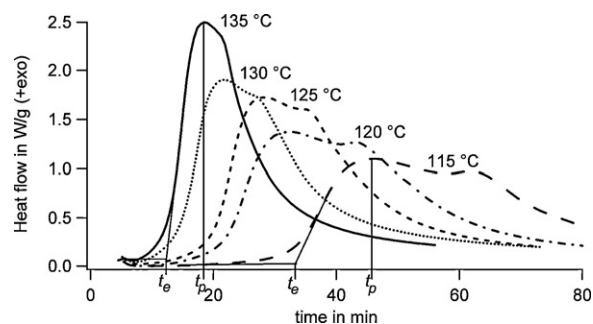


Fig. 2. Isothermal oxidation thermograms of CO with PS. The determination of the t_e and t_p is illustrated on the curves for 135 and 115 °C.

cyanate solution (30 g/100 mL) was added and the sample was vortexed for 2–4 s. Then 50 μ L of the iron(II) solution was added; the sample was vortexed for 2–4 s, incubated for 5 min at room temperature and the absorbance at 500 nm was measured against a blank containing all of the reagents except the oil sample, with a UV/vis spectrophotometer (Perkin Elmer, Shelton, CT). Peroxide values were calculated from a standard curve of ferric chloride as described by Shantha and Decker [25] and expressed as milliequivalents (mequiv.) of peroxide per kg of oil. The iron(II) solution was prepared by mixing 0.5 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water with 0.4 g of BaCl_2 in 50 mL water, acidifying with 2 mL of 10 M HCl, and removing the BaSO_4 by filtration.

2.3.4. Viscosity measurements

The kinematic viscosities of the oils at 40 and 100 °C were determined with a SVM model 3000 Stabinger viscometer from Anton-Paar GmbH (Österreich, Austria).

2.4. Data analysis

The determination of the peak maximums and the onsets was conducted using the software supplied with the DSC instrument. Further analysis of data was conducted using Microsoft Excel 2007 software (Richmond, WA).

3. Results and discussion

3.1. Dynamic DSC

The thermograms of the samples under the DDSC condition showed a prolonged oxidation process that started at the OT and did not finish even when a temperature of 300 °C was reached and the scan was stopped (Fig. 1). This indicated that autoxidation of the samples initiated without autoignition, which is in contrast to the results reported by Gamlin et al. [23]. The lack of autoignition may be from the lower oxygen pressure used in our experiment, 620 kPa vs. 3400 kPa used by Gamlin et al.

The OT and SMT results of the DDSC experiments are summarized in Table 2. The standard error of the values is estimated to be

Table 2
Average onset temperatures (OT) and signal maximum temperatures (SMT) from the DDSC (heating rate 10 °C/min, 620 kPa oxygen).

Oil	OT (°C)	SMT (°C)
CO + SMCO	157	174
CO + PS	162	183
CO	165	188
PAO	177	210
PAO + SMCO	217	229
SMCO	230	281
PAO + PS	237	249

Table 3
Example of IDSC data.

CO			SMCO		
Temperature (°C)	t_e (min)	t_p (min)	Temperature (°C)	t_e (min)	t_p (min)
115	15.88	26.02	185	8.88	84.47
115	15.78	27.11	185	4.38	67.03
120	29.87	40.44	190	4.13	43.30
125	16.31	24.74	195	3.63	37.70
130	11.99	18.73	200	3.42	30.21
130	5.24	11.38	205	3.13	21.70
135	9.52	15.41			

1.8 °C. The SMT values were generally higher than OT by about 20 °C. The actual difference varied from oil to oil. In the case of SMCO, for instance, the difference was 50 °C. The OT and SMT in Table 2 are arranged in increasing order. The data can be used to rank the oils according to their OS. The OS, according to the OT values, was CO + SMCO < CO + PS < CO < PAO < PAO + SMCO < SMCO < PAO + PS (most stable). The SMT gave a similar ranking with the only difference being that SMCO had a higher SMT than PAO + PS.

If we compare the CO-based blends, we conclude that the addition of SMCO decreased the OS of CO. The addition of PS to CO also had a negative effect, but to a lesser extent. SMCO had significantly higher OS than the neat CO. This can be attributed to the effect of the replacement of the double bonds of CO with sulfide moieties. Since the addition of sulfur compounds to CO decreased the OS, we can speculate that the major reason for the improvement of the OS is the removal of the double bonds, which results in the removal of oxidatively susceptible allylic and bis-allylic hydrogen atoms from the triglyceride molecules.

3.2. Isothermal DSC

Since the investigated oils had wide variations in their oxidative stabilities, it was not feasible to carry out the IDSC tests for all samples at the same set of temperatures. The oxidatively unstable oils would start oxidizing so fast at high temperatures that it will not be possible to determine t_e , or even t_p . On the other hand, the oxidatively stable oils oxidized too slowly at low temperatures and the energy released per minute was so low that the line of steepest slope and the peak could not be reliably determined. Thus, the t_e and t_p could not be measured for all the samples at the same temperatures. This observation is similar to the findings reported by Qiu et al. [9]. Because of this, different temperature ranges were used to determine t_e and t_p for each of the oils.

A typical data set from IDSC experiments for samples with low (CO) and high (SMCO) OS is summarized in Table 3. The general tendency is for t_e and t_p to decrease with increasing temperature, but some scatter was observed, as can be seen for CO. The more oxidatively stable SMCO showed values for t_e at 185 °C that were comparable to the values of t_e for the less oxidatively stable CO at a much lower temperature, 135 °C. The higher OS of SMCO was more pronounced in the t_p values. The t_p value of SMCO at 185 °C was much higher than t_p of CO at 135 °C.

If the autoxidation of a sample is a single step reaction, then its rate constant will obey the Arrhenius law: $k = Z \exp(-E_a/RT)$. In the equation, k is the rate constant, Z is a pre-exponential factor, E_a is activation energy, R is the universal gas constant, and T is the absolute temperature.

From the above equation, it can be derived that the time, t_c , for a sample to reach a given degree of oxidation, C , in an isothermal process will be [26]:

$$\ln\left(\frac{1}{t_c}\right) = \ln Z' - \frac{E_a}{RT} \quad (1)$$

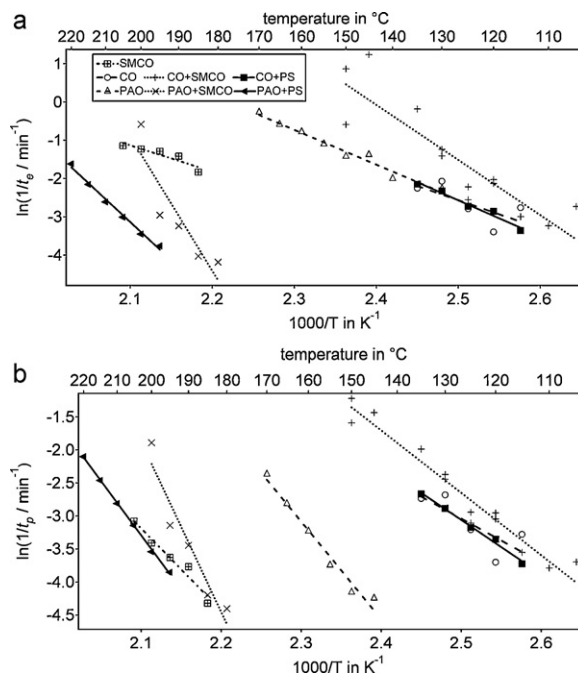


Fig. 3. Arrhenius plot of the isothermal data. The times are in minutes. (a) onset induction time (t_e); (b) peak time (t_p)

where Z' is proportional to Z . From the above equation, it follows that, by measuring the time to reach a given degree of oxidation as a function of temperature, we can obtain E_a and Z' of the oxidation process. Eq. (1) can be rewritten as: $\ln(1/t_e) = \ln Z^e - E_a^e/RT$ and $\ln(1/t_p) = \ln Z^p - E_a^p/RT$, using t_e or t_p as times for reaching the corresponding degrees of oxidation.

Arrhenius plots, based on the data from the isothermal experiments, are displayed in Fig. 3. The data in Fig. 3A is for t_e , and Fig. 3B is for t_p . Each data point is a result of a single measurement. The points in the upper (short times) right (low temperatures) corner of the graph indicate less stable oils than the ones with times in the bottom left corner. The results from the Arrhenius fits are summarized in Table 4.

For each sample, the autoxidation activation energies determined using t_e , E_a^e , differ from the ones determined using t_p , E_a^p . This, as well as the fact that multiple peaks were observed in some DSC scans, indicated that autoxidation is not a single step process.

The calculated values for E_a of CO from this work, 56 and 51 kJ/mol, were in the lower range of the values reported in the literature: 67, 75, 43 [21]; 78 [27]; 88 [28]; and 105 kJ/mol [18].

The activation energies of PAO autoxidation from this work, E_a^e 74 kJ/mol, E_a^p 120 kJ/mol, were lower than the values reported (118 and 130 kJ/mol) by Gamlin et al. [23].

Table 4

Parameters determined from the Arrhenius plots in Fig. 3. The values are given \pm standard error.

Oil	From onset induction time, t_e		From peak time, t_p	
	E_a^e (kJ/mol)	$\ln(Z^e)$	E_a^p (kJ/mol)	$\ln(Z^p)$
CO	56 \pm 31	14.5 \pm 9	51 \pm 21	12 \pm 6
SMCO	63 \pm 27	15 \pm 7	109 \pm 13	24 \pm 3
PAO	74 \pm 5	20 \pm 1	120 \pm 8	30 \pm 2
CO + PS	78 \pm 7	21 \pm 2	68 \pm 4	17 \pm 1
CO + SMCO	120 \pm 20	34 \pm 5	79 \pm 5	21 \pm 2
PAO + PS	164 \pm 8	38 \pm 2	135 \pm 2	31 \pm 1
PAO + SMCO	334 \pm 60	84 \pm 16	235 \pm 31	58 \pm 8

Table 5

Calculated isokinetic temperatures for transition from antioxidant to pro-oxidation action of sulfides in CO and PAO.

Oil	Additive	T_{iso}^e (°C)	T_{iso}^p (°C)
Corn oil	SMCO	120	100
	PS	135	135
PAO	SMCO	215	220
	PS	330	730

3.3. Isokinetic temperature

The Arrhenius plots show that the effect of the sulfur additives on the oxidative stability is temperature dependent. It can be shown, that there is a temperature below which the oxidation rate will decrease by the addition of the sulfur additives, and above which it will increase. This temperature is the isokinetic temperature. This term is usually used for one-step reactions of related compounds [29–31]. It is also applied for description of the first step of autoxidation of different lipids [32], or to autoxidation of lipids with phenolic antioxidants [33].

The isokinetic temperature, T_{iso} , can be calculated as follows: $T_{iso} = (E_{aB} - E_{aA}) / R(\ln Z_B - \ln Z_A)$, where the subscripts A and B refer to the oils with and without additive, T_{iso} is the isokinetic temperature, and R is the universal gas constant. Sulfur additives act as antioxidants below the isokinetic temperature and as prooxidants above it.

The isokinetic temperature obviously depends on the base oil and the additive used. Possible factors that affect the isokinetic temperature include the degree of unsaturation of the oil and the type of sulfur additive. Our results suggest that the isokinetic temperature depends strongly on the degree of unsaturation of the oil and, to a lesser degree, on the type of sulfur additive.

The calculated isokinetic temperatures are summarized in Table 5. The data illustrates that sulfur-containing materials will act as antioxidants in PAO for temperatures of 200 °C and higher. This temperature range corresponds to that encountered in most application conditions for PAO. The isokinetic temperature for the sulfur compounds in CO is about 100–135 °C.

These findings are in agreement with the results from the DDSC measurements (Table 2). The sulfur compounds decreased the OT and SMT values of CO since they were above the isokinetic temperatures (Table 2). The decrease was more pronounced in the SMT values which occurred at higher temperatures than OT. SMCO decreased the OT and SMT of CO more than PS, since the isokinetic temperature of SMCO was lower than that of PS. The sulfur compounds increased the OS of PAO, since its oxidation in the DDSC test occurred well below the isokinetic temperature for PAO. The SMCO had weaker antioxidant effect on PAO than PS in the DDSC experiment; this was because SMCO increased the PAO stability up to the isokinetic temperature. The antioxidant effect of additives in PAO, as determined from SMT values, was smaller than that based on the OT values. This can be explained by the fact that SMT values are higher than OT values and sulfur additives display a diminishing antioxidative effect with an increase of the temperatures.

Becker and Knorr [11] conducted OS tests at 130 °C. This temperature is very close to the isokinetic temperature determined in our experiments. This explains why the authors observed a weak effect of the sulfur compounds on the autoxidation stability of rapeseed oil. Since the rapeseed oil has lower unsaturation content than CO [1], we would expect the rapeseed oil to have a higher isokinetic temperature than CO and the sulfur compounds to have a slightly stronger antioxidative effect.

Qiu et al. [9] investigated the oxidation properties of naphthenic oil at 150 °C with RBOT. From the description of the oil, we can assume that it had very low unsaturated content. They observed

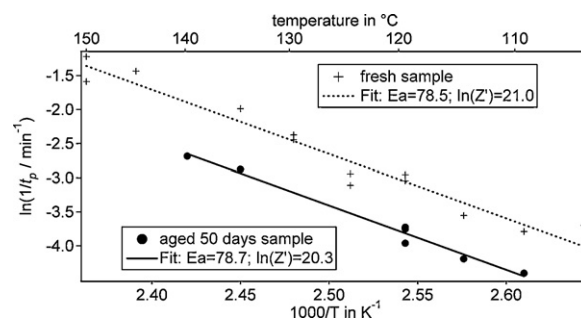


Fig. 4. Effect of aging at low temperature on the oxidation stability of CO with SMCO.

improved OS with most of the sulfides. They reported that 7 out of 10 sulfur compounds increased the RBOT time by 10% or more. On the other hand, their DDSC test resulted in peaks at around 200 °C. The DDSC results showed that most of the sulfides had negligible influence on OS. They reported that 7 out of 10 sulfides changed the SMT value by less than 1.3 °C. Only 3 out of 10 showed improved OS, and one of these three increased SMT by a mere 0.08 °C. This suggested that, for sulfides in naphthenic oil, the isokinetic temperature was around 200 °C, similar to our PAO results.

Bala et al. [10] reported that the oil with 26% aromatics displayed decreased OS at 160 °C when sulfides were added. We can speculate that it had a low isokinetic temperature, similar to CO in this work. It is well known that the hydrogens in the alpha position to an aromatic ring are more susceptible to oxidation, similar to the allylic hydrogens in unsaturated compounds. The hydrotreated oil with 98% saturates, on the other hand, had an isokinetic temperature above 160 °C, similar to PAO in this work.

3.4. Low-temperature antioxidant action of sulfur compounds

The antioxidant mechanism of sulfur compounds is through non-radical decomposition of peroxides [7,8]. Our data suggest that the sulfur-containing compounds have stabilizing action at low temperature. To check the effect of SMCO on low temperature oxidation stability, a sample of CO with SMCO was stored in a refrigerator (~5 °C) for 50 days. The initial concentration of peroxide in the sample was determined to be 9.6 mequiv./kg, but dropped to 6.5 mequiv./kg, or by 32% after 50 days. The stored sample showed increased t_o and t_p compared to the fresh sample (Fig. 4). The activation energies of the fresh and aged samples were essentially the same. The difference between the values was well below their standard errors (~5 kJ/mol). It can be calculated from the fits that the t_p values in the temperature range of 110–140 °C dropped 53 ± 3%; the decrease is in the same order as the decrease of the peroxide value (32 ± 4%). This data supports the notion that SMCO increases OS by removing the peroxides, thereby decreasing the rate of the initiation reaction. The removal of peroxides is active even at low temperatures. The PAO sample had a low initial peroxide value (1.7 ± 0.2 mequiv./kg) and the extended storage with added sulfur compounds did not change it significantly (1.5 ± 0.3 mequiv./kg for the SMCO; 1.9 ± 0.2 mequiv./kg for the PS).

4. Conclusions

Two sulfide compounds, a commercial PS and a newly synthesized bio-based monosulfide (SMCO), were investigated for their properties as antioxidant additives in CO and PAO. Pressurized differential scanning calorimetry in two modes, dynamic (DDSC) and isothermal (IDSC), was used for evaluating OS. The additives were added to result in 0.6% sulfur in the final blend. DDSC ranked the blends in the following order of increasing OS: CO + SMCO < CO + PS < CO < PAO < PAO + SMCO < SMCO ≲ PAO + PS.

IDSC showed that the influence of both sulfides on OS is temperature-dependent. The sulfides acted as antioxidants or pro-oxidants, below or above an isokinetic temperature, respectively. The isokinetic temperature was dependent on the base oil chemistry and, to a lesser degree, on the type of sulfur-containing additive. We propose that the isokinetic temperature is a strong function of the degree of unsaturation of the base oil. For highly saturated oils, the isokinetic temperature was high; while for unsaturated oils, it was low. For CO, which contains a significant amount of unsaturated double bonds, the isokinetic temperature was in the range of 100–130 °C. For the fully saturated PAO, the isokinetic temperature was above 200 °C. The commercial polysulfide showed a higher isokinetic temperature than the biobased mono-sulfide material. This hypothesis also explains the results from the DDSC experiment, as well as the known literature data. The implication of the isokinetic temperature is that accelerated test methods for evaluation of the OS of oils will underestimate its value at ambient temperature when sulfur compounds are present. This is because accelerated methods are conducted at high temperatures, where sulfide compounds become pro-oxidants instead of antioxidants.

For the SMCO in CO, IDSC showed that extended storage at low temperature leads to better OS than the freshly prepared solution. The increase in the OS was correlated with the removal of the hydroperoxides by the SMCO.

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