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Oxidative stabilities of engine oils contaminated by vegetable oil

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Abstract

Samples of engine oils of CC or CD API grades contaminated with edible rapeseed oil (2–10%) have been oxidized in the cell of a pressure differential scanning calorimeter (PDSC). The PDSC experiments were carried out under 1400 kPa oxygen pressure at 190°C. From the resulting PDSC exotherms their extrapolated onset and peak maximum times have been determined and compared with results obtained under the same conditions for engine oils without addition of vegetable oil. The presence of rapeseed oil in engine oils drastically decreases their resistance to oxidation.

Keywords: Oil; Oxidation; Oxidative stability; PDSC; Rapeseed oil; Stability

1. Introduction

Vegetable oils and their derivatives have potential as alternative diesel fuels but the problems associated with the use of such fuels must be overcome. Besides the current uncompetitive price of vegetable oil based fuels (VOBF) they can create a variety of practical problems largely resulting from incomplete combustion in the engine. VOBFs can cause nozzle coking, ring sticking, formation of engine deposits, scuffing of cylinder lines, etc. The other group of problems are those associated with thickening, gelling, and decrease of oxidative stability of engine lubricating oils as

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a result of their contamination with vegetable oil or products of its incomplete combustion.

The best methods for quality assessment of VOBFs and lube oils are engine tests, but they are expensive and time consuming. The laboratory methods for quality assessment of engine oils contaminated by vegetable oils are mainly based on viscometric measurements [1,2]. Thermal analysis techniques seem also to be highly applicable for such purposes because the DSC/PDSC methods are popular for the determination of oxidative stabilities of engine oils [3–8] and vegetable oils [9–14].

The present study was undertaken to investigate the potential of PDSC in the evaluation of oxidative stabilities of engine oils containing additions (2–10%) of vegetable oil.

Table 1
Technical parameters of F-13 and F-14 oils

Parameter [a]	Result of determination	
	F-13	F-14
Kinematic viscosity/(mm^2 s^{-1})		
at 40°C	35.97	80.00
at 100°C	5.68	9.25
Viscosity index	95	90
Carbon residue mass/%	0.012	0.060
Sulphur content mass/%	0.93	1.07
Flash temperature/°C		
open cup	220	250
closed cup	195	198
Pour point/°C	−12	−12
Density at 20°C/(g cm^{-3})	0.877	0.866

[a] Besides sulphur content determined in accordance with ASTM D 1552-67 Standard all measurements were carried out in accordance with Suitable Polish Standards (PN).

2. Experimental

2.1. Engine oils

The model engine oils were prepared from base oil and DI additive packages, overbased detergents, viscosity improver (VI) additive package, and pour point depressant. Base oil was blended using 50% F-13 and 50% F-14 petroleum-based oils, the properties of which are listed in Table 1. The DI additive packages and overbased detergents used are characterized in Table 2. All model engine oils fulfilled requirements of the SAE 15W/40 viscosity grade and depend on the level of treatment with DI packages; they were of CC or CD API grades as specified in Table 3. Engine oils containing rapeseed oil (2–10%) were prepared by mass.

Table 2
Technical parameters of DI additive packages and overbased detergents

Determination	DI additive packages			Overbased detergents	
	DI/A	DI/B	DI/C	K	L
Kinematic viscosity at 100°C/ ($mm^2\ s^{-1}$)	105.50	68.04	166.10	220.66	34.16
Flash point/°C	180	140	162	159	156
Base number/ [(mg KOH) g^{-1}]	158	119	116	285	277
Sulphated ash/ mass%	17.00	14.91	13.35	27.00	39.40
Elemental analysis/mass%					
Zn	1.40	1.85	1.28		
P	1.17	1.65	1.08		
Ca	5.25	4.65	3.90	7.80	12.00
S	3.60	4.10	3.70	3.80	1.80
N	2.68	0.78	0.88		

Table 3
Composition of model engine oils

Code	API grade	Composition of oils [a]
A-I	CC	Base oil +6% DI/A
A-II	CD	Base oil +9.5% DI/A
B-I	CC	Base oil +6% DI/B +0.5% L
B-II	CD	Base oil +9.5% DI/B +0.5 L
C-I	CC	Base oil +6% DI/C +0.5% K
C-II	CD	Base oil +9.5% DI/C +0.5 K

[a] Base oil = 50% F-13 oil +50% F-14 oil.

2.2. *Rapeseed oil*

The rapeseed oil (RSO) was obtained from a local factory; it was "pure rapeseed" without addition of other vegetable oils. The RSO was fresh (peroxide value = 0.1 mmol O_2^{2-} per 1 kg of oil, acid value = 1.6 mg KOH per 1 g of oil and iodine value = 118 g of I_2 per 100 g of oil) and its fatty acid composition obtained by fatty acid methyl esters gas-liquid chromatography (GLC) is listed in Table 4.

2.3. *Apparatus and procedure*

A Du Pont 1090 B thermal analyzer with 1091 disc memory and a Du Pont 910 differential scanning calorimeter equipped with a pressure cell (PDSC, model no.

Table 4
Fatty acid composition of rapeseed oil

Fatty acid $C_{m:n}$ [a]	Content/%
$C_{14:0}$	0.1
$C_{16:0}$	4.8
$C_{16:1}$	0.2
$C_{18:0}$	1.6
$C_{18:1}$	59.5
$C_{18:2}$	20.2
$C_{18:3}$	8.6
$C_{20:0}$	0.4
$C_{20:1}$	1.8
$C_{20:2}$	0.1
$C_{22:2}$	0.3
$C_{22:1}$	1.8
$C_{24:0}$	0.1
$C_{24:1}$	0.1
Unidentified	0.4

[a] m is the number of carbon atoms; n is the number of double bonds.

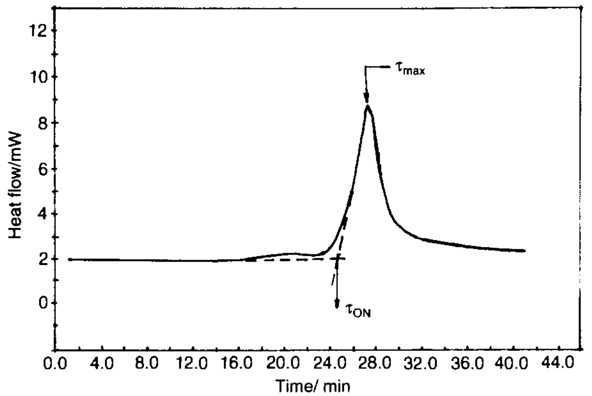

Fig. 1. Determination of parameters τ_{ON} and τ_{max} from the PDSC exotherm for oxidation of model engine oil.

900830-902) were used. The instrument was calibrated using high purity indium as the standard. Weighed samples of oils (3–4 mg) were placed in the open aluminium pan; the reference pan was left empty. Experiments were performed under 1400 kPa pressure of oxygen and at 190°C. Samples of pure RSO were investigated at temperatures in the range 120–160°C. The run data were recorded on 8 in floppy discs and then plotted. From the resulting PDSC heat flow curves the times for the extrapolated onset of oxidation τ_{ON} (obtained with the Du Pont OXIDATIVE STABILITY V 2.0. program) and the maximum of the peak τ_{max} (obtained from plots) were determined, as shown in Fig. 1.

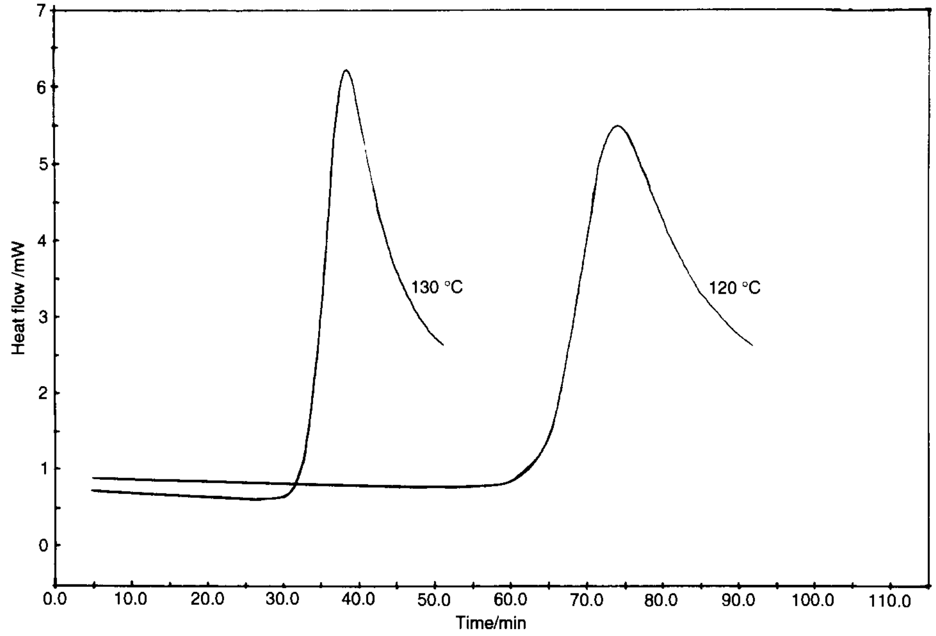

Fig. 2. PDSC exotherms for oxidation of rapeseed oil at 120°C and at 130°C; oxygen pressure is 1400 kPa.

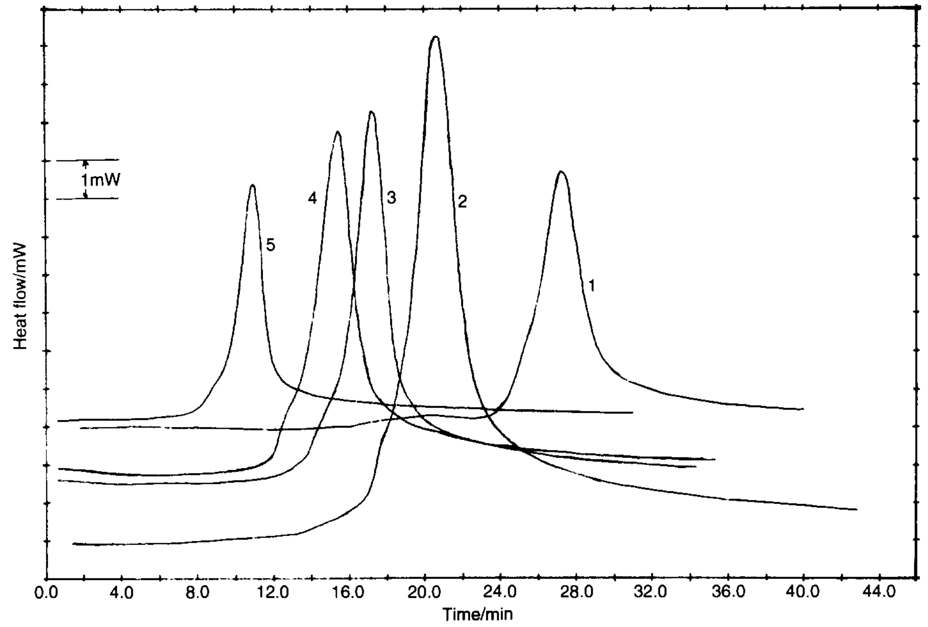

Fig. 3. PDSC exotherms obtained at 190°C and under 1400 kPa oxygen pressure for oxidation of (1) B-I engine oil, and B-I engine oil containing (2) 2% (3) 4% (4) 6% and (5) 10% of rapeseed oil.

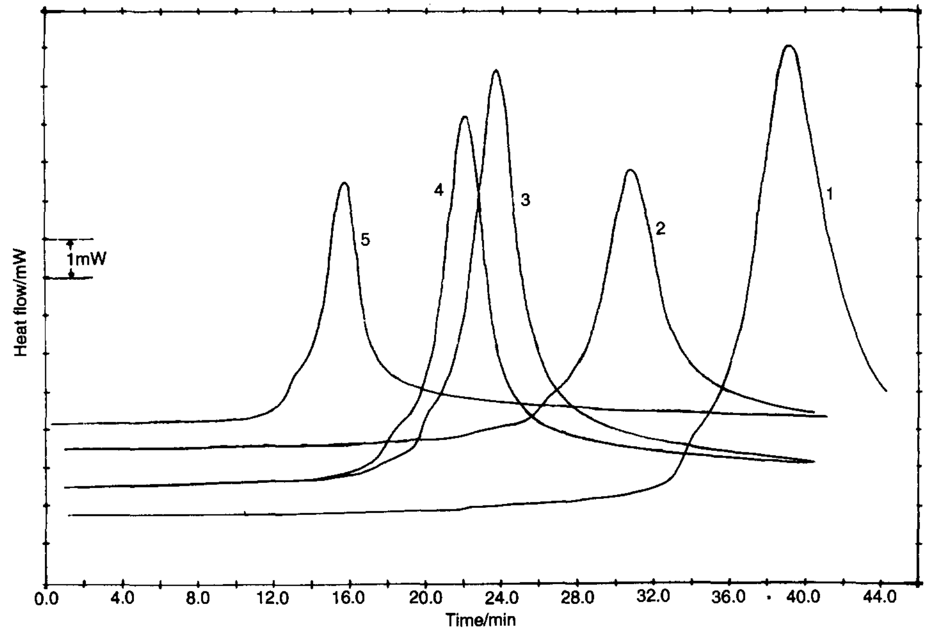

Fig. 4. PDSC exotherms obtained at 190°C and under 1400 kPa oxygen pressure for oxidation of (1) B-II engine oil, and B-II engine oil containing (2) 2%, (3) 4% (4) 6% (5) 10% of rapeseed oil.

Table 5
PDSC exotherm times τ_{ON} and τ_{max} obtained for model engine oils under 1400 kPa of oxygen at 190°C

Code	τ_{ON}/ min	τ_{max}/ min
A-I	20.9	24.2
A-II	43.5	47.5
B-I	24.6	27.2
B-II	34.7	39.0
C-I	25.4	28.4
C-II	31.5	33.4

Table 6
PDSC exotherm times τ_{ON} and τ_{max} obtained for rapeseed oil under 1400 kPa of oxygen

Temperature/ °C	τ_{ON}/ min	τ_{max}/ min
120	64.7	73.7
130	33.0	38.4
140	18.9	21.4
150	9.5	12.3
160	4.7	6.6

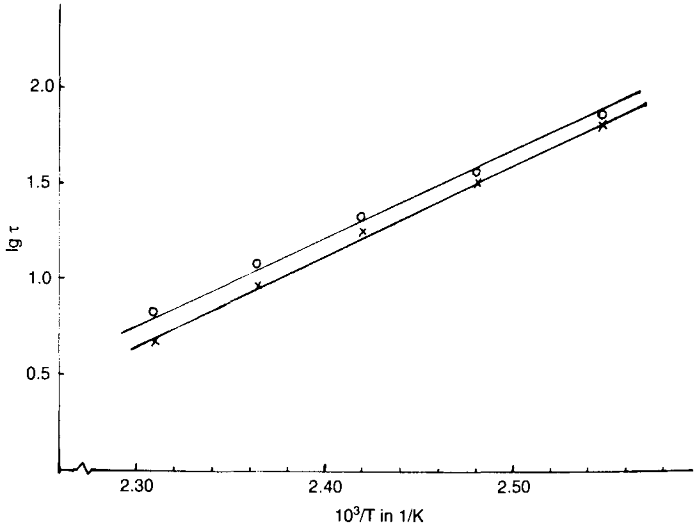

Fig. 5. Lg τ_{max} (top line) and lg τ_{ON} (bottom line) versus reciprocal temperatures (K^{-1}) of PDSC exotherms for oxidation of rapeseed oil.

3. Results and discussion

The examples of PDSC exotherms obtained for oxidation of pure RSO, engine oils and engine oils contaminated with RSO are shown in Figs. 2–5. The times τ_{ON} and τ_{max} determined from PDSC exotherms of the oils studied are listed in Tables 5–7. These times can be used as a measure for determination of the resistance of oils to oxidation. The RSO is much less stable than engine oils and it cannot be inhibited by the DI packages due to their limited solubilities in RSO. For this reason the times τ_{ON} and τ_{max} for oxidation of RSO at 190°C could not be precisely measured. The RSO was studied at five different temperatures in the range 120–160°C. Because the lg τ_{ON} and lg τ_{max} values obtained for RSO show linear dependences on the reciprocal of exotherm absolute temperatures (Fig. 5) they were correlated (correlated coefficients >0.99) with the equations

$$\lg \tau_{ON} = 4793.38\ T^{-1} - 10.369 \tag{1}$$

and

$$\lg \tau_{max} = 4406.08\ T^{-1} - 9.343 \tag{2}$$

From these equations the values $\tau_{ON} = 1$ min and $\tau_{max} = 1.5$ min were calculated for oxidation of RSO at 190°C. Comparison of these values with those obtained for engine oils illustrates the difference in oxidative stabilities of engine and vegetable oils.

The oxidative stabilities of CD grade engine oils were better than oils of CC grade. However it appears that for selected API quality grade oils their stabilities were also dependent on the DI packages used in the formulation of oils. When

Table 7
PDSC exotherm times τ_{ON} and τ_{max} obtained for model engine oils contaminated with rapeseed oil; temperature is 190°C and oxygen pressure is 1400 kPa

Model engine oil+rapeseed oil		τ_{ON}/ min	τ_{max}/ min
Code	Rapeseed oil content/mass%		
A-I-1	2	10.4	14.7
A-I-2	4	9.1	11.9
A-I-3	6	8.1	11.0
A-I-4	10	7.5	10.5
A-II-1	2	35.2	39.7
A-II-2	4	28.5	31.1
A-II-3	6	21.7	25.4
A-II-4	10	18.2	21.3
B-I-1	2	17.5	20.6
B-I-2	4	15.0	17.3
B-I-3	6	13.0	15.5
B-I-4	10	9.0	11.0
B-II-1	2	27.7	30.8
B-II-2	4	20.7	23.7
B-II-3	6	19.1	22.1
B-II-4	10	13.5	15.7
C-I-1	2	21.7	24.6
C-I-2	4	16.4	19.2
C-I-3	6	15.1	17.6
C-I-4	10	11.2	13.6
C-II-1	2	23.2	27.1
C-II-2	4	17.9	21.1
C-II-3	6	16.5	19.8
C-II-4	10	10.8	15.0

engine oils were contaminated by RSO their resistance to oxidation was strongly reduced. For the oils of B-II and C-II type (CD grade) the addition of 2% RSO reduces their resistance to oxidation to the level shown by the oil of CC grade. For the oil of A-II type the same result was obtained when the concentration of RSO was greater than 6%. It seems probable that reduction of the oxidative stabilities of engine oils by admixture with RSO is caused by easier initiation, the first step in the radical promoted autoxidation of oils. Based on dynamic DSC [7] and isothermal PDSC [6,8] studies of engine oil oxidation it has been shown that the apparent activation energies for oxidation of such oils were about 135–170 kJ mol^{-1}. For comparison, the activation energy of oxidation calculated from Eq. (2) for the pure RSO used in this work is only 84.3 kJ mol^{-1}.

4. Conclusions

PDSC was used successfully to investigate the oxidative stability of engine oils containing vegetable oil. The method offers a simple, fast and precise technique for such investigations, with inherent advantages: milligram amounts of sample without its previous preparation and well defined measuring conditions. The PDSC studies of lube oils can be used as analytical tests or as the preliminary test prior to time consuming engine tests.

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