Specific Heat Capacity Of Some Mineral, Synthetic And Semi-Synthetic Automotive Lubricant Oils After Thermal Degradation

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ABSTRACT

The knowledge of the specific heat capacity of the derived of the petroleum and of its mixtures it is of great practical importance in the branch of the petrochemical engineering, because it is associated with the refinery operations of petroleum and other correlated processes. This work aims to characterize thermal degradation process of automotive mineral, synthetic and semi-synthetic lubricant oils, in relation to its specific heat capacities. Lubricants were degraded at temperatures varying from 150 to 210ºC, and times of 1 to 48 hours. After degradation, oils were characterized by DSC. The analyzed lubricating oils present an increase in your heat transfer capacity in function of the increase of the temperature.
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INTRODUCTION

Modern lubricants, with high performance, can do much more than simply reducing attrition and wear. Lubricant oils are really important, presenting different functions, as refrigeration, cleaning, fencing off and protection against corrosive agents[1]. Lubricant oil degradation under operation conditions is a problem that involves meaningful economical losses. Oxidation is the primary agent of degradation, and has given rise to many studies. Establishing thermodynamic parameters of reaction is difficult due to complexity of these systems[2-4].

It is of fundamental importance to know the thermal behavior of the automotive lubricant oils, their chemical composition and physical properties for a

strict process control and the definition of standards for each specific use[5]. The specific heat capacity (C_p) is as one of such physical properties. The molar heat capacity has a great importance in thermochemical processes and it is related to the heat of transformation, dQ_p, at a constant pressure, p, as shown below in Eq. 1:

$$dH = \delta Q_p \tag{1}$$

as δQ_p depends on the heat exchange and does not depend on the reversibility of these processes, the specific heat capacity (Cp) is defined by Eq. 2:

$$C_p = \frac{dH}{dT} = \frac{\delta Q_p}{dT} \tag{2}$$

The knowledge of the specific heat capacity (Cp) of the derived of the petroleum and of its mixtures it is of great practical importance in the branch of the petrochemical engineering, because it is associated with the refinery operations of petroleum and other correlated processes[6]. In the development of the equipments, the knowledge of the specific heat capacity values, in several temperature intervals, is of fundamental importance, because these data can help in the establishment of conditions of lingering storage or of operations to low temperatures. The specific heat capacity can be used for evaluation of other basic thermodynamic properties of other fuels[7].

Consistent experimental data about the specific heat capacity of derived of the petroleum are quite limited in the literature, and some data are available in small temperature intervals for the great majority of these derived. Differences in the composition of the automotive lubricant oils can result in significant differences in its specific heat capacity. In the last years, the Differential scanning calorimetry has been enough used in the determination of the specific heat capacity of hydrocarbons mixtures[8]. This happens; therefore through this method it can be obtained results with great sensibility and precision. In the present work, the specific heat capacities of some automotive lubricant oils were determined by Differential scanning calorimetry after thermal degradation, to evaluate the proposed method.

EXPERIMENTAL

The samples of automotive lubricant oils were acquired in the local trade, being all produced by Brazilian industries. In this study, mineral lubricant oils were used with and without addictives, synthetic and semi-synthetic (mixed), all destined to the application in the gasoline, alcohol and natural gas motors, whose characteristics are described in the TABLE 1.

For thermal degradation, lubricants were heat treated at 150, 170, 190 and 210°C, with air flux, in a system similar to a distillation one, as presented in figure 1. An initial lubricant volume of 300 ml was used. Samples were withdrawn after times that varied from 1 to 48 hours. Specific heat capacities were evaluated for degraded and non-degraded lubricant oils.
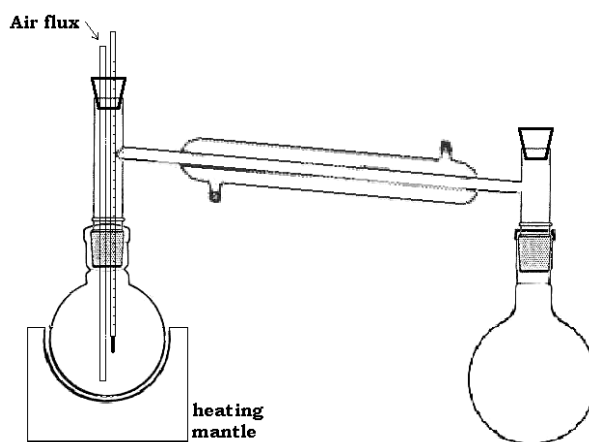

Figure 1: DSC curves: (a) lubricant oil sample, (b) blank and (c) reference material

DSC measurements

A differential scanning calorimeter Shimadzu, model DSC-50, was used. The automotive lubricant oil samples were placed in aluminum crucibles and heated from room temperature up to 190°C at a heating rate of 5°Cmin⁻¹, under a dynamic atmosphere of nitrogen (50 mLmin⁻¹), according to the procedure described in TABLE 2.

Three measurements were carried out for each sample: 1) Measurements with an empty crucible; 2) Measurements with a reference material (alumina),

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TABLE 1: Characteristics of the analyzed lubricating oils

Lubricants	Base	Addictives	Specification
Mineral	Paraffin	Antiwaste, antioxidant, detergent / dispersant, rust inhibitors and it skims, increased of the viscosity index	API SJ SAE 40W
Mineral without addictives	Paraffin	Non contain	API SJ SAE 40W
Synthetic	Synthetic	Antiwaste, antioxidant, detergent, dispersant, rust inhibitors and it skims, increased of the viscosity index	API SJ SAE 20W/50
Semi-synthetic	Paraffin and Synthetic	Antiwaste, antioxidant, detergent, dispersant, rust inhibitors and it skims, increased of the viscosity index	API SJ SAE 20W/50

TABLE 2: Experimental conditions to determine the specific heat capacities of edible vegetable oils

Heating hate ($^{\circ}$C min $^{-1}$)	Temperature ($^{\circ}$C)	Time (min)
5.0	30.0	5.0
10.0	200.0	5.0

with a known specific heat capacity; 3) Measurement of specific heats of the lubricant oil samples, with a fixed mass of 10.0 ± 0.5 mg.

RESULTS AND DISCUSSION

According to Santos[5], the relationship between heat capacity of the sample Cs (sample crucible support + sample crucible + sample), of the reference material Cr (reference material support + reference material crucible + reference material) and the heating rate (α) is expressed as:

$$C_s - C_r = \frac{T_s - T_r}{\alpha R} \qquad (3)$$

where Ts is the oil sample temperature; Tr is the reference material temperature; R is the instrument constant (thermal resistance of the sample, reference material and furnace) and Ts - Tr is the DSC displacement, which is proportional to the difference between Cs and Cr. If the DSC displacement is S and the proportionality constant is k, it can be stated that:

$$C_s - C_r = kS \qquad (4)$$

The automotive lubricant oil sample support and the reference material support have their heat capacities respectively represented by C_s^h and C_r^h The
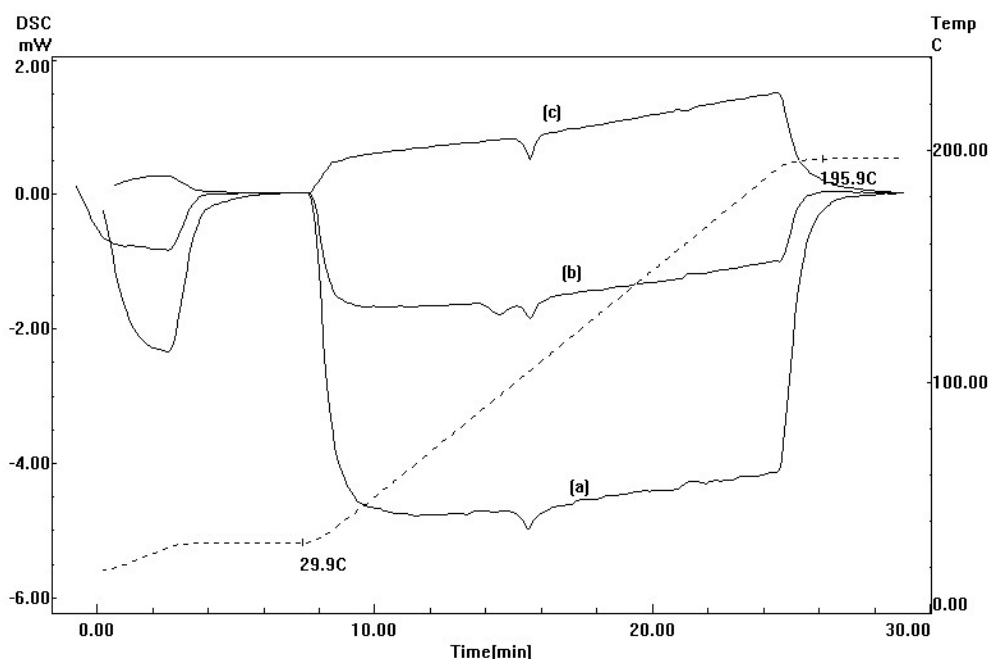

Figure 2: Schematic representation of the degradation system

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specific heat capacities of the reference material and of the lubricant oil sample are represented by c_0 and c, and the mass values of the reference material and of the oil sample are denominated m_0 e m, respectively. Thus, the following relations are obtained:

$$C_s^h - C_r^h = kS_1 \tag{5}$$

$$(C_s^h + m_0 c_0) - C_r^h = kS_2 \tag{6}$$

$$(C_s^h + mc) - C_r^h = kS_3 \tag{7}$$

Where S_1, S_2, S_3 are the thermal displacements of the DSC respectively related to the blank, the reference and the lubricant sample. The figure 2 shows the DSC curves for the lubricant oil sample, the blank and the reference material.

From equations (5), (6) and (7) the following equation is obtained

$$\frac{mc}{m_0 c_0} = \frac{S_3 - S_1}{S_2 - S_1} \tag{8}$$

as the specific heat capacity of the reference material is known, the specific heat capacity of the lubricant oil samples can be calculated by:

$$c = \frac{m_0 c_0}{m} \cdot \frac{S_3 - S_1}{S_2 - S_1} \tag{9}$$

as S_1, S_2 and S_3 are continuous functions relating to the temperature, the specific heat capacities can be determined continuously[5].

The TABLE 3 shows the results of this analysis for the samples of non-degraded lubricant oils.

It can be verified that the mineral lubricant oils presented a transfer heat capacity of more accentuated that the synthetic and semi-synthetic oils. This fact is probably due the chemical structure of these samples, once, the minerals are constituted basically of hydrocarbons in the strip from 20 to 25 carbons, while the synthetic ones, in your great majority, de-

TABLE 3: Specific heat capacity of the non degraded lubricant oils

Lubricant Oils	Cp (J g^{-1}ºC^{-1})							
	40ºC	60ºC	80ºC	100ºC	120ºC	140ºC	160ºC	180ºC
Mineral	2.534	2.865	3.069	3.101	3.648	4.052	4.689	5.458
Mineral without addictives	2.329	2.661	2.832	2.867	3.345	3.724	4.297	4.986
Synthetic	2.382	2.714	2.890	2.944	3.430	3.825	4.424	5.122
Semi-synthetic	2.316	2.675	2.861	2.894	3.360	3.732	4.314	5.015

TABLE 4: Specific heat capacity of the degraded mineral based lubricating oils

Lubricant oils	Sample conditions	Cp (J g^{-1}ºC^{-1})							
		40ºC	60ºC	80ºC	100ºC	120ºC	140ºC	160ºC	180ºC
Mineral	150 ºC/24 h	2.370	2.711	2.898	2.940	3.464	3.874	4.468	5.213
	150 ºC/48 h	2.763	3.199	3.315	3.368	3.945	4.402	5.226	5.400
	170 ºC/24 h	2.379	2.715	2.902	2.945	3.445	3.854	4.456	5.181
	170 ºC/48 h	2.245	2.555	2.739	2.777	3.223	3.665	4.214	4.876
	190 ºC/24 h	2.398	2.750	2.930	2.980	3.474	3.872	4.473	5.164
	190 ºC/48 h	2.238	2.593	2.799	2.852	3.341	3.737	4.303	4.826
	210 ºC/24 h	2.328	2.678	2.874	2.927	3.426	3.833	4.414	5.086
	210 ºC/48 h	2.269	2.595	2.789	2.841	3.333	3.703	4.265	4.947
Mineral without Addictives	150 ºC/24 h	2.298	2.606	2.775	2.803	3.302	3.699	4.307	5.022
	150 ºC/48 h	2.217	2.509	2.656	2.674	3.136	3.522	4.090	4.881
	170 ºC/24 h	2.379	2.736	2.909	2.948	3.455	3.863	4.496	5.214
	170 ºC/48 h	2.281	2.593	2.789	2.827	3.311	3.703	4.291	4.978
	190 ºC/24 h	2.243	2.569	2.725	2.746	3.226	3.612	4.191	4.874
	190 ºC/48 h	2.075	2.342	2.466	2.510	2.945	3.330	3.913	4.572
	210 ºC/24 h	1.314	1.384	1.464	1.497	1.747	2.000	2.378	2.754
	210 ºC/36 h	0.691	1.202	0.911	0.539	0.592	0.723	0.907	1.120

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rived of esters, and the semi-synthetic ones, a mixture of these two types of oils. It is still verified, that the presence of the addictive ones (mainly addictive EP), it provokes an increase in the specific heat, due to the breaking of the lubricating film. With the heating, this fact generates a responsible heat for the chemical reaction that frees the compositions that will act as lubricants.

The TABLE 4 and 5 shows the variation of the specific heat capacity in function of the thermal deg-radation of the automotive lubricant oils.

After degradation of the samples, a variation a little significant is verified in relation to the specific heat capacity in function of the time and of the deg-radation temperature, except for the mineral lubri-cating oil without addictive, that it presents a fall in the specific heat capacity values to 210°C, due to the polymerization process, because it was observed that in this temperature, after 36 hours, the sample was plenty of polymerized.

TABLE 5: Specific heat capacity of the degraded synthetic based lubricating oils

| Lubricant oils	Sample conditions	Cp (J g^{-1} °C^{-1})							
		40°C	60°C	80°C	100°C	120°C	140°C	160°C	180°C
Synthetic	150 °C/24 h	2.344	2.661	2.838	2.897	3.401	3.809	4.432	5.158
	150 °C/48 h	2.300	2.636	2.808	2.842	3.343	3.726	4.297	4.962
	170 °C/24 h	2.347	2.682	2.877	2.927	3.435	3.813	4.412	5.140
	170 °C/48 h	2.292	2.586	2.757	2.794	3.276	3.664	4.241	4.976
	190 °C/24 h	2.359	2.701	2.877	2.934	3.443	3.831	4.418	5.088
	190 °C/48 h	2.282	2.617	2.806	2.865	3.354	3.736	4.276	4.971
	210 °C/24 h	2.442	2.788	2.982	3.037	3.557	3.949	4.526	5.246
	210 °C/48 h	2.356	2.696	2.870	2.913	3.423	3.829	4.432	5.171
Semi-Synthetic	150 °C/24 h	2.324	2.671	2.844	2.899	3.389	3.770	4.317	4.999
	150 °C/48 h	2.312	2.620	2.777	2.803	3.266	3.643	4.225	4.922
	170 °C/24 h	2.288	2.629	2.793	2.824	3.291	3.657	4.224	4.904
	170 °C/48 h	2.328	2.686	2.872	2.915	3.407	3.782	4.343	5.027
	190 °C/24 h	2.350	2.699	2.889	2.950	3.453	3.831	4.403	5.093
	190 °C/48 h	2.193	2.525	2.709	2.752	3.220	3.556	4.070	4.655
	210 °C/24 h	2.421	2.779	2.996	3.053	3.571	3.963	4.560	5.273
	210 °C/48 h	2.327	2.677	2.851	2.913	3.400	3.798	4.416	5.121
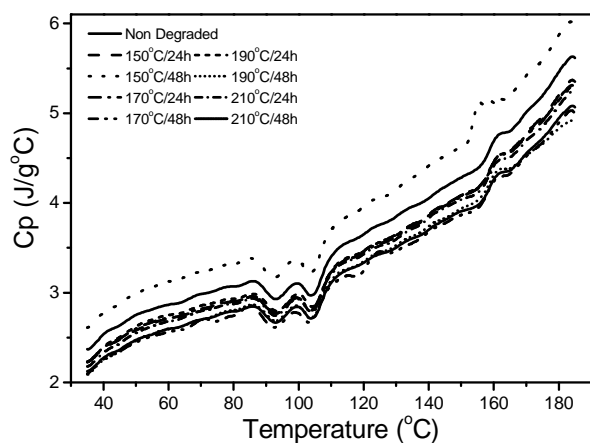
Figure 3: Specific heat capacity of the mineral lubricant oils in function of the time and deg-radation temperature.
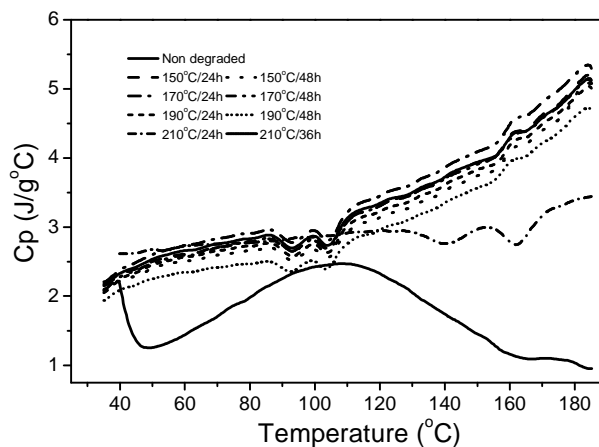

Figure 4: Specific heat capacity of the mineral lubricant oils without addictives in function of the time and degradation temperature.
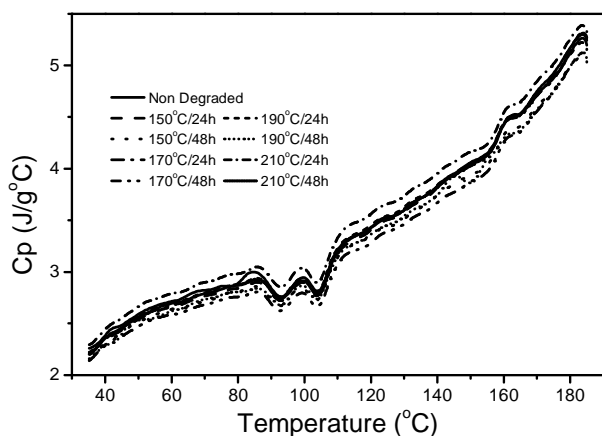
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Figure 5: Specific heat capacity of the synthetic lubricant oils in function of the time and degradation temperature
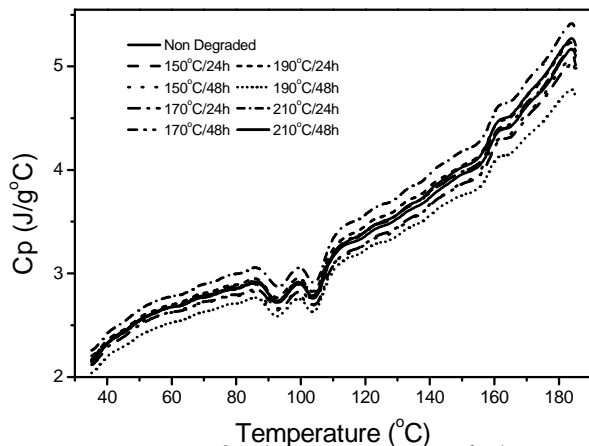

Figure 6: Specific heat capacity of the semi-synthetic lubricant oils in function of the time and degradation temperature

The figures 3 to 6 illustrate the behavior of the specific heat capacity of the automotive lubricating oils function of the time and degradation temperature.

CONCLUSIONS

In general terms, an increase is verified, in all the cases, of the specific heat capacity in function of the temperature, in the interval of 40-180°C, getting to bend the specific heat capacity. The significant increase happens starting from the 100°C. It can be verified although, the analyzed lubricating oils present an increase in its transfer heat capacities in function of the increase of the temperature, then these lubricant oils be used commonly relatively not in temperatures very discharges. In higher temperatures, it happens a heating of the lubricated parts that can cart your deterioration with the time of use of the lubricant.

ACKNOWLEDGEMENTS

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