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Assessment of gamma radiolytic degradation in waste lubricating oil by GC/MS and UV/VIS

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ABSTRACT

The hydrocarbons degradation by gamma irradiation of the waste automotive lubricating oil at different absorbed doses has was investigated. The waste automotive oil in a Brazilian oil recycling company was collected. This sample was fractioned and 50% and 70% (v/v) Milli-Q water were added. Each sample was irradiated with 100, 200 and 500 kGy doses using a gamma source Co-60—GAMMACELL type, with 5×10^3 Ci total activity. Gas chromatography–mass spectrometry (GC/MS) was used to identify degraded organic compounds. The mass spectra were analyzed using the mass spectral library from NIST, installed in the spectrometer. The sample irradiated at 500 kGy dose with 70% (v/v) Milli-Q water addition formed eight degradation products, namely diethanolmethylamine ($C_5H_{13}NO$), diethyldiethylene glycol ($C_8H_{18}O_3$), 1-octyn-3-ol, 4-ethyl ($C_{10}H_{18}O$) and 1.4-pentanediamine, N1, N1-diethyl ($C_9H_{22}N_2$). The color changing of the waste lubricating oil, for different absorbed doses, was determined by UV/VIS spectrophotometer. The related sample showed the lowest absorbance value evidencing the formation of 2-ethoxyethyl ether ($C_8H_{18}O_3$) compound.

1. Introduction

The automotive lubricating oils, through use, undergo thermal and oxidative degradation, acquiring undesirable impurities such as dust, metal scrapings, water or chemicals compounds, making their substitution necessary (EPA, 2008). The consumption of lubricating oil in Brazil is around $10^6\,m^3$/year (Conselho em Revista, 2005). Approximately, $6.5\times10^5\,m^3$/year are consumed in the lubrication process, and from $3.5\times10^5\,m^3$/year remainder only 20% are treated or recycled. The rise in consumption of automotive lubricating oil in the world wide has increased ending in large used oil volume and its waste. Thus, a great deal of research have been done for improvement of processes and treatments, seeking higher efficiency and lower costs (Cherednichenko et al., 2006; Hamad et al., 2005; Fakhri, 2004; Beaupied, 2004; Deutsch, 2001). The scientific literature has reported the use of the advanced oxidation process (AOP) by electron beam irradiation or gamma irradiation, as an efficient and clean technology for water waste, sludge, petroleum effluents and used lubricating oils treatment, improving metal removal, organic compounds degradation and microbiological sterilization (Duarte et al., 2004; Zhang and Yu, 2004; Popov and Getoff, 2005; Wasiewicz, et al., 2006; Scapin et al., 2007a, b). In this work, the efficacy and technical feasibility of the gamma irradiation, for organic compounds degradation in used automotive lubricating oils, was studied.

2. Experimental

2.1. Sampling

A used oil sample was collected from a Brazilian recycling company (*TASA LUBRIFICANTES LTDA*), and fractioned in three steps:

Step 1: Each 5 mL sample was transferred into 5 mL glass vials and labeled A_1, A_2, A_3 and A_4 samples;

Step 2: Each 7 mL sample was transferred into 14 mL glass vials and for each one 7 mL of Milli-Q water was added. These samples were mixed for 10 min in a mixer (SPEX-MILL, CAT. NO. 76156) and named B_1, B_2, B_3 and B_4;

Step 3: Each 4 mL sample was transferred into 14 mL glass vials. In each one, 10 mL of the Milli-Q water was added. These samples were also mixed for 10 min and named C_1, C_2, C_3 and C_4.

2.2. Irradiation processing

The irradiation was performed in a Co-60 irradiator (GAMMA-CELL-220, 5×10^3 Ci). The A_1, B_1 and C_1 samples were used as

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Table 1
Identified organic compounds by GC/MS, their retention time and relative peak area for MO (mineral oil), A_1 (used oil), C_3 and C_4 (irradiated) samples.Main kinetic reactions contributing to PCE decomposition in air under EB irradiation for the initial concentration of PCE being 322 ppm.

Retention time (min)	9.149	10.418	9.603	13.233	10.651	14.412	7.369	10.106
Compounds	$C_5H_{13}NO_2$	$C_{10}H_{18}O$	$C_8H_{18}O$	$C_9H_{22}N_2$	$C_{10}H_{20}O_5$	$C_4H_8O_2$	$C_5H_{13}NO$	$C_6H_{14}BNO_2$
Samples	Relative peak area (%)							
MO	ND	ND	ND	ND	ND	ND	ND	ND
A_1	12.55	ND	8.36	11.78	ND	ND	ND	ND
C_3	16.04	ND	9.93	10.22	ND	ND	ND	3.42
C_4	19.99	19.34	18.01	15.47	4.95	4.19	4.03	3.36

ND–not detected.

control samples, without irradiation. The A_2, B_2 and C_2 samples were irradiated with 100 kGy absorbed dose; A_3, B_3 and C_3 with 200 kGy and A_4, B_4 and C_4 with 500 kGy, in atmospheric air. After the irradiation, the samples were centrifuged at 3000 rpm for 2 min; the oil and aqueous phases were separated and stored under refrigeration (4 ± 2 °C) until analysis.

2.3. Organic compounds analysis

The control samples (A_1, B_1 and C_1) and irradiated samples (A_2, B_2, C_2, A_3, B_3, C_3, A_4, B_4 and C_4) were analyzed by GC/MS spectrometer (Shimadzu Co., model QP-5000) using a DB-5 ms capillary column from J & W scientific and helium carrier gas (flow: 1.3 mL/min). Initially, those samples were diluted in dichloromethane (1:10 v/v), and 1 μL was injected in the column, using splitless mode. The column was maintained at 75 °C for 1 min and heated to 200 °C, at a ratio of 15 °C/min. The final temperature (250 °C) was maintained for 1 min. The organic compounds were identified by NIST database library coupled to CG/MS spectrometer.

Using the MO, A_1, C_3 and C_4 samples, the color changing for different absorbed doses was measured by UV/VIS spectrophotometer (Varian Co., model Cary 1E) using 1.0 cm quartz cell. A total of 100 μL sample was diluted in 5 mL of carbon tetrachloride and absorption spectrum for each sample was obtained.

3. Results and discussion

The CG/MS methodology ruggedness was evaluated analyzing three replicates of pure mineral oil samples, named MO. For each sample, two measurements were carried out and relative standard deviation (RSD %) was calculated, which value was less than 5%.

The pure mineral oil (MO sample) chromatography analysis identified the eicosane ($C_{20}H_{42}$), heptadecane ($C_{17}H_{36}$) and hexadecane ($C_{16}H_{34}$) as the most abundant compounds. In the used oil (A_1 sample), the eicosane ($C_{20}H_{42}$), tridecane ($C_{13}H_{28}$), hexadecane ($C_{16}H_{34}$), 2-(2-hydroxyethyl-methyl-amino) ethanol ($C_5H_{13}NO$) and 1-ethoxy-2-(2-ethoxyethoxy) ethane ($C_8H_{18}O_3$) were identified as the most abundant organic compounds. Those results confirm the thermal and oxidative degradation of the automotive lubricating oil. However, the main characteristics of the mineral oil were kept.

As the same, the A_2, A_3, A_4, B_2, B_3, B_4 and C_2 samples did not show significant alteration in their composition, concerning mass spectra, when compared to A_1 sample, presenting the same organic compounds.

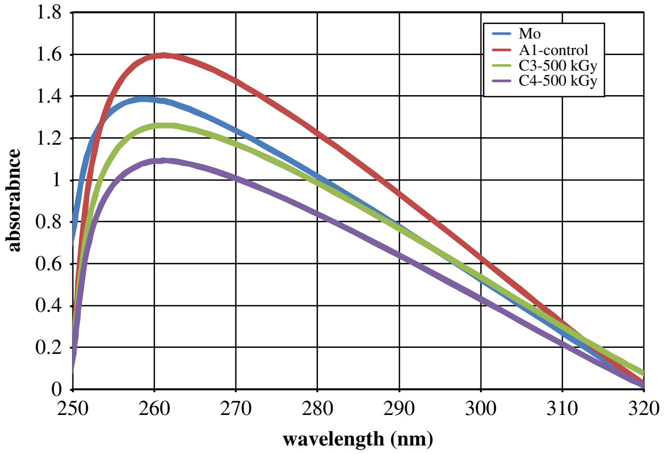

Fig. 1. UV/VIS absorption spectrum for MO, A_1, C_3 and C_4 samples.

The samples C_3 and C_4 (irradiated at 200 and 500 kGy with H_2O addition) showed the most significant changes in their composition. The 2-(2-hydroxyethyl-methyl-amino) ethanol ($C_5H_{13}NO_2$); 1-octyn-3-ol, 4-ethyl ($C_{10}H_{18}O$); 1-ethoxy-2-(2-ethoxyethoxy) ethane ($C_8H_{18}O_3$); 1,4-pentanediamine, N1, N1-diethyl ($C_9H_{22}N_2$); 1,4,7,10,13-pentaoxacyclopentadecane ($C_{10}H_{20}O_5$); ethylene glycol ether monovinil ($C_4H_8O_2$); ethanol, 2-(1-methylethyl) amino ($C_5H_{13}NO$) and diptych (boroxazolidin), B-ethyl ($C_6H_{14}BNO_2$) compounds were identified. Their retention time and relative peak area are presented in Table 1. The C_4 sample showed an increase in relation to A1 sample, for $C_5H_{13}NO_2$, $C_8H_{18}O_3$ and $C_9H_{22}N_2$ compounds (Table 1). They are classified as flammable, therefore additional flammability was given for this sample. The $C_5H_{13}NO_2$ compound, known commercially as methyldiethanolamine (MDEA), has several industrial applications such as corrosion inhibitor and gaseous waste treatment product. The $C_8H_{18}O_3$, known commercially as butildiglicol, is used as an organic solvent in a variety of synthetic resins and in paints and varnishes formulations. It is also a clearing agent and responsible for the brightness and viscosity increase of the lubricating oil. The formation of the $C_{10}H_{18}O$, $C_9H_{22}N_2$, $C_{10}H_{20}O_5$, $C_4H_8O_2$, $C_5H_{13}NO$ and $C_6H_{14}BNO_2$ compounds was observed only in the C_4 sample; currently, they do not offer industrial applications.

The sample C_3 (irradiated with 200 kGy absorbed doses) showed the $C_5H_{13}NO_2$, $C_8H_{18}O$, $C_9H_{22}N_2$ and $C_6H_{14}BNO_2$ formation, but in lower quantities than C_4 sample.

In Fig. 1, the UV/VIS absorption spectrum for MO, A_1, C_3 and C_4 samples is shown. The spectrum shows clarification process promoted by irradiation, since the sample A_1 showed greater absorbance value (at 260 nm) than other samples, and C_4 sample presented the lowest absorbance, demonstrating used oil clarification.

4. Conclusions

The application of gamma radiation in used lubricating oil showed to be efficient for organic compounds degradation. The increasing of the $C_5H_{13}NO_2$, $C_8H_{18}O_3$ and $C_9H_{22}N_2$ C_4 compounds gave additional flammability and $C_5H_{13}NO_2$ plus $C_8H_{18}O_3$ degradation products show several industrial applications, while $C_8H_{18}O_3$ promoted oil clarification. The gamma irradiation process demonstrates to be a promising technology for used lubricating oil treatment.

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