2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

SULPHUR REMOVAL FROM USED AUTOMOTIVE LUBRICATING OIL BY IONIZING RADIATION

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ABSTRACT

Following the worldwide evolution with the purpose of a higher control of vehicular emissions, the specialists have looked for clean technologies and efficient procedures to make vehicular emissions free of pollutants. Much attention is given to the sulphur concentration in the gasoline, diesel and lubricating oils. The ionizing radiation is a promising technology for the removal of this pollutant when compared to other conventional treatment methods. In this work, the ionizing radiation was used to remove in significant levels the presence of sulphur in automotive motor oil. A 1000mL sample of used automotive lubricating oil from a gas station was collected. This sample was fractioned and irradiated with 10, 20 50, 100, 200 and 500kGy doses in a ^{60}Co irradiator (GAMMACELL-220 - 12 kCi). The 50 and 70% (v/v) of MilliQ water and 30% (v/v) of hydrogen peroxide was used to improve the radiolysis The sulphur element before and after the irradiation was determined by X-ray fluorescence technique (WDXRF) using the Fundamental Parameters Method. The results showed approximately 70% sulphur removal at 500kGy irradiation dose with 70% (v/v) of MilliQ water addition.

1. INTRODUCTION

The lubricating mineral oils are derived from petroleum used in automotive and industrial engines. The automotive lubricant oils require some additives for their applications, such as diethylcarbamates and sulphonates organometallic compounds [1]. They act as antioxidants, dispersants and detergents. During their use, the automotive lubricant oils are partially degraded producing oxygen compounds (organic acids and ketones), aromatic compounds of high viscosity (potentially carcinogenic), resins and shellacs. Furthermore, some metallic elements can also be found in the oil by worn out mechanisms or corrosion process.

Lubricating oils are not totally consumed during their use and lose their lubricating property; therefore they should be replaced periodically, according to the engine specifications. In the automotive sector, the volume of used oil generated is significant, due to the sizeable fleet of vehicle. This residue may be classified as highly toxic [2], thus it should not be disposed nor reused without adequate treatment.

Usually, the technologies for oil recycling utilize the following steps: cyclonic distillation with dehydration, flash distillation, clarification, neutralization, and filtration. Each step provides products that receive adequate treatments, mainly metal removal to be then reutilized as raw material or in other products [3].

The ionizing radiation process has been used for different applications, especially for industrial and domestic effluents treatment (organic and biologic compounds degradation, metal removal) due to its high efficiency and clean technology application [4, 5, 6].

In this work, the gamma radiation was used to verify the level of sulphur removal in one used automotive oil sample. Two experiments were accomplished: The first with and without the addition of hydrogen peroxide and the second with and without the addition of MilliQ water. This sample was fractioned and irradiated with 10, 20 50, 100, 200 and 500kGy doses in a ^{60}Co irradiator (GAMMACELL-220 - 12 kCi).

The elemental concentration was determined by X-ray fluorescence technique, using the Fundamental Parameters Method. The values obtained were compared with those from one sample recycled by conventional process.

2. EXPERIMENTAL

2.1. Sampling

A 1000mL sample of used automotive lubricating oil from a gas station was collected. This sample was separated in four groups and fractioned as described below:
Group-A: 5 ml from the initial sample was transferred into 6 glass vials of 5mL, and labelled as samples named A1, A2, A3, A4, A5, and A6;

Group-B: 4 ml from the initial sample was transferred into 4 glass vials of 5mL, respectively. In each vial, 1ml of the hydrogen peroxide (H_2O_2 - 30% - MERCK) was added. These samples were then mixed for 10 minutes in the mixer (SPEX-MILL, CAT. N^O. 76156), named samples B1, B2, B3 and B4;

Group-C: 7 mL from the initial sample was transferred into 4 glass vials of 14 mL, respectively. The volume of each vial was completed with water Milli-Q and mixed for 10 minutes in the mixer, then named samples C1, C2, C3 and C4;

Group-D: 4 mL from the initial sample was transferred into 4 glass vials of 14 mL, respectively. The volume of each vial was completed with water Milli-Q and mixed for 10 minutes in the mixer, then named samples D1, D2, D3 and D4;

2.1. Processing

The irradiation was performed in a ^{60}Co irradiator (GAMMACELL-220 - 12 kCi). The Group A samples were irradiated with the following absorbed doses: 10, 20, 50, 100, 200 and 500 kGy, respectively except A1 sample that was used as "blank". The Groups B, C and D were irradiated with 100, 200 and 500 kGy, except B1, C1 and D1 which were not irradiated.

The elemental concentration was determined by a wavelength dispersion X-ray fluorescence spectrometer (RIGAKU Co., model RIX 3000) using the Fundamental Parameters Method [7]. The samples preparations were carried out through the following steps. Initially, a 50 ml Pt/Au mould was filled with 2.00000±0.00005g of wax (MERCK, wax C micro powder). Afterward, 1.00000±0.00005 of each sample was added.

The mixture was heated in a hot plate at 60±1 ^{0}C until melting; subsequently it was homogenized, cooled and taken off from the mould, obtaining a 25 mm diameter and 10 mm thickness disc. The methodology was evaluated using SRM 1084 Wear Metal in Lubricating Oil from National Bureau of Standards. The results were evaluated by statistical tests, recommended by EURACHEM/CITAC Guide [8].

3. RESULTS AND DISCUSSION

The SRM 1084 Wear Metal in Lubricating Oil from National Bureau of Standards reference material data presented a precision of 2% as relative standard deviation. The accuracy of the method presented Z-score value Z = 0.6, demonstrating the validation of the methodology for sulphur determination in oil samples.

In Table 1, the sulphur concentration and percent removal level (%RL) for the A, B, C and D Groups samples and a sample recycled by conventional process (CRP) are shown.

The results show that the gamma radiation promotes the decrease of the sulphur concentration for all of the analyzed samples and allows the following observations:

a) For the Group-A samples, the better percent removal level was 14% (A-6); it was observed that there was not a linear correlation between the %RL and the absorbed dose. However, higher doses showed to provide higher %RL values;

b) For the Group-B samples, only with the H_2O_2-30% addition, it was possible to decrease the sulphur concentration at 19%. The use of the gamma radiation increased to 25 and 26% at 100 and 200 kGy irradiation doses, respectively; although the variations of the doses have not presented a significant increase in the %RL;

c) For the Group-C samples, it was verified that the water addition also increase the sulphur removal (%RL = 32%); but significant removal could be not observed with the absorbed doses variation;

d) For the Group-D samples, it was verified a little increase in %RL (at 0 and 100 kGy absorbed doses) in relation to Group-C samples, 33% and 36% RL, respectively. Significant removal could be observed at 200 and 500 kGy, where D-4 sample presented the best %RL value (68%). The experiment evidence the water addition (70% v/v) contributed to increase the radiolysis process.

Table 1 - Sulphur concentration and percent removal level (%RL) for the A, B, C and D Groups

Groups	samples	($\mu g\ g^{-1}$)	(%RL)
A	A1 - Blank	12961±70	0
	A2 - 10kGy	12541±68	3
	A3 - 20kGy	12477±68	4
	A4 - 50 kGy	11786±64	9
	A5 - 100 kGy	11420±62	12
	A6 - 200 kGy	11166±61	14
B	B1 - H_2O_2(30%)	10562±58	19
	B2 - H_2O_2(30%) + 100kGy	9705±53	25
	B3 - H_2O_2(30%) + 200kGy	9616±52	26
C	C1 - H_2O(50%)	8770±48	32
	C2 - H_2O(50%) + 100kGy	8772±48	32
	C3 - H_2O(50%) + 200kGy	8674±47	33
	C4 - H_2O(50%) + 500kGy	8620±47	33
D	D1 - H_2O(70%)	8303±45	36
	D2 - H_2O(70%) + 100kGy	8235±45	36
	D3 - H_2O(70%) + 200kGy	7549±41	42
	D4 - H_2O(70%) + 500kGy	4188±23	68
	CRP	5495±30	58

The comparison between the proposed treatments with the conventional process is shown in Figure 1. The dilution with H_2O-Milli Q 70% (v/v) showed better removal than CRP sample, 68 and 58% RL, respectively.

The use of the H_2O_2-30% improve the sulphur removal but to reach higher removal would be necessary the increase of irradiation dose and/or more addition of the reagent, what would not be suitable due to the cost rising.

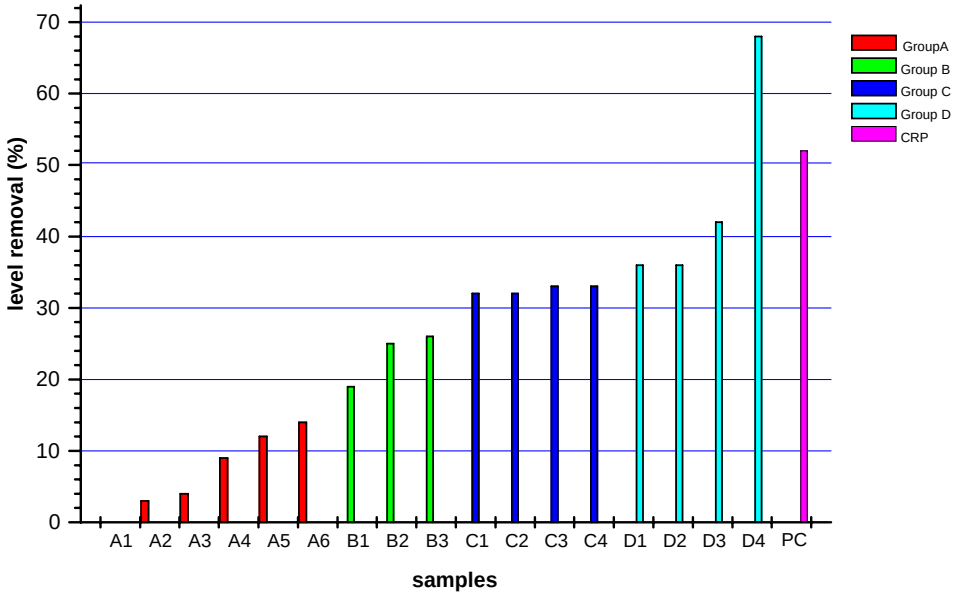

Figure 1 – Proposed and conventional treatments for sulphur removal

4. CONCLUSIONS

The use of gamma radiation together with the procedures used in our experiment showed to be a promising treatment for the sulphur removal in used automotive lubricant oil. In terms of environmental legislation, the procedure is adequate and clean, since the use of chemical agents was not necessary for the sulphur removal. This fact is very important in the worldwide trend seeking for clean technologies, mainly for used lubricating oils recycling process or re-using applications.

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