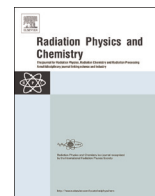




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Petroleum and diesel sulfur degradation under gamma radiation

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HIGHLIGHTS

- Sulfur compound degradation in petroleum and diesel by ionizing radiation.
- Radiation interaction with benzothiophene.
- Organic sulfur compounds analysis by GC–MS.

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ABSTRACT

Hydrodesulfurization (HDS) is currently the most common method used by refineries to remove sulfur compounds from petroleum fractions. However, it is not highly effective for removing thiophene compounds such as benzothiophene. Additionally, this process generates high costs for the oil industry. In the present work, ionizing radiation was used in order to study the effect on the degradation of petroleum and diesel sulfur compounds. Crude oil and diesel fuel samples were studied, without any pretreatment, and irradiated using a cobalt-60 gamma cell in a batch system at absorbed doses of 30 kGy and 50 kGy. The sulfur compounds were extracted and then analyzed by gas chromatography associated with mass spectrometry (GCMS). A high efficiency of ionizing radiation was observed regarding the degradation of sulfur compounds such as benzothiophene and benzenethiol and the formation of fragments, for example 1,2-dimethylbenzene and toluene.

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1. Introduction

Crude oil is a highly complex mixture of hydrocarbons with small amounts of heteroatoms like sulfur, oxygen, nitrogen and organic metals. Among these, sulfur is the most abundant and is considered an undesirable compound by refineries. Sulfur is present in petroleum as mercaptans, sulfides, cyclic sulfides, disulfides, thiophenes, benzothiophenes, dibenzothiophenes and naphthobenzothiophene; these are referred to as organosulfur compounds (Moustafa and Andersson, 2011; Speight, 2006).

Recent studies have been carried out in order to produce low-sulfur fuel oils. One reason is due to environmental laws that have become stricter over the years. Another point is the amount of money wasted by the petroleum industry using methods that are not always efficient.

The problems generated by sulfur compounds are related to the concentrations, which affect the quality of the final products and the price. At the refinery, these compounds cause the corrosion of

metal parts and catalyst poisoning, and also incur costs for the process to extract it from crude oil and products. The most frequently used process to extract sulfur is the hydrodesulfurization (HDS), which significantly removes sulfur compounds such as thiol, sulfide and disulfide, but it demands high amounts of energy, since a high temperature is necessary, around 300–430 °C, along with a high pressure of 2×10^7 Pa. In addition, high hydrogen consumption, expensive catalysts and a lack of efficacy regarding the removal of thiophene compounds are the disadvantages of this process. There are also environmental problems, such as acid rain, caused by the oxidation of sulfur compounds to SO_x when the fuel is combusted. Stringent environmental laws have been enacted to decrease the sulfur concentration in petroleum and derivatives (Zaykina et al., 2002).

Due to these reasons, an effective method needs to be developed, either as a single process or a complement to existing ones. Therefore, ionizing radiation, which is known as an efficient mediator of oxidation processes, is used in order to enhance sulfur removal from petroleum and diesel.

The use of ionizing radiation for oil processing has been studied since 1960 and has undergone a great evolution since then.

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According to previous studies, radiation is expected to oxidize sulfur compounds that are considered difficult to remove by conventional treatment. The increase in compounds that undergo oxidation as well as the decomposition of sulfur compounds is related to the dose. When liquid hydrocarbons are irradiated, radicals such as H, CH₃, C₂H₅, OH[•] and O[•] are formed and reactions like recombination, disproportionation, dissociation, molecular breakage and polymerization occur. These reactions are important in the process of desulfurization and the formation of less aggressive sulfur compounds such as sulfoxides, sulfones and sulfuric acids (National Energy Technology Laboratory, 2006; Zaykin et al., 2007, 2013; Zaykina et al., 2004).

Some researchers have demonstrated that the radiation process can reduce the quantity of mercaptans, disulfides and sulfides from heavy oil products. Sulfoxides and sulfones are generated as a result of the molecular transformation caused by oxidation induced by radiation. In other studies, electron beam exposure associated with ozone reduced the sulfur content in heavy oil and the formed sulfones, which were later removed by a simple process (National Energy Technology Laboratory, 2006; Zaykin et al., 2007; Zaykina et al., 2004).

The reduction in the sulfur content in petroleum and diesel by ionizing radiation is not completely established. Therefore, the present work aimed to contribute to the development of this technology, by studying the interaction of ionizing radiation from a Co⁶⁰ source and sulfur compounds present in diesel and crude oil. For this, in the first phase, a molecular model of sulfur (benzothiophene) was studied. In the second phase, the behavior of Brazilian diesel and petroleum under ionizing radiation was studied.

2. Experimental

2.1. Samples

The commercial reagent used in this investigation as a molecular model was benzothiophene (BT) from Merck Inc. It was prepared as a standard solution with 1391.6 mg l⁻¹ in methanol. From this standard, a 50 ml working solution diluted in distilled water was prepared. For the calibration curve and sample irradiation, the highest concentration was 139.2 mg l⁻¹. The oils used in this research were Brazilian petroleum and diesel from Campos Basin, Rio de Janeiro. The samples were maintained under refrigeration in amber glass bottles.

2.2. Radiation processing

All the irradiations were performed in a batch system; gamma irradiation was carried out at room temperature using a cobalt-60 gamma irradiator, gamma cell type. The BT, petroleum, and diesel samples were placed in completely filled 20 ml vials. The delivered doses for BT were 1 kGy, 2 kGy, 3 kGy, 4 kGy, 5 kGy, 10 kGy, 15 kGy and 20 kGy; the dose rate was 1.45 kGy/h. The delivery doses for petroleum and diesel samples were 30 kGy and 50 kGy; the dose rate for these samples was 1.27 kGy/h. The Dosimetry Research Group calibrates this system routinely with a Fricke dosimeter to determine the absorbed dose rate.

2.3. Chemical analyses

The chemical analyses were carried out based on previous research in petroleum and diesel analyses.

2.3.1. Benzothiophene chemical analyses

After irradiation, the BT content in the samples was analyzed using an O.I Analytica 4560 Purge and Trap Sample Concentrator linked gas chromatography column coupled to a mass spectrometry from Shimadzu (GC/MS-QP5000). The samples were injected onto a fused silica capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm) coated with DB-5. Helium was the gas carrier at a constant velocity of 42 cm/s. The temperature program was started at 30 °C programmed to 100 °C at 10 °C/min and then programmed to 300 °C at 15 °C/min. The mass spectrometer was operated in electron impact mode at 70 eV. The injector and interface temperatures were held at 250 °C and 230 °C, respectively.

2.3.2. Petroleum and diesel analyses

The total sulfur concentration was analyzed by X-ray fluorescence using EDX (Shimadzu, model Rany 720). The samples were prepared by the deposition of 25 μl of diesel/petroleum on Whatman no. 42 filter paper; the working range of the concentration was 334–10,000 mg l⁻¹.

In the second step, the diesel samples were prefractionated in an open glass column with an i.d. of 10 nm and a length of 200 nm, packed with 1.5 g of activated charcoal from Fmaia. 0.5 ml of diesel was dissolved in 5 ml of hexane and then passed through the column. The eluent was changed from hexane (20 ml) to benzene (50 ml), and the fractions of the column were collected in glass sample tubes 10 ml at a time (Later et al., 1981).

Petroleum samples were distilled according to ASTM-D1160. First, they were weighed directly in the distillation balloon, and then the system was submitted to 5 min of vacuum and heated until 400 °C. The balloon and system's maximum temperatures were measured during the process, which lasted approximately 20 min. The distillate was collected under cooling at -43 °C and the volume was measured (ASTM-D1160).

The sulfur compounds present in the distilled petroleum were separated based on a method developed by Nishioka and collaborators in 1987, using palladium chloride physically adsorbed on silica gel (PD-IISG). To prepared this, 100 ml of a 0.01 g l⁻¹ solution of PdCl₂ in deionized water was used with magnetic stirring for 30 min. The solution was mixed with 20 g of SG and the liquid phase was separated from the solid by decantation. The obtained solid was dried at 90 °C for 12 h and heated at 200 °C for 24 h (Nishioka, 1987).

An aliquot of 0.5 ml of distilled petroleum was dissolved in 5 ml of n-hexane/chloroform 1:1 and was eluted in an open column that was packed with 5 g of Pd-II-SG and pretreated with n-hexane/chloroform 1:1. The compounds were eluted with 80 ml of n-hexane/chloroform 1:1 and collected in 10 ml glass sample tubes (Nishioka, 1987; Xiaolan et al., 2006). Fig. 1 presents the separation scheme.

The samples were analyzed by a gas chromatography coupled to a mass spectrometer (GC-MS; Shimadzu model QP5000). A DB5 column and helium were used. The injector and interface

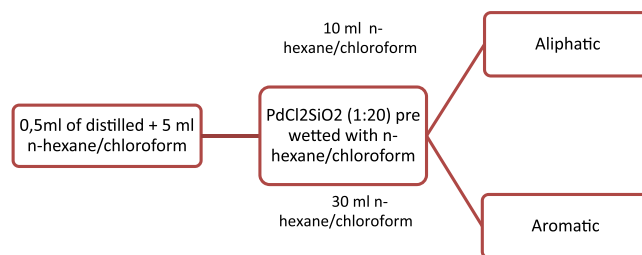


Fig. 1. Distilled petroleum separation by open column chromatography using PdCl₂SiO₂ as the stationary phase.

temperatures were held at 280 °C; the program temperature started at 40 °C, where it remained for 1 min. The heating range used was 4 °C/min until 280 °C, where it remained during 5 min. The mass spectrometer was operated in electron impact mode at 70 eV.

The irradiation treatment efficiency was evaluated by the chemical analyses of triplicate samples before and after irradiation.

3. Results and discussion

3.1. Benzothiophene

The calibration curve was obtained with a regression coefficient of 0.9944, and the obtained experimental variability ($N=10$), expressed as the standard deviation, was 10%. After irradiation, the samples were analyzed to quantify BT, and its transformation as a function of the absorbed dose was calculated. Fig. 2 shows BT removal (%) as a function of the absorbed dose (kGy). The efficiency of the process was related to the radiation dose. The results show that almost all BT was degraded with 20 kGy.

The formation of some other fragments occurred as a result of BT decomposition, such as benzothiophene, thiophene, toluene and dimethylbenzene in very small amounts, as shown in Fig. 3.

In this phase, it was observed that the presence of water directly affects the efficiency of the irradiation process; it is known that water suffers decomposition into hydrogen atoms and hydroxyl radicals with radiation (Eqs. (1) and (2)) (Getoff, 1986; Qu et al., 2007). In order to evaluate whether the degradation was mainly caused by the reaction with hydroxyl radicals, a radical blocking study was carried out with methanol. Methanol preferentially reacts with hydroxyl radicals, oxidizing and reversing the effects of radiation. An assay with benzothiophene diluted in water was performed with the addition of 20%, 40% and 60% methanol, with irradiation at 5 kGy, 10 kGy, 15 kGy and 20 kGy. The removal of BT as a function of the absorbed dose is presented in Fig. 4.



From Fig. 4, it is possible to infer that the presence of methanol interferes with benzothiophene degradation by ionizing radiation, i.e. comparing the 20 kGy dose of all samples with the different methanol concentrations. With the addition of 60% methanol and a dose of 20 kGy the transformation was not significant. This may have happened because the radicals produced by water radiolysis

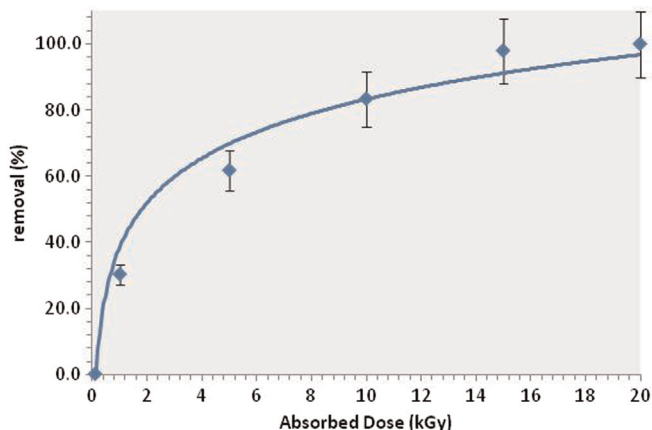


Fig. 2. Benzothiophene removal as a function of the absorbed dose.

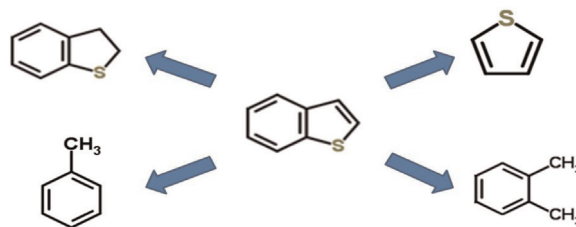


Fig. 3. Fragments formed after benzothiophene gamma irradiation.

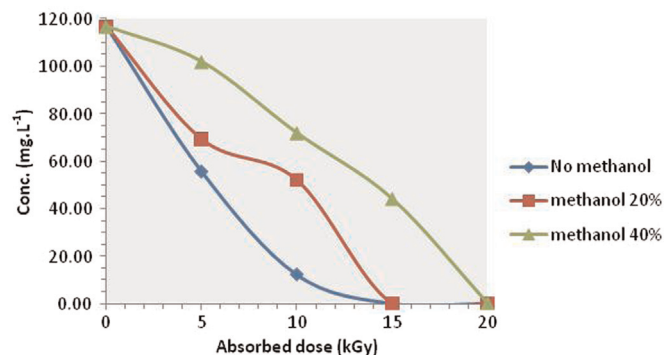
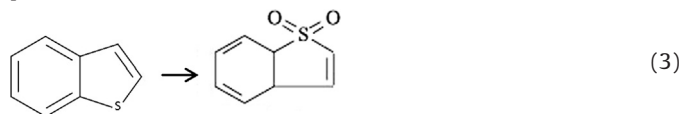


Fig. 4. Degradation of BT with different methanol concentrations after irradiation with different absorbed doses.

reacted preferentially with the OH of the methanol by oxidizing it. However, with the addition of 20% methanol and a dose of 20 kGy, the degradation was 86%. It is possible to conclude that benzothiophene degradation mainly occurs via hydroxyl radicals. According to the literature, a possible mechanism of benzothiophene oxidation is shown in Eq. 3. The formation of sulfoxides and sulfone groups (Zaykina et al., 2004) could also occur, but these groups were not identified by GC-MS analyses during the experiments.



3.2. Diesel

3.2.1. X-ray fluorescence

The total sulfur content in diesel was determined by X-ray fluorescence analyses. A calibration curve was made in the concentration range of 334–10,000 ppm, with a regression coefficient of 0.9944. The obtained experimental variability ($N=3$), expressed as the standard deviation, was 15%. The analysis with X-ray fluorescence showed that the sulfur concentration in the diesel was 2561 ± 29 ppm.

After irradiation, the sulfur concentration presented no variation, which was expected, because the radiation effects are supposed to transform sulfur compounds into less aggressive compounds. In other words, although there may have been chemical changes, molecular sulfur was still present in samples. Therefore, H_2S , which is the volatile form of sulfur, was not released.

3.2.2. Organosulfur compound analysis

In diesel samples, ten major sulfur compounds were identified by GC-MS, including eight aromatic compounds and two aliphatic compounds. Sulfur is in the ring in five of these eight aromatic

Table 1
Organosulfur compounds identified in diesel samples.

ID	Chemical name	Structural formula
D1	Butane, 1-(ethylsulfinyl)	
D2	1-Phenyl-2-ethylprop-1-ene (1-3)sultine	
D3	Benzo b thiophene	
D4	Benzo b thiophene, 5-methyl-	
D5	Benzo b thiophene, 2,5-dimethyl-	
D6	Benzene, (hexylsulfonyl)	
D7	Benzo b thiophene, 2,5,7-trimethyl-	
D8	Benzenemethanethiol, alpha-phenyl-	
D9	Benzenemethanethiol, alpha-methyl-alpha-phenyl-	
D10	Undecanoic acid, 11-mercapto	

compounds and is connected to the aliphatic portion in two compounds. In Table 1, the organosulfur compounds with their respective identification and structural formula are presented. Compounds D4, D5 and D7 are benzothiophene derivatives.

The benzenemethanethiol, alpha-methyl, alpha-phenyl and benzo-b-thiophene and 2,5-dimethyl were in higher concentrations in the diesel samples. In Fig. 5, the peak areas of compounds D1–D10 as a function of the absorbed dose of 30 kGy or 50 kGy are presented.

The variation in the concentration of the sulfur compounds in irradiated samples was calculated as a percentage related to the non-irradiated samples. The results are in Table 2.

It was possible to observe that there was a reduction in almost all compounds at 50 kGy, and, as result of this decomposition, simpler compounds were formed. Aliphatic molecular compounds increased at 30 kGy, especially 11-mercapto undecanoic acid, which was expected since the degradation of the other compounds generated CH_3 free radicals, particularly those with monosubstituted branches like benzothiophene.

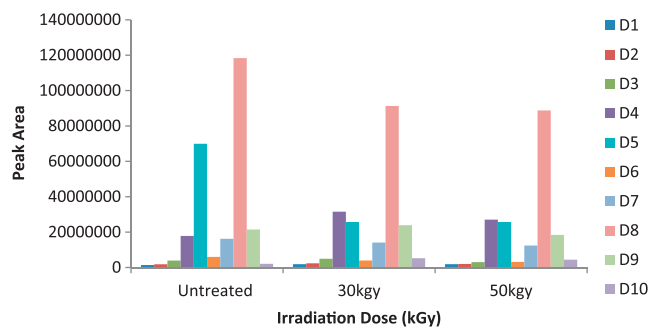


Fig. 5. Relationship between the area and dose of the sulfur compounds in diesel.

Table 2
Sulfur compound removal (%) from diesel samples after irradiation in comparison with the non-irradiated sample.

ID	30 kGy	50 kGy
D1	–32.7*	–0.84
D2	–29.7	15.4
D3	–25.7	38.1
D4	–76.6	14.1
D5	63.1	0.01
D6	33.9	19.5
D7	13.1	11.9
D8	22.8	2.7
D9	–11.4	23.0
D10	–148.9	16.1

* Negative numbers represent an increase in the concentration.

Analyzing Fig. 3 and Table 2, it can be inferred that there was a reduction in benzothiophene at 50 kGy, but the same result was not observed with the mono-substituted benzothiophenes at the same dose; contrary to what was expected, these compounds showed an increase at both doses. The di- and tri-substituted benzothiophenes were reduced by 63% in the first case and on average by 17% in the second one. From these data, it can be concluded that the formation of light $\text{C}_n\text{H}_{2n+1}$ radicals occurred, which recombined to generate saturated hydrocarbons. This increased the concentration of mono-substituted benzothiophene.

Benzenemethanethiol-alpha-phenyl showed some reduction, but when a methyl was added to the molecule forming benzenemethanethiol-alpha-methyl-alpha-phenyl, there was an increase with 30 kGy and a subtle reduction with 50 kGy. Benzene (hexylsulfonyl) decreased only a little, but 11-mercapto undecanoic acid, 1-phenyl-2-ethylprop-1-ene(1-3)sultine, butane and 1-(ethylsulfinyl) were increased.

3.3. Petroleum

Due the complexity of crude oil compared to diesel, it was necessary to employ chemical separation techniques such as distillation and separation by open column chromatography using palladium chloride before GC–MS analyses. The results obtained will be presented considering these steps.

3.3.1. Crude oil distillation

Crude oil distillation was performed in order to facilitate the chemical separation of organic compounds. It was also important to simulate thermal cracking in the distillation process that occurs at refineries, i.e. the breakage of long aliphatic chains into smaller chains.

During the distillation process of crude oil, the temperature was controlled in the distillation balloon and at top of system, where different fractions pass through in steam form. The

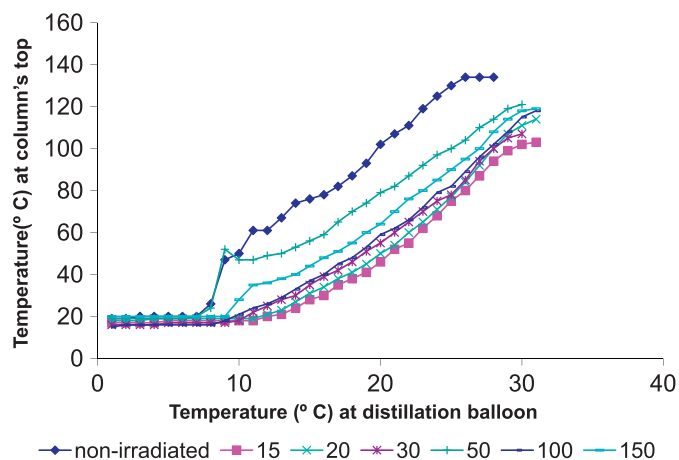


Fig. 6. Distillation balloon and system temperature variation with different doses.

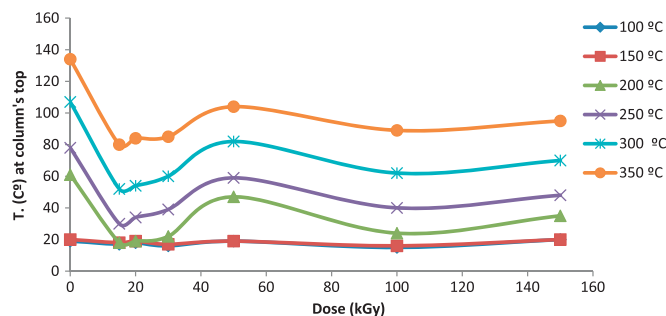


Fig. 7. Temperature variation at the top of the column with different doses.

variation in temperature for each radiation dose is presented in Fig. 6. In the distillation of non-irradiated crude oil, the temperature at the top of the column was higher, reaching 140 °C when the distillation balloon was heated to 400 °C. Between 350 °C and 400 °C there was a plateau, indicating the presence of heavy hydrocarbon chains. For samples that were irradiated in different doses, the temperature at the top of the column was lower, indicating the presence of light hydrocarbons. The petroleum irradiated with an absorbed dose of 15 kGy showed the lowest temperature; on the other hand, for higher doses, the temperature at the top of the column increased again. The mass of the oil before distillation and the distilled volume were measured for the non-irradiated and irradiated samples. Using the oil's apparent density, the distillation yield was calculated, which was $52 \pm 6\%$.

The influence of the absorbed dose on temperature behavior at the top of the column in relation to the distillation balloon temperature can be observed in Fig. 7. At temperatures from 100 °C to 150 °C, it can be noted that the temperature at the top remained unchanged in the samples. From 200 °C, the temperature at the top of the column varied for all absorbed doses, i.e. it decreased at 15 kGy and 20 kGy, and increased at 30 kGy and 50 kGy. This behavior can be explained by the cracking of heavier hydrocarbon compounds by ionizing radiation; in other words, lighter hydrocarbon compounds were generated, and thus distillation occurred at lower temperatures. In addition, the samples irradiated with higher doses started to show the same behavior as the non-irradiated samples, which means that with higher doses, the polymerization of hydrocarbons occurred. This was caused by the recombination of free radicals formed by the interaction with radiation.

3.3.2. Petroleum X-ray fluorescence

X-ray fluorescence was used to assess the petroleum samples. The analyses were carried out using the same parameters that were applied to the diesel samples. The total sulfur content in the sample was 6330 ± 16 ppm. After irradiation, there was no variation in the sulfur concentration. However, after irradiation and distillation at 400 °C, the sulfur species were transferred to the heavier fraction. This was confirmed by X-ray fluorescence, as

Table 3
Sulfur concentration after distillation of non-irradiated and irradiated crude oil.

Dose (kGy)	Distilled petroleum (ppm)
Non-irradiated	1485 ± 14
30	699 ± 50
50	1561 ± 50

Table 4
Organosulfur compounds identified in petroleum samples.

ID	Chemical name	Structural formula
P1	4-Fluorothiophenol	
PS2	1H, 3H-Theieno [3,4-c] thiophene, 4,6, dimethyl	
PS3	5-Hydroxy-2-methylthiopyrimidine	
PS4	2,6-Dimethyl-3-formylthiacyclohex-3-ene	
PS5	Cyclohexane, isothiocyanato	
PS6	1,2-dithiolane-3 pentanoic acid	
PS7	1-Heptadecanethiol	
PS8	4,5-Dimethyltetrahydro-1,3-oxazine-2-thione	
PS9	Benzenesulfonic acid, 4-methyl, dodecyl ester	

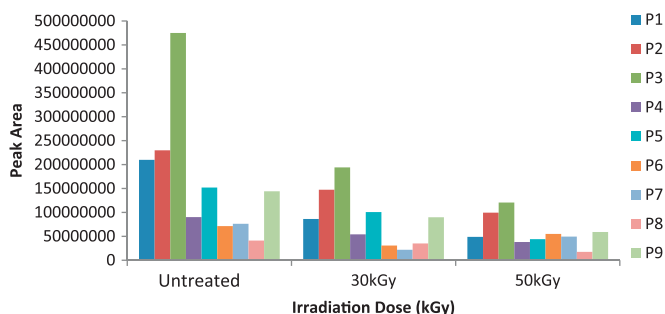


Fig. 8. Peak area variation, after separation with palladium chloride, of the main petroleum sulfur compounds as a function of absorbed dose.

Table 5
Sulfur compound removal (%) in petroleum samples in comparison to the non-irradiated sample.

ID	30 kGy	50 kGy
P1	58.8	76.6
P2	14.6	57.4
P3	59.1	74.6
P4	39.9	57.6
P5	33.7	70.9
P6	37.7	59.02
P7	35.8	56.7
P8	56.8	22.8
P9	71.2	35.1

shown in Table 3. The crude oil underwent partial desulfurization in the light fraction, especially at the 30 kGy dose. These results are in agreement with literature data obtained with oil from Saudi Arabia (Basfar and Mohamed, 2011) and Kazakhstan (Zaykina et al., 2002).

3.3.3. Organosulfur compound analysis

After the distillation and chemical separation using palladium chloride as the stationary phase in open column chromatography, the cyclic and aromatic compounds were separated from the aliphatic compounds by the use of appropriate solvents. However, aliphatic compounds with a high molecular weight, such as 1-heptadecanethiol, coeluted with the cyclic and aromatic compounds. In Table 4, the name, identification and molecular structure of the selected compounds are shown. The peak areas of the compounds identified in Table 4, as function of the absorbed dose, are presented in Fig. 8. It is possible to visualize the reduction in the concentration of all compounds at a dose of 30 kGy. It is also possible to note that, at 50 kGy, there was a reduction in some compounds while others showed an increased concentration.

The removal of sulfur compounds in irradiated samples was calculated as a percentage related to the non-irradiated samples. The results are shown in Table 5.

In Fig. 8 and Table 5, it can be noted that all sulfur compounds decreased. The highest reductions with 50 kGy were seen for 4-fluorothiophenol, 5-methyl-6-phenyltetrahydro-1,3-oxazine-2-thione and cyclohexane isothiocyanato with reductions of 76%, 74% and 70%, respectively. The remaining sulfur compounds showed reductions of approximately 50% with the exception of 1,2-dithiolane-3-pentanoic acid and 1-heptadecanethiol, which showed better results with 30 kGy. These compounds were reduced by 56% and 71%, respectively.

One of the important factors that must be considered in organic sulfur degradation is the form in which sulfur is bound to carbon.

For example, compounds like PS-1, PS-3 and PS-5, which do not have sulfur inside a cycle or aromatic ring, are easily reduced at 50 kGy, because their connection to carbon is weaker. In contrast, compounds such as PS-2, PS-4, PS-6, which have the sulfur inside a cycle or aromatic ring, have less of a tendency to be reduced than other compounds. The reduction of these compounds is related to the breakage of the external branch, i.e. CH_3 , because cycles and aromatic rings redistribute the energy from radiation. Also, the presence of nitrogen and oxygen should be considered, like in PS-8 and PS-9, as these atoms interact preferentially and competitively with electrons generated by the radiation process when compared to sulfur. Furthermore, steric hindrance makes the interaction of electrons with sulfur more difficult.

4. Conclusion

The reduction of sulfur compounds by gamma radiation in diesel was not satisfactory. However, in petroleum samples, radiation promoted the degradation of sulfur compounds. In addition, it was demonstrated that, after distillation, crude oil underwent partial desulfurization. Therefore, it was concluded that it is possible to use ionizing radiation as a degradation process, associated with HDS or some other well-developed process, thereby aggregating environmental benefits.

Acknowledgments

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