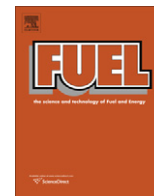


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Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process

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ABSTRACT

Ultrasound-assisted oxidative desulfurization (UAOD) process was applied to diesel oil and petroleum product feedstock containing model sulfur compounds (benzothiophene, dibenzothiophene and dimethylbenzothiophene). The influence of oxidant amount, volume of solvent for the extraction step and time and temperature of ultrasound treatment (20 kHz, 750 W, operating at 40%) was investigated. Using the optimized conditions for UAOD, sulfur removal up to 99% was achieved for model compounds in petroleum product feedstock using a molar proportion for H₂O₂:acetic acid:sulfur of 64:300:1, after 9 min of ultrasound treatment at 90 °C, followed by extraction with methanol (optimized solvent and oil ratio of 0.36). Using the same reagent amount and 9 min of ultrasound the removal of sulfur was higher than 75% for diesel oil samples. Sulfur removal without ultrasound using the same conditions was lower than 82% for model compounds and 55% for diesel oil samples showing that ultrasound improved the efficiency of oxidative desulfurization. In comparison to conventional hydrodesulfurization, the proposed UAOD process can be performed under relatively mild conditions (atmospheric pressure and 90 °C, without using metallic catalysts).

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1. Introduction

Sulfur compounds are the most notorious and undesirable petroleum contaminants and a large portion of these compounds can be transferred to diesel oil during refining process. In general, sulfur occurs as hydrogen sulfide, organic sulfides and disulfides, benzothiophene, dibenzothiophene, and their alkylated derivatives [1]. Upon diesel combustion, sulfur compounds are converted to sulfur oxides (SO_x) that contribute to acid rain and environmental pollution [2]. Although environmental regulation has been applied in many countries to reduce the sulfur levels in diesel and other fuels [3], sulfur removal still represents a major operational and economic challenge for petroleum refining industry [4].

Hydrodesulfurization (HDS) is the current industrial method to remove aliphatic and acyclic sulfur-containing compounds from diesel oil. This process is usually applied using CoMo and NiMo-type catalysts and allows removing sulfur compounds by their conversion to H₂S [5,6]. However, it is important to point out that this process requires high temperature (up to 400 °C), high hydrogen pressure (up to 100 atm), use of metal catalysts and large reactors,

with long reaction time resulting in higher operational costs [6–9]. Studies on HDS indicated that this process is efficient for mercaptans, thioethers, sulfides, disulfides and thiophene removal, but it has shown limitations regarding the treatment of alkylated aromatic sulfur compounds, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) [10–17]. Moreover, HDS is hindered by nitrogen compounds present in diesel oil [4,6]. In this sense, to overcome the limitations of HDS, several non-conventional methods have been developed. Some “non-HDS” based desulfurization technologies were reviewed by Babich and Moulijn [6] showing the application of alternative methods as biodesulfurization, selective adsorption, extraction with ionic liquids and oxidative desulfurization, which have been developed in order to remove the most refractory sulfur compounds.

Oxidative desulfurization (ODS) has been considered a promising method for deep desulfurization technology because it can be carried out under mild conditions, such as relatively low temperature, pressure and cost of operation when it is compared with HDS [4,6,18]. Several oxidation systems have been studied, such as H₂O₂/photocatalysts [19], H₂O₂/heteropolyanion (phase transfer catalyst) [2,20], isobutyraldehyde/molecular oxygen [21], ionized ozone [22] and nitrogen dioxide or nitric acid [23]. Hydrogen peroxide has been considered a powerful oxidant of sulfur compounds

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[7] and its effect when combined with other substances, such as $\text{H}_2\text{O}_2/\text{Na}_2\text{CO}_3$ [24], H_2O_2 /heteropolyanion catalysts and phase transfer agent [2,25], H_2O_2 /inorganic acids [26], H_2O_2 /formic acid [27,28], and H_2O_2 /acetic acid [5,9,23,29,30], has been studied. Thereby, the oxidation of sulfides to sulfoxides and sulfones is generally performed by reaction with peroxyacid generated *in situ* by the reaction of hydrogen peroxide and an appropriate carboxylic acid [28,31]. These oxidized molecules are substantially more polar than the respective sulfides and a solvent extraction step can be a convenient way to remove selectively the oxidized sulfur compounds from oil phase [5,18,20,30,31].

Associated to ODS, recent works have reported the use of ultrasound in petroleum fractions processing [20,24,32]. Studies related to chemical effects of ultrasound have shown that cavitation (the generation and violent collapse of vapor bubbles in a liquid subject to ultrasound) plays a major role [33–35]. These waves can cause the formation, growth and implosive collapse of bubbles, creating shock waves in liquids [33,34]. Furthermore, cavitation produces extreme local conditions and a microenvironment with high temperature and high pressure, which may also create active chemical intermediates allowing the reaction to proceed instantaneously [36]. Ultrasound effect is associated to the enhancement of reaction rates in view of the formation of radicals, cleavage of bonds and mass transfer, which could provide useful chemical effects [35,36]. However, despite the possible improvements caused by the use of ultrasound in the last years few works directly related to its application in petroleum industry have been published [7,20,24,27,32].

In the present work the use of ultrasonic energy to improve the oxidation and removal of sulfur compounds from diesel oil and petroleum product feedstock using relatively mild conditions and avoiding the use of metal catalysts was studied. The operational parameters for the ultrasound-assisted oxidative desulfurization (UAOD) procedure were investigated as hydrogen peroxide and acetic acid volumes, methanol and diesel oil volume ratio for sulfur compounds extraction, the effect of temperature during reaction and the ultrasound irradiation time. The reuse of reagents and a comparison of reactional conditions for sulfur removal without ultrasound were also evaluated. The UAOD procedure was applied for sulfur removal for model compounds in a hydrotreated petroleum product feedstock and for diesel oil samples.

2. Experimental

2.1. Apparatus

Experiments using the UAOD procedure were performed using an ultrasonic processor manufactured by Sonics and Materials, Inc. (Model VC 750, 20 kHz and 750 W of nominal power, Newton, USA). For all experiments an ultrasonic probe ($\frac{1}{2}$ in., full wave titanium probe solid, 254 mm long, Order Number 230-0217) was dipped directly into the oil/reagents mixture. Experiments were performed in a 250 mL three-neck conic glass reactor (Sonics and Materials, Inc., Order Number 830-00013) with temperature control (Servylab, Model MCT 100 Plus, São Leopoldo, Brazil). After ultrasound treatment, a glass separator funnel was used for the solvent extraction step. Tests without ultrasound were carried out for comparison using a high speed mechanical stirrer (Model MA 102, Marconi, Piracicaba, Brazil).

Total sulfur concentration in oil phase was determined using a sulfur analyzer (Antek Instruments, Model 9000 series sulfur/nitrogen analyzer, Texas, USA) by ultraviolet fluorescence, following the direct injection method [37]. The determination of sulfur in the aqueous phase (hydrogen peroxide and acetic acid) was performed by inductively coupled plasma optical emission spectrometry (ICP

OES) using a Spectro Ciros CCD spectrometer (Spectro Analytical Instruments, Kleve, Germany) with axial view configuration equipped with a cross flow nebulizer coupled to a double pass spray chamber. The plasma, auxiliary and nebulizer gas flow rates were 14.5, 1.0 and 0.95 L min⁻¹, respectively, and the radiofrequency power was 1650 W [38]. The wavelength of 180.731 nm was monitored for sulfur determination. The remaining operational parameters were set as recommended by instrument manufacturer. Argon 99.996% (White Martins-Praxair, São Paulo, Brazil) was used for plasma generation.

A viscometer (Stabinger, Model SVM 3000, Anton Paar GmbH, Graz, Austria) was used for the determination of dynamic viscosity and density of samples after and before the treatment according to ASTM D 7042-04 [39]. An infrared spectrometer PerkinElmer Model Spectrum One FTIR (PerkinElmer, Beaconsfield, Bucks, England) was used for characterization of obtained products in the range of 4000–650 cm⁻¹.

2.2. Reagents and materials

Oxidizing reagents used for UAOD procedure were hydrogen peroxide (H_2O_2 , 50% w/w, Synth, Diadema, Brazil) and glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, 1.05 kg L⁻¹, Vetec, Rio de Janeiro, Brazil). Benzothiophene ($\text{C}_8\text{H}_6\text{S}$, $\geq 99\%$ pure, Merck, Darmstadt, Germany), dibenzothiophene ($\text{C}_{12}\text{H}_8\text{S}$, $\geq 98\%$ pure, Merck), 4,6-dimethyldibenzothiophene (4,6-DMDBT, $\text{C}_{14}\text{H}_{12}\text{S}$, $\geq 97\%$ pure, Merck) and dibenzothiophene sulfone (DBTO, $\text{C}_{12}\text{H}_8\text{O}_2\text{S}$, $\geq 97\%$, Merck) were used as model sulfur compounds.

Solvents such as toluene (C_7H_8 , 0.87 kg L⁻¹) and methanol (CH_3OH , 0.79 kg L⁻¹) were obtained from Vetec (Rio de Janeiro, Brazil). Reference solutions for sulfur determination in oil and solvent phase were prepared by dissolving DBT in toluene. For sulfur determination in aqueous phase, reference solutions were prepared by serial dilution of stock solution (1000 mg L⁻¹) (Spex CertiPrep, Metuchen, USA) in ultra-pure water (18.2 M Ω cm, Milli-Q Ultra-pure Water Purification Systems, Millipore, Billerica, USA). For cleaning of reactor, ultrasonic probe and all the other materials, ultra-pure water, toluene and ethanol were used.

Table 1 summarizes the properties and sulfur concentration of all evaluated samples. Model sulfur compounds (BT, DBT and 4,6-DMDBT) were added to aliquots of a sulfur free hydrotreated petroleum product feedstock (in the diesel boiling point range, with sulfur concentration lower than 0.3 mg kg⁻¹) and enriched samples (feedstock 1–6, Table 1) were used for process parameters optimization. In addition to model compounds, diesel oil samples were used for experiments (Table 1).

2.3. Procedure

Reactions for sulfur removal were performed combining different mixtures of glacial acetic acid and 50% w/w H_2O_2 directly into the glass reactor containing 25 mL of diesel oil. The ultrasound probe was introduced into the reactional mixture (1 cm of the ultrasound probe was immersed into the liquid). The ultrasound amplitude control was set at 40%. In a first step, the effect of the volume of H_2O_2 solution was studied using volumes ranging from 0 to 5 mL 50% w/w H_2O_2 to a mixture of 25 mL feedstock and 2.5 mL glacial acetic acid. After choosing the H_2O_2 :sulfur molar proportion, the effect of glacial acetic acid was studied. Volumes of glacial acetic acid ranging from 0 to 50 mL were investigated for a mixture of 25 mL of feedstock and the previously selected volume of 50% w/w H_2O_2 . The effect of the temperature on the reaction was evaluated in the range of 20–90 °C. Using the selected temperature conditions, the reaction time was also investigated from 5 to 15 min. All the experiments were carried out at atmospheric pressure.

Table 1
Properties of petroleum derivatives samples and sulfur removal after UAOD treatment (25 mL of oil, molar proportion of H₂O₂:acetic acid:sulfur of 64:300:1, reaction at 90 °C, 9 min of ultrasound at 20 kHz, set at 40%, n = 3).

Sample	Compounds	Sulfur concentration (mg kg ⁻¹)	Sulfur removal (%)	Density (g cm ⁻³ , 20 °C)	Viscosity (mm ² s ⁻¹ , 20 °C)
<i>Hydrotreated petroleum product feedstock enriched with model compound</i>					
Feedstock 1	BT	285	64.8 ± 2.4	0.8362	10.0100
Feedstock 2	DBT	208	96.3 ± 0.7	0.8362	10.0100
Feedstock 3	4,6-DMDBT	180	98.6 ± 1.6	0.8362	10.0100
Feedstock 4	BT + DBT + 4,6-DMDBT	60 + 160 + 161	85.8 ± 3.2	0.8362	10.0100
Feedstock 5	BT + DBT + 4,6-DMDBT	288 + 210 + 182	80.2 ± 2.0	0.8362	10.0100
Feedstock 6	BT + DBT + 4,6-DMDBT	302 + 301 + 301	72.8 ± 1.2	0.8362	10.0100
Diesel oil A ^a	Diesel sample	136 ± 5	75.8 ± 1.2	0.8681	6.6855
Diesel oil B ^a	Diesel sample	319 ± 3	87.7 ± 1.8	0.8510	4.2119
Diesel oil C ^a	Diesel sample	249 ± 4	76.8 ± 1.9	0.8672	7.2414

^a Diesel oil samples were obtained from petroleum refining process and they have been previously deep hydrotreated (A and C) and hydrotreated (B).

After ultrasound treatment the phase separation was spontaneously achieved in less than 1 min. The treated oil phase was extracted three times with methanol, using a glass separator funnel with manual and constant shaking according to the procedure described in previous work [32]. The solvent volume required to extract the oxidized sulfur compounds in 25 mL of feedstock was evaluated in the range of 0–25 mL of methanol. Oil and solvent phases were separated and sulfur concentration was determined in both phases. In addition, sulfur was also determined in the aqueous phase by ICP OES. For experiments with model compounds, aqueous phase was washed with toluene for characterization of obtained products. Sulfur conversion efficiency was calculated taking into account the sulfur concentration remaining in oil phase. Finally, using all the optimized conditions, it was studied the possibility to reuse the aqueous phase (H₂O₂ and acetic acid) to treat fresh amounts of the feedstock. For comparison, experiments were carried using the optimized conditions for UAOD process but mechanical stirring (7000 rpm) was used instead of ultrasound. In this case, reagents addition, separation of oil and aqueous phase and extraction were carried as previously optimized for UAOD process. Fig. 1 shows the overall procedure and the sequence of optimizations performed.

3. Results and discussion

3.1. Optimization of reagents amount for UAOD procedure

Oxidative desulfurization schemes based on the use of organic acids and hydrogen peroxide have been reported in literature

[5,29,30,32]. In the present work, initial studies were performed in view of reducing the reagent consumption in oxidative desulfurization reactions. Experiments were focused on the effect of ultrasound irradiation for the improvement of the reaction efficiency that could be observed in the reaction of acetic acid and hydrogen peroxide leading to the formation of a peroxyacid reagent and also in the oxidation of sulfur compound. Dibenzothiophene was used as model sulfur compound due to its resistance to HDS process. Tests were carried out modifying the acetic acid:sulfur and H₂O₂:sulfur molar proportions. These experiments were always performed using 25 mL of enriched feedstock. Hydrogen peroxide 50% (w/w) solution and glacial acetic acid were added to the oil and molar proportion was changed by adding different volumes of these oxidizing solutions. Ultrasound irradiation conditions were used according to previous work [32]. A systematic optimization of reagents concentration was performed keeping the ultrasound energy at 40% of amplitude [32].

Initially, 25 mL of feedstock 2 (208 mg kg⁻¹ of sulfur as DBT) were treated with 15 mL of glacial acetic acid and volumes of 50% (w/w) H₂O₂ ranging from 0 to 5 mL, that represents an equivalent molar proportion of H₂O₂:sulfur from 0:1 to 640:1. Results of sulfur removal as a function of H₂O₂:sulfur molar proportion are shown in Fig. 2. It could be observed that the efficiency of removal was improved by increasing the relative amount of H₂O₂. A sulfur removal higher than 95% was observed when molar proportion for H₂O₂:sulfur of 64:1 was used (0.5 mL of 50% (w/w) H₂O₂). For higher values of molar proportion, the removal was reduced. This decrease could be explained probably by the dilution of aqueous

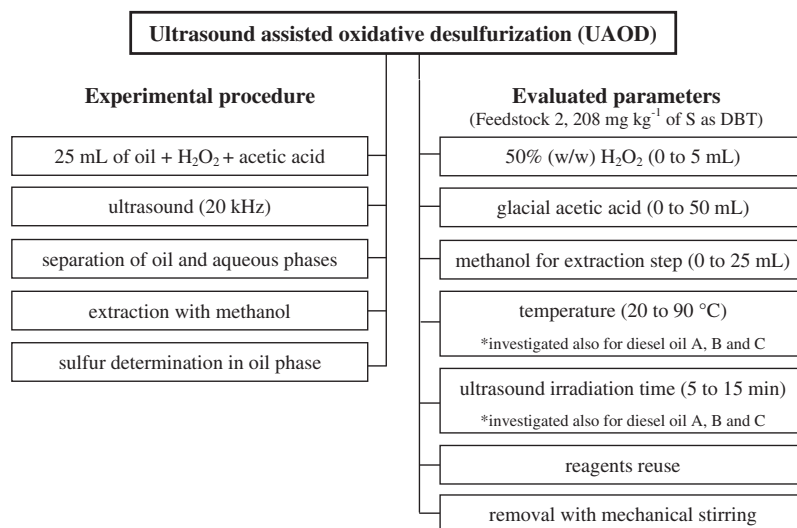


Fig. 1. Experimental workflow for general desulfurization procedure.

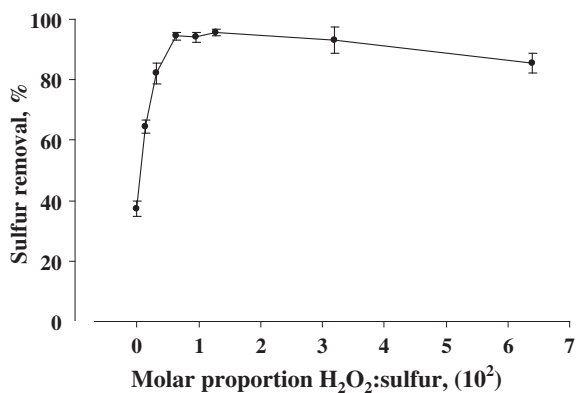


Fig. 2. Effect of hydrogen peroxide on sulfur removal from feedstock 2 (25 mL of feedstock, molar proportion for acetic acid:sulfur of 300:1, 9 min of ultrasound 20 kHz, set at 40%, extraction with methanol, $n = 3$).

phase (composed by acetic acid and hydrogen peroxide) with the increase of H₂O₂ volume, reducing the efficiency of this mixture for the oxidation process.

Further, the effect of acetic acid volume was evaluated. In this case, the use of 0–50 mL of glacial acetic acid that represents a molar proportion of acetic acid:sulfur ranging from 0:1 to 6440:1 was evaluated, for desulfurization of 25 mL of feedstock 2 (208 mg kg⁻¹ of sulfur as DBT) using 0.5 mL of 50% (w/w) H₂O₂ (H₂O₂:sulfur molar proportion of 64:1). Ultrasound irradiation time was 9 min (20 kHz, run at 40%) for all the experiments. Methanol was used for extraction step after UAOD procedure. Results for sulfur removal for different acetic acid:sulfur molar proportion are shown in Fig. 3. An increase on sulfur removal could be observed when the amount of acetic acid was increased in relation to the initial sulfur concentration in the oil. Slightly increasing the amount of acetic acid allowed improving the efficiency on sulfur removal. Removal of sulfur was higher than 94% when 2.5 mL of glacial acetic acid was used (molar proportion of acetic acid:sulfur was 300:1). The use of higher amounts of acetic acid also resulted in high removal efficiency (up to 97%), but volumes higher than 2.5 mL were considered as not necessary. In addition, it is important to minimize the use of oxidizing reagents and the consequent chemical residues.

When acetic acid was not used in the mixture the sulfur removal was only about 35% (Fig. 3, 0 mL of acetic acid). This same behavior was observed in the study of hydrogen peroxide molar proportion when H₂O₂ was not used (Fig. 2, 0 mL of H₂O₂). It must

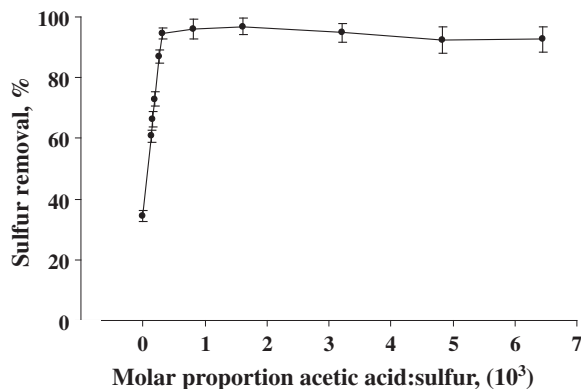


Fig. 3. Effect of acetic acid on sulfur removal from feedstock 2 (25 mL of feedstock, molar proportion for H₂O₂:sulfur of 64:1, 9 min of ultrasound 20 kHz, set at 40%, extraction with methanol, $n = 3$).

be considered that all results presented in Figs. 2 and 3 were obtained after methanol extraction step. In addition, it is important to point out that a sulfur removal of 32–35% was obtained using only liquid–liquid extraction with methanol and this removal efficiency was the same obtained for experiments without acetic acid or without H₂O₂. Hence, it is possible to consider that the sulfur removal for experiments without acetic acid or H₂O₂ could represent only the extractability of sulfur compounds by methanol and with no addition of acetic acid or H₂O₂ low removal efficiency was obtained. Results obtained in these studies suggest the necessity of combining the use of acetic acid and H₂O₂ in order to obtain higher efficiency on sulfur removal. Based on this study, it was found that the more suitable amounts of H₂O₂ and acetic acid were 0.5 and 2.5 mL, respectively, for sulfur removal from 25 mL of feedstock (molar proportion for H₂O₂:acetic acid:sulfur was 64:300:1) that resulted in a reduced amount of reagents in comparison to the amounts suggested in previous works using oxidative mixtures [5,29,30,32].

3.2. Solvent volume for extraction step

According to previous studies [30–32] organosulfur compounds are generally polar and an extraction step can be applied to remove sulfur compounds, mainly in its oxidized form. As a general requirement the solvent must have high polarity and to be insoluble in the oil [24,28–30]. Based on previous work using UAOD procedure [32], methanol amount for extraction of sulfur from oil phase was evaluated in order to reduce the solvent consumption. For these experiments, UAOD procedure was performed during 9 min using 25 mL of feedstock 2, 0.5 mL of 50% (w/w) H₂O₂ and 2.5 mL of acetic acid (molar proportion for H₂O₂:acetic acid:sulfur of 64:300:1). At the end of ultrasound irradiation and separation of oil and aqueous phases, a liquid–liquid extraction was performed. After extraction step, sulfur concentration in oil phase was determined. An additional experiment was carried out but without the extraction step. In this particular case, after ultrasound irradiation, oil and aqueous phases were separated and sulfur concentration was directly determined in the not extracted oil phase. Results for sulfur removal obtained regarding extraction step with different solvent and oil volume ratios were also investigated and the results are shown in Table 2. It was observed that the removal efficiency was higher with the increase of solvent volume reaching 91% of sulfur removal with a solvent and oil volume ratio of 0.24. Using the volume ratio of 0.36, sulfur removal was increased to 95%. The same sulfur removal was observed for higher volumes of methanol. Then, the total solvent volume for extraction step was kept as 9 mL for sulfur extraction using 25 mL of oil and this solvent and oil volume ratio (0.36) was used for further experiments. In addition, sulfur was determined in all phases of UAOD procedure (oil, aqueous and solvent used in extraction step) in order to evaluate the sulfur mass balance. Using optimized conditions it was observed that aqueous phase contained about 55% of

Table 2

Sulfur removal using UAOD procedure followed by oil phase extraction with methanol with different solvent and oil volume ratio (25 mL of feedstock 2, molar proportion for H₂O₂:acetic acid:sulfur of 64:300:1, 9 min of ultrasound 20 kHz, set at 40%, $n = 3$).

Solvent	Solvent and oil ratio	Sulfur removal (%)
No extraction	–	71.4 ± 7.8
Methanol	0.12	80.8 ± 2.5
Methanol	0.24	90.7 ± 2.2
Methanol	0.36	95.6 ± 2.1
Methanol	0.49	94.3 ± 2.4
Methanol	1.00	94.5 ± 2.8

sulfur, 42% was found in methanol and only 3% remained in oil, showing that recovery was quantitative. At the end of UAOD process the total oil loss was lower than 1%.

3.3. Effect of temperature

The effect of temperature on the oxidative reaction under ultrasound was evaluated from 20 to 90 °C. The upper limit was determined by the boiling point of the more volatile component in the mixture. Experiments were performed using 25 mL of oil, 0.5 mL of 50% w/w H₂O₂ and 2.5 mL of acetic acid (according to the optimizations for molar proportion using DBT as model compound). Ultrasound (at 20 kHz, set at 40%) was applied during 9 min and oil phase was extracted with methanol. Fig. 4 presents the temperature effect on sulfur removal from three diesel oil samples (A, B and C) obtained from different Brazilian crude oils and from a sulfur free petroleum product feedstock enriched with DBT (feedstock 2), used as model sulfur compound. Results showed that at higher temperatures (90 °C), sulfur removal was higher than 75% for all evaluated samples. As expected, the feedstock containing the model sulfur compound (feedstock 2) showed the best result (sulfur removal higher than 95%). Based on these results, subsequent experiments were carried out keeping the temperature at 90 °C.

3.4. Effect of reaction time

The reaction time necessary to oxidize the sulfur compounds was evaluated. The amount of H₂O₂ and acetic acid was also 0.5 and 2.5 mL, respectively, for the treatment of 25 mL of oil. Reactions were carried out at 90 °C for diesel oil samples A, B and C and for the sulfur free petroleum product feedstock enriched with DBT (feedstock 2). At this temperature, reactions were performed at reaction times from 5 to 15 min (ultrasound at 20 kHz, set at 40%) and the results of sulfur removal are shown in Fig. 5.

It can be observed that sulfur removal increases from 5 to 15 min of ultrasound for all samples (at 90 °C). Sulfur removal higher than 90% was obtained for the feedstock containing the model sulfur compound (feedstock 2), even with only 5 min of ultrasound treatment. The effect of increasing time was more prominent on the hydrotreated diesel oil (B) which presents mainly benzothiophene and its derivatives which are more difficult to react by oxidation. Sulfur removal was higher than 75% for all diesel oil samples, for 9 min of ultrasound. It was also observed that removal efficiency was different for diesel oil samples A, B and C due to the different composition of each sample. Lower removal of these contaminants was obtained for diesel oil A and C

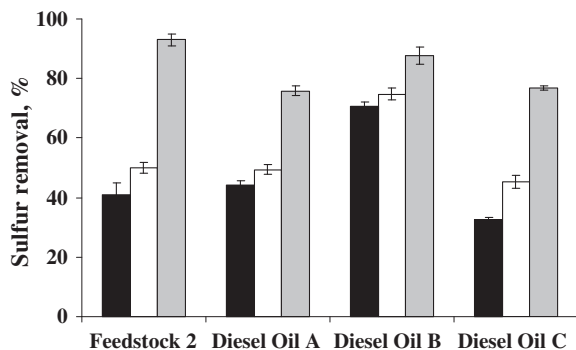


Fig. 4. Effect of temperature of the reaction on sulfur removal from feedstock 2 (enriched with DBT) and diesel oil samples A, B and C at ■ 20, □ 50 and ▒ 90 °C (25 mL of feedstock with molar proportion for H₂O₂:acetic acid:sulfur of 64:300:1, or diesel oil, using 9 min of ultrasound 20 kHz, set at 40%, extraction with methanol and oil volume ratio of 0.36, *n* = 3).

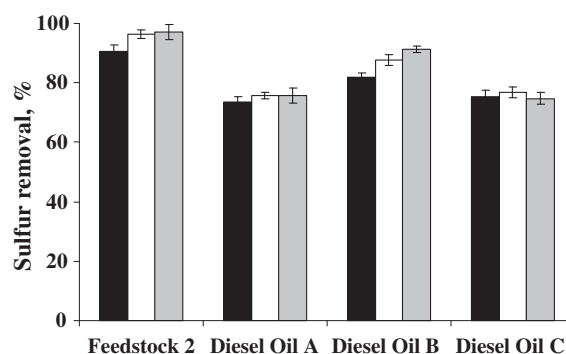


Fig. 5. Effect of reaction time on sulfur removal from feedstock 2 (enriched with DBT) and diesel oil samples A, B and C for ■ 5, □ 9 and ▒ 15 min (25 mL of feedstock or diesel oil, molar proportion for H₂O₂:acetic acid:sulfur of 64:300:1, reaction at 90 °C, ultrasound 20 kHz, set at 40%, extraction with methanol and oil volume ratio of 0.36, *n* = 3).

(lower sulfur concentration, mainly dibenzothiophene and its derivatives), whereas higher sulfur removal was observed for diesel oil B (higher sulfur concentration but lower nitrogen content). It is important to point out that diesel oil samples contain from 110 to 230 mg kg⁻¹ nitrogen which also could decrease sulfur removal. As previously reported in literature [40–42], this effect can be mainly due to the interference of nitrogen compounds in the extraction/adsorption step, but also the consumption of H₂O₂ could be considered for some compounds, as indole. In this study it was observed that the efficiency on sulfur removal was lower when higher concentrations of nitrogen were present in diesel oil samples. In addition, the concentration of nitrogen is relatively higher in the samples studied in this work in relation to the concentration of sulfur (samples contain about 110–230 mg kg⁻¹ of nitrogen and 136–319 mg kg⁻¹ of sulfur) which is typical for samples obtained from Brazilian refineries. Based on these results, as 15 min of ultrasound gives no or only small improvement on the removal, 9 min of ultrasound application was chosen for further studies.

3.5. Application of UAOD procedure for sulfur removal in petroleum derivatives

After UAOD parameters optimization (molar proportion for H₂O₂:acetic acid:sulfur of 64:300:1, 9 min of ultrasound at 20 kHz, set at 40%, reaction temperature kept at 90 °C and extraction with methanol and oil volume ratio of 0.36), the proposed procedure was applied for sulfur removal in an hydrotreated petroleum product feedstock enriched with different model compounds. For this study, BT, DBT and 4,6-DMDBT, the most refractory sulfur compounds in HDS process, were used. According to the results showed in Table 1, the UAOD procedure was efficient for oxidation of DBT and even 4,6-DMDBT with sulfur removal higher than 96%. Contrarily, it was observed a poor efficiency on BT oxidation (about 65% of sulfur removal for feedstock 1) as expected based on the reactivity of sulfur compounds in ODS process. Even for feedstock 4, 5 and 6 also containing benzothiophene compounds, sulfur removal was always higher than 72%. It was observed a colorless solid material in aqueous phase for experiments for UAOD using feedstock 2 (DBT as model compound). In order to characterize this product, aqueous phase was washed with toluene and the solvent was evaporated. The obtained material presented a melting point of 232–235 °C which is in agreement with literature data for dibenzothiophene sulfone, the main product of dibenzothiophene oxidation. In addition, solid material was characterized by infrared spectroscopy and

characteristic signal for sulfone compounds ($1350\text{--}1080\text{ cm}^{-1}$) were observed confirming the oxidation of the former sulfur compound.

Table 1 also presents the results for sulfur removal from a deep hydrotreated (diesel oil A and C) and hydrotreated (diesel oil B) samples showing the feasibility of the proposed UAOD procedure for sulfur removal from real samples. Sulfur removal was higher than 75% for all samples. The disagreement between sulfur removal efficiency could be explained by different reactivity of the organosulfur compounds in each diesel oil sample. All samples used in this work have been already treated by conventional HDS process. Consequently, only refractory sulfur compounds, not removed by HDS treatment, should remain in the sample. According to analysis of samples without any treatment by gas chromatography with pulsed flame photometric detector (GC-PFPD, data not shown) diesel oil B presents mainly BT and its related compounds (about 60%) and about 2% of 4,6-DMDBT. This sample also presents the highest nitrogen content, (230 mg kg^{-1}). Diesel oil A and diesel oil C present about 35% of DBT alkylated derivatives.

In order to evaluate the improvement obtained by the application of ultrasound in the reactional mixture a procedure applying the same previously optimized conditions, but using a fast mechanical stirring system was also investigated. Then, 25 mL of feedstock 2 were treated with 0.5 mL of 50% (w/w) H_2O_2 and 2.5 mL of acetic acid (molar proportion for H_2O_2 :acetic acid:sulfur of 64:300:1) with mechanical stirring (7000 rpm) during 9 min, at $90\text{ }^\circ\text{C}$, using methanol for sulfur extraction. The efficiency of sulfur removal was about 70–80% that is lower in comparison to the removal when ultrasonic irradiation was used (sulfur removal about 95%). Even for longer times (30 min) for reaction with mechanical stirring the removal was lower than 82% showing that ultrasound allowed to achieve better removal efficiency.

Concerning the oil properties after UAOD treatment, the density and viscosity were determined at the end of the experiments. The values for these properties in all samples after the application of proposed UAOD procedure were very close to the original values (agreement for the values after the treatment and the original value higher than 99%). It is important to mention that for practical purposes, the use of peroxyacid or ultrasound did not cause significant changes in these properties of diesel oil.

3.6. Reagents reuse

For the UAOD procedure proposed in this work the reagents reuse for fresh oil batches was also evaluated. In this sense, 25 mL of feedstock 2 was treated with the molar proportion for H_2O_2 :acetic acid:sulfur of 64:300:1 previously optimized, by ultrasound irradiation at $90\text{ }^\circ\text{C}$ (9 min, run at 40%). When the irradiation time was finished, phases were immediately separated. The efficiency on removal was about 95% for the first use of the reagents as previously observed. Then, the phase containing acetic acid and H_2O_2 , was used to react with another aliquot of 25 mL of fresh feedstock. After consecutive use, the removal was reduced to 75%, 65% and 50% for 2nd, 3rd and 4th cycles of treatment, respectively, always using the same reagents in aqueous phase. If a fresh portion of H_2O_2 was added in each cycle, the efficiency on sulfur removal was reduced in the same proportion and then it is not useful for improving the removal. However, this result suggests that the aqueous phase could be reused, as example, for up to four batches and a final step with a new oxidant mixture could be used to assure higher sulfur removal.

In order to reduce the extraction solvent consumption, it was also evaluated the use of the same portion of solvent for consecutive extractions steps. Two aliquots of 25 mL samples named as “a” and “b” from feedstock 2, were separately treated with the molar proportion for H_2O_2 :acetic acid:sulfur of 64:300:1. After ultra-

sound irradiation (9 min, run at 40%, at $90\text{ }^\circ\text{C}$), the oxidized oil “a” was extracted with 9 mL of methanol (sulfur removal about 95%). Then, the oxidized oil “b” was extracted, using the same portion of methanol previously used for oil “a”. The obtained results showed a reduction of sulfur removal when methanol was reused for extraction of the oxidized sulfur compounds in oil “b”. The sulfur removal for the oxidized oil “b” was about 85%. As observed for the aqueous phase, the result above suggests that sequential extractions steps could be applied with the same aliquot of solvent, using a fresh portion of solvent only in the first step of extraction.

4. Conclusions

The use of ultrasound irradiation combined with hydrogen peroxide and acetic acid for sulfur removal was studied in a batch laboratory system. Sulfur removal was almost 98% for feedstocks enriched with model sulfur compounds (DBT and 4,6-DMDBT) and at least 75% for diesel oil samples, which were better than those obtained without ultrasound. The UAOD procedure allowed a high efficiency for sulfur removal in less severe pressure and temperature conditions (atmospheric pressure and temperatures up of $90\text{ }^\circ\text{C}$) when compared to the conventional HDS processes. Moreover, metallic catalysts were not required in the proposed procedure to achieve high efficiency of sulfur removal. Based on the obtained results it could be possible to consider that the proposed UAOD procedure is useful for sulfur removal in diesel oil. It was possible to use smaller amounts of hydrogen peroxide, acetic acid and methanol for sulfur extraction and also to reduce the reaction time in comparison to the conventional procedures using oxidesulfurization reactions. Results obtained in this study for diesel oil samples showed that the use of ultrasound technology in the petroleum industry seems to be a promising alternative for sulfur removal.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.fuel.2011.01.030](https://doi.org/10.1016/j.fuel.2011.01.030).

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