**Evaluation of Nitrogen Effect on Ultrasound-Assisted Oxidative Desulfurization Process**

# Evaluation of nitrogen effect on ultrasound-assisted oxidative desulfurization process

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## Abstract

A novel procedure based on ultrasound-assisted oxidative desulfurization was applied for diesel oil treatment, which was performed simultaneously to ultrasound-assisted oxidative denitrogenation (UAODN) in order to minimize N interference over S oxidation. The effect of ultrasonic irradiation time, reagent amount and the nature of extraction solvent were evaluated. A petroleum product feedstock containing quinoline was used as a model nitrogen compound and acetic acid and hydrogen peroxide were used as oxidizing agents. Nitrogen removal above 95% was obtained for the model oil after 5 min of ultrasonic irradiation (20 kHz, 750 W, 40%). Additionally, this study showed that quinoline can reduce the oxidative desulfurization efficiency of an oil containing dibenzothiophene. The application of oxidative treatment without ultrasound showed that nitrogen and sulfur removal efficiencies for five diesel oil samples were considerably lower (lower than 22 and 40% for nitrogen and sulfur, respectively). The UAODN procedure was applied for the treatment of a hydrotreated petroleum product feedstock and samples of diesel oil with nitrogen and sulfur content up to 226 and 375 mg $kg^{-1}$, respectively. Under optimized conditions, nitrogen content below 20 mg $kg^{-1}$ was obtained and the feasibility of ultrasound for simultaneous denitrogenation and desulfurization was demonstrated.



## 1. Introduction

The production of diesel oil and other fuels with low levels of polluting compounds is required to meet fuel specifications and thus the removal of some contaminants such as sulfur, nitrogen, oxygen and metals is necessary [1,2]. Hydrodesulfurization (HDS) is currently the industrial refining process used for sulfur removal from petroleum fractions, and it generally occurs simultaneously with hydrodenitrogenation (HDN). In most cases, sulfur and nitrogen compounds are refractory to conventional HDS and HDN processes, and moreover the respective catalysts can be poisoned by nitrogen compounds. In order to overcome these drawbacks, usually the hydrotreatment process has been operated under severe conditions of pressure and temperature (generally from 20 to 100 bar and from 300 to 400 °C, respectively) [2]. Furthermore, pollution caused by $NO_x$ and $SO_x$ emissions has been a critical point to the environment [1,3,4].

Although hydroprocessing has been considered a very important step in petroleum refining industry, it requires expensive processes in cases of deep sulfur and nitrogen removals. In order to satisfy the legislation for commercial fuels, new emerging technologies have been developed and many works on sulfur removal procedures, such as biodesulfurization [5,6], extraction with ionic-liquids [7,8], and oxidative desulfurization (ODS) [9-12] have been reported.

The presence of nitrogen compounds is known to impair desulfurization activity, mainly due to competitive reactions of nitrogen com- pounds with hydrogen as well as nitrogen adsorption onto catalyst surface [13,14]. The inhibiting effect of nitrogen compounds such as quinoline, indole and carbazole on the hydrodesulfurization process has been observed even at nitrogen concentrations below 15 mg kg¬[15]. Due to this limitation, some non-conventional processes for nitrogen removal have been proposed, resulting in better efficiency. Some of these processes are based on the use of microbiological denitrogenation [16-18], ionic-liquids [19], selective adsorption [20,21] and oxidative denitrogenation (ODN) [22,23].

The oxidative process for desulfurization and denitrogenation is a promising methodology for high efficiency sulfur and nitrogen removal as it can be conducted at relatively low temperature and atmospheric pressure, and does not require hydrogen consumption. In this process, sulfur and nitrogen compounds can be oxidized by some reagents as hy- drogen peroxide/formic acid [3], hydrogen peroxide/acetic acid [24] or hydroperoxide/$MoO_3$-$Al_2O_3$ [23]. Due to the higher polarity, oxidized sulfur or nitrogen compounds can be removed by a liquid-liquid extrac- tion or adsorption step [22,25-27].

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The use of ultrasound (US) in chemistry can intensify chemical reac- tions due to several effects, especially those related to cavitation phenomenon [28-30]. Cavitation occurs when mechanical vibrations are generated and transmitted to a liquid medium, producing a series of compression and rarefaction cycles that may exceed the attractive forces of the molecules in the medium, producing cavitation bubbles. In some conditions, the collapse of bubbles in liquids provides a micro- environment with temperature and pressure up to 20,000 K and 1000 atm, respectively [31].

The feasibility of combining oxidizing conditions and US energy for sulfur removal has been proposed in some works [32-36]. However, in a similar way to conventional hydrodesulfurization process, the presence of nitrogen compounds decreases the efficiency of sulfur removal, and most of works do not evaluate the efficiency of ultrasound-assisted ODN, or even the effect of nitrogen in ODS processes.

In the present work, an ultrasound-assisted oxidative denitrogenation (UAODN) procedure using an oxidizing system based on hydrogen per- oxide and acetic acid is proposed for the oxidation of nitrogen and its re- moval from a petroleum product feedstock. The inhibiting effect of quinoline on the oxidative desulfurization of dibenzothiophene was also evaluated. Selected ultrasound-assisted oxidative desulfurization (UAODS) conditions were performed simultaneously to UAODN for the treatment of diesel oils with nitrogen concentration ranging from 86 to 226 mg $kg^{-1}$ and sulfur concentration ranging from 136 to 375 mg $kg^{-1}$. The effect of S:N molar ratio on UAODS was evaluated from 1:0.1 to 1:2, respectively.

## 2. Experimental

### 2.1. Apparatus

Ultrasonic treatment was performed using a 20 kHz and 750 W nominal power ultrasonic processor (Sonics and Materials Inc., Model VC 750, Newtown, USA) with a titanium ultrasonic probe (13 mm diam- eter, 254 mm long), which was dipped directly into the reaction mix- ture. Experiments were performed in a 250 mL three-neck conic glass reactor (Sonics and Materials, Inc.) with a glass jacket for temperature control using a circulating water bath (Model MCT 110 Plus, Servylab Ltda., São Leopoldo, Brazil). After US treatment, a glass separator funnel was used for the solvent extraction step. Comparative experiments without US were performed with a high speed mechanical stirrer (Model PT 3100 D, Polytron, Switzerland) using a stainless steel dispers- ing aggregate (20 mm of diameter) at 2000 rpm.

Analysis of reaction products after quinoline oxidation with acetic acid and $H_2O_2$ in toluene was performed using gas chromatography coupled to mass spectrometry (GC-MS, Agilent 6850/5973 Network). Chromatographic and detection conditions are shown in Table 1.

Total nitrogen and sulfur concentration in petroleum product feed- stock and diesel oil samples were determined using a total nitrogen and sulfur analyzer with chemiluminescence and fluorescence detectors (direct injection method, Antek Instruments, Model 9000 series nitrogen/sulfur analyzer, Texas, USA), according to ASTM D 4629-96 and D 5453-06 for nitrogen and sulfur determination, respectively [37,38].

A viscometer (Stabinger, Model SVM 3000, Anton Paar GmbH, Graz, Austria) was used for the determination of kinematic viscosity ($mm^2\ s^{-1}$) and density ($g\ cm^{-3}$) of samples before and after the treat-ment according to ASTM D 7042-04 method [39].

Table 1
Conditions used in GC-MS for quinoline and oxidative products analysis.

| Parameters | Conditions |
|---|---|
| Injector | |
| Temperature | 250 °C |
| Carrier gas flow rate (He) | 1.2 mL min¬ |
| Injection volume | 1 μL |
| Split/Splitless | 20:1 |
| Oven | |
| Initial temperature | 50 °C (3 min) |
| | 80 °C (3 °C $min^{-1}$) |
| Final temperature | 300 °C (10 °C $min^{-1}$, hold 10 min) |
| Detector | MS |
| Temperature | 280 °C |
| Column | HP-5MS (30 m × 0.25 mm × 0.25 μm) |

### 2.2. Reagents and materials

In the proposed UAODN procedure, 50% hydrogen peroxide ($H_2O_2$, Synth, Diadema, Brazil) and glacial acetic acid (AcOH, $C_2H_4O_2$, 1.05 kg $L^{-1}$, Vetec, Rio de Janeiro, Brazil) were used. Quinoline ($C_9H_7N$, 98%, Aldrich, St. Louis, USA) was used as a model nitrogen compound for the optimization of process parameters. A synthetic oil solution was then prepared by dissolving quinoline in a hydrotreated petroleum product feedstock, resulting in a solution with total nitrogen concentration of 252 mg $kg^{-1}$. In order to evaluate the effect of nitrogen content on desulfurization process, dibenzothiophene (DBT, $C_{12}H_8S$, ≥98%, Merck, Darmstadt, Germany) was used as model sulfur compound. Quinoline was added to a hydrotreated petroleum product feedstock (similar composition to diesel oil) containing 211 mg kg¬of sulfur (as dibenzothiophene), resulting in S:N molar ratios of 1:0.1, 1:0.3, 1:0.5, 1:1 and 1:2. The properties of the hydrotreated petroleum product feedstock employed in this study are shown in Table 2.

Toluene ($C_7H_8$, 0.87 kg $L^{-1}$), ethanol (EtOH, $C_2H_5OH$, 0.79 kg $L^{-1}$) and methanol (MeOH, $CH_3OH$, 0.79 kg $L^{-1}$) were purchased from Vetec. Reference solutions for sulfur and nitrogen determination in the oil phase were prepared by dissolving a white mineral oil (AccuStandard, Inc., 5000 mg $kg^{-1}$ sulfur content, New Haven, USA) and pyridine ($C_5H_4N$, ≥99.5%, Merck) in toluene. The ultrasonic probe and all the glass materials were cleaned with toluene, ethanol and deionized water.

### 2.3. Experimental procedures

For the initial experiments, UAODN conditions were similar to those previously optimized for diesel oil desulfurization [40]. In this way, 25 mL of quinoline enriched petroleum product feedstock were heated at 90 °C and sonicated for 9 min running at 40% amplitude with 2.5 mL glacial acetic acid and amounts of 50% $H_2O_2$ ranging from 0 to 1.0 mL. After selecting the $H_2O_2$ amount, the effect of glacial acetic acid volume (0 to 2.5 mL) was investigated for petroleum feedstock and for diesel oil samples (25 mL). Using the selected reagent amounts, reaction times of 1 to 9 min were investigated and US amplitude of 30 to 70% was evalu- ated. It is important to point out that all the experiments were carried out at atmospheric pressure (n = 3).

After US treatment, the separation of oil and aqueous phases was spontaneous (less than 1 min), and the oil phase was further extracted by manual shaking using a polar solvent (EtOH, MeOH or $H_2O$) and a glass separator funnel. Nitrogen and sulfur were determined in oil phase after the extraction step in order to evaluate the efficiency of the proposed procedure. Fig. 1 shows the overall procedure and the sequence of optimization performed.

In order to evaluate the quinoline oxidation after UAODN process, 25 mL of quinoline solution in toluene (150 mg $kg^{-1}$ as N), 5 mL of 50%

Table 2
Properties of hydrotreated petroleum product feedstock.

| Property | Feedstock (oil) | |
|---|---|---|
| Hydrogen content (%, w/w) | 13.6 | |
| Carbon content (%, w/w) | 86.4 | |
| Sulfur (original, mg $kg^{-1}$) | 3.6 | |
| Nitrogen (original, mg $kg^{-1}$)Density | ÷0.5 | |
| 20 °C/4 °C (g $cm^{-3}$) | 0.8362 | |
| Distillation temperature (initial b.p., °C) | 10% (v/v) | 266 |
| | 50% (v/v) | 328 |
| | 90% (v/v) | 361 |

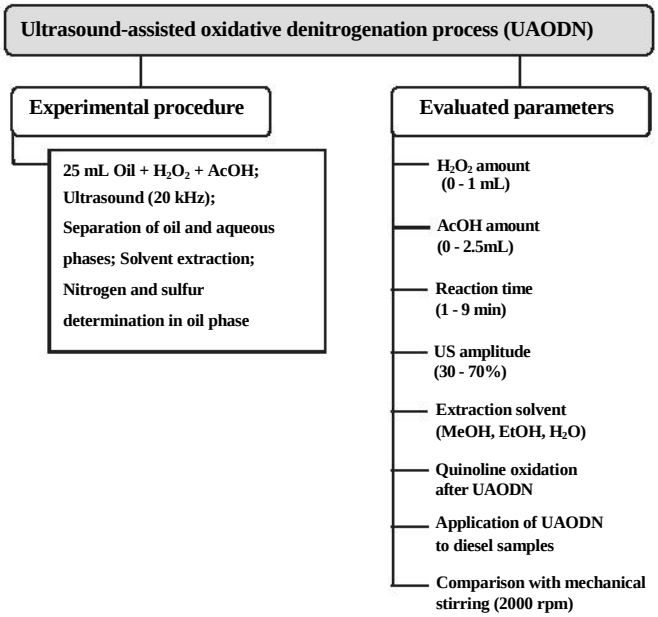


Fig. 1. Experimental conditions and evaluated parameters for UAODN process.

$H_2O_2$ and 15 mL of glacial acetic acid were treated at 80 °C for 9 min with magnetic stirring at 350 rpm. Final reaction medium presented two different phases in the reaction vessel. Toluene phase was washed with 15 mL of water and dried with anhydrous $Na_2SO_4$. After filtration, the organic phase was analyzed by GC-MS.

After optimization of UAODN conditions, the procedure was applied to the ultrasonic treatment of five diesel oil samples, named D1, D2, D3, D4 and D5, as shown in Table 3. In addition, experiments using optimized US conditions but with mechanical stirring (2000 rpm) were carried, and the effect of US over ODS and ODN efficiency was evaluated.

All statistical calculations were performed using GraphPad InStat software (GraphPad InStat Software Inc., Version 3.0, 1997). A 95% confidence level was adopted for all comparisons. Comparisons between two averages were performed using a Student-test, whereas the Tukey-Kramer test was used for comparison of three or more averages.

### 2.4. Energy consumption

The energy input to the reaction was determined by calorimetry, according to Kimura et al. [41]. This evaluation was performed with 25 mL of diesel oil 1, applying ultrasound at 20 kHz, set at 40% of amplitude, for 5 min. The temperature was monitored using a digital thermometer and the power (P) was determined according to the equation $P = m\,C_p\,dT$, where dT is the variation of temperature, $C_p$ is the specific heat of diesel oil 1 (2130 J $kg^{-1}$ $K^{-1}$), and m is the diesel oil mass (kg). The determined power (Joules) can be related to the sonication time (s), to give the power (watts) transferred to the solution. In addition, the power intensity (W $dm^{-3}$) [42] was also determined for the used ultrasonic system. According to the procedure described, the energy input for the treatment of 25 mL of diesel oil was about 10 W and the power intensity was 400 W $dm^{-3}$.

Table 3
Properties of diesel oil samples used in UAODN treatment.

| Samples[a] | Nitrogen concentration (mg $kg^{-1}$) | Sulfur concentration (mg $kg^{-1}$) | S:N molar ratio | Density (g $cm^{-3}$, 20 °C) | Viscosity ($mm^2$ $s^{-1}$, 40 °C) |
|---|---|---|---|---|---|
| D1 | 143 ± 3 | 136 ± 5 | 1:2.40 | 0.8681 | 3.9156 |
| D2 | 226 ± 4 | 249 ± 4 | 1:2.07 | 0.8672 | 4.1792 |
| D3 | 158 ± 4 | 226 ± 5 | 1:1.60 | 0.8682 | 4.3167 |
| D4 | 119 ± 5 | 319 ± 3 | 1:0.85 | 0.8510 | 2.7072 |
| D5 | 86 ± 1 | 375 ± 9 | 1:0.52 | 0.8484 | 2.3580 |

[a] Diesel oil samples obtained from petroleum refining process that had previously been hydrotreated by conventional process.

## 3. Results and discussion

### 3.1. Quinoline oxidation after UAODN process

A solution of quinoline in toluene (150 mg $kg^{-1}$ of N) was treated by reaction with acetic acid and $H_2O_2$ using US. After the oxidative step, the organic phase was treated for further analysis by GC-MS. An aliquot was analyzed in order to confirm the formation of ion m/z 145, corresponding to the oxidation of quinoline (m/z 129) to the N-oxide form. Fig. 2 shows that quinoline was oxidized, demonstrating the feasibility of using acetic acid and $H_2O_2$ to convert nitrogen compounds present in diesel oil to more polar molecules. No other oxidation product was observed and the mass spectrum was showed up to m/z 150 in order to facilitate viewing.

### 3.2. Effect of $H_2O_2$ volume on nitrogen removal

Quinoline was selected for the evaluation of UAODN proposed process because this compound that naturally occurs in crude oils is normally present also in related fuels [4,22,43]. A hydrogenated petroleum product feedstock containing 252 mg $kg^{-1}$ of total nitrogen (as quinoline) was treated by ultrasound-assisted reaction with acetic acid and hydrogen peroxide, similarly to a previous work [32].

In this study, 25 mL of petroleum product feedstock and 2.5 mL of acetic acid were mixed with a variable volume of 50% $H_2O_2$ (ranging from 0 to 1 mL). Ultrasound amplitude was set at 40% and US was applied during 9 min keeping the reaction mixture at controlled temperature (90 °C). At the end of this step, the petroleum product feedstock and AcOH/$H_2O_2$ phases were spontaneously separated. The oil phase was extracted three times (3 mL each) using MeOH by manual shaking [40]. After US treatment and extraction step, nitrogen concentration was determined in oil phase and the results are shown in Fig. 3.

When hydrogen peroxide was not used, 92% of nitrogen removal was achieved (Fig. 3). This result can be explained by the extraction of nitrogen compounds by acetic acid during sonication and/or by methanol in liquid-liquid extraction step since no oxidizing agent was used for the reaction. When 0.1 mL of $H_2O_2$ was used, a small increase in nitrogen removal efficiency (95%) was observed. For $H_2O_2$ volumes higher than 0.25 mL, no significant improvement was observed (ANOVA, $p > 0.05$) and nitrogen removal did not exceed 97%. In spite of quinoline being extracted by acetic acid and methanol not requiring the use of $H_2O_2$, it is still necessary to achieve better ODS efficiency, as shown in previous works [32,34,44]. In addition, it can contribute to oxidize other nitrogen compounds which are not soluble in solvent phase and have to be converted to N-oxidized compounds before the extraction from oil. In this way, the amount of $H_2O_2$ was kept at 0.25 mL for further experiments.

### 3.3. Effect of acetic acid volume on nitrogen removal

Oxidation experiments were carried out in a combined system using 25 mL of hydrotreated petroleum product feedstock containing 252 mg $kg^{-1}$ of nitrogen, 0.25 mL of 50% $H_2O_2$ and volume of acetic acid ranging from 0 to 2.5 mL. The oxidative reaction system was kept at 90 °C and 9 min of US irradiation was applied (set at 40% of

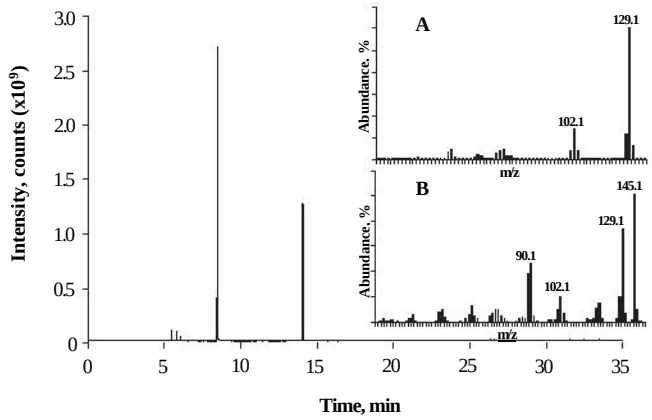


Fig. 2. Chromatogram of quinoline solution after oxidation and the mass spectrum of the peak in 8.49 min (quinoline, A) and in 14.04 min (N-oxide, B).

amplitude). At the end of reaction, oil and aqueous phases were separat- ed and the oil phase was extracted three times (3 mL each) using MeOH. To evaluate the effect of acetic acid in the oxidizing mixture, an experi- ment without acetic acid was also performed. The effect of acetic acid on denitrogenation efficiency is shown in Fig. 4.

Nitrogen removal higher than 95% was obtained using 2 mL of glacial acetic acid. The use of higher volumes resulted in slightly better nitro- gen removal. However, it is important to point out that the use of 2.5 mL of acetic acid did not result in significant improvement in UAODN efficiency. No statistical difference was observed in the experi- ments using 2 or 2.5 mL acetic acid and, therefore, acetic acid volumes higher than 2 mL were considered unnecessary.

It is important to emphasize that the effect of the carboxylic acid on nitrogen removal is more pronounced than $H_2O_2$, as can be observed in experiments without $H_2O_2$ (Fig. 3) and without acetic acid (Fig. 4). For the reactions where only acetic acid and 25 mL of diesel oil were used, nitrogen removal higher than 92% was achieved, while less than 88% was removed when using only $H_2O_2$. Higher efficiency using only acetic acid can be associated to its extractive effect over nitrogen compounds, which may be more pronounced than those presented by $H_2O_2$. In addition, it is important to point out that a pronounced extractive effect was also observed for methanol, which was able to extract about 79% of nitrogen by applying a liquid-liquid extraction step direct- ly to the oil (without UAODN treatment). This extractive effect of nitrogen compounds can be an important contribution to oxidative desulfurization once nitrogen can be removed by extraction and thus, oxidative reagents would be available to react with sulfur compounds.

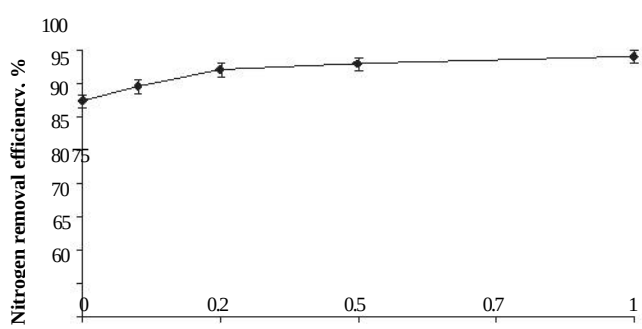


Fig. 3. Effect of the volume of 50% $H_2O_2$ on nitrogen removal from petroleum product feed- stock (25 mL of oil containing 252 mg kg$^{-1}$ of N as quinoline and 2.5 mL of acetic acid, 9 min of US 20 kHz, set at 40%, extraction with MeOH; error bars represent the standard deviation, n = 3).

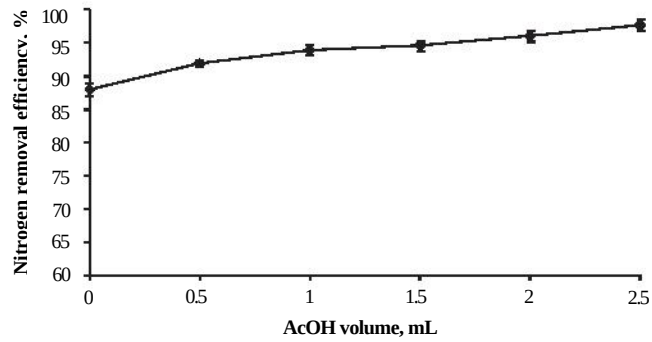


Fig. 4. Influence of acetic acid volume on N removal from petroleum product feed- stock (25 mL of oil containing 252 mg kg$^{-1}$ of nitrogen as quinoline and 0.25 mL of 50% $H_2O_2$, US 20 kHz, set at 40%, extraction with MeOH; error bars represent the standard de- viation, n = 3).

### 3.4. Study of ultrasonic irradiation time and amplitude

Regarding the reduction of the UAODN process time, several exper- iments containing 25 mL oil, 2 mL acetic acid and 0.25 mL of 50% $H_2O_2$ were performed with reaction times ranging from 1 to 9 min in a system heated at 90 °C. The extraction step after oxidation reaction was per- formed with MeOH and the obtained results are shown in Fig. 5.

It is possible to observe that nitrogen removal efficiency up to 93% was obtained under only 1 min of sonication. However, after 5 min of US, nitrogen removal was 97% and no significant improvement was ob- tained for longer sonication times. In this sense, the time of 5 min was selected for further experiments.

Ultrasonic amplitudes of 30 to 70% were evaluated in a series of 5 min sonication experiments at 90 °C under optimized conditions (2 mL of acetic acid and 0.25 mL of 50% $H_2O_2$ for the treatment of 25 mL of diesel oil). No statistical difference in nitrogen removal was observed for evaluated amplitudes (ANOVA, $p > 0.05$) and a denitrogenation efficiency of at least 95% was obtained. Therefore, am- plitude of 40% was selected for subsequent experiments, as it was previ- ously observed to be more efficient for sulfur removal [32,40].

### 3.5. Extraction step

Some works have reported the hydroxylation of both quinoline rings after the oxitreatment of diesel oil containing quinoline. The presence of these hydroxyl groups increases polarity, enabling the use of alternative nitrogen removal methods such as adsorption and solvent based extrac- tion. It is important to point out that the solvent in liquid-liquid oil extraction must present high polarity and be insoluble in fuel matrix [3,25]. Therefore, methanol, ethanol and water were evaluated as sol- vent in the extraction step. A solvent:diesel oil ratio of 0.36 was chosen based on preliminary results using ultrasound-assisted oxidative

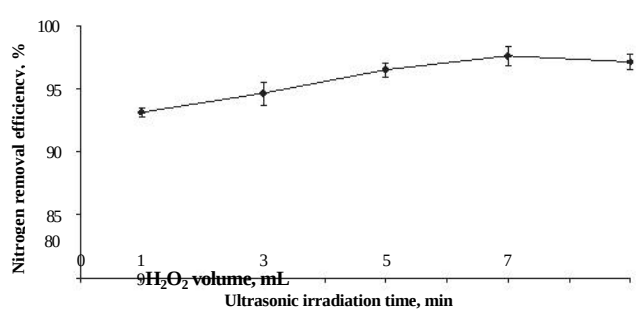


Fig. 5. Influence of US irradiation time on N removal (25 mL of oil containing 252 mg kg$^{-1}$ of N as quinoline, 2 mL of acetic acid, 0.25 mL of 50% $H_2O_2$ solution, US 20 kHz, set at 40%, extraction with MeOH; error bars represent the standard deviation, n = 3).

process with further liquid-liquid extraction [40]. Thus, experiments were performed with 25 mL of diesel oil enriched with quinoline, following the experimental conditions previously optimized.

Using ethanol, the denitrogenation efficiency was 91.6 ± 2.5% (n = 3), but a partial solubility of this solvent in diesel oil after the extraction step (ca. 5% in mass) was observed, making ethanol useless for this purpose. Nitrogen removal of 95.5 ± 1.1% was obtained using methanol and a similar efficiency (96.4 ± 1.9%) was observed when water was used as the extraction solvent. In order to avoid the addition of water to petroleum derivatives after the refining process, and considering that methanol is more efficient than water to extract oxidized sulfur compounds [32], methanol was chosen to perform the extraction after the oxidative denitrogenation process as well as for subsequent experiments. It is important to mention that due to the wide number of nitrogen and sulfur compounds in fuels, the characteristics of oxidized compounds may require a change in solvent. In this way, it would be necessary to evaluate the ideal solvent for each organonitrogen and/or organo-sulfur class when this process is applied to other structures [45].

### 3.6. Effect of quinoline on the oxidative desulfurization of dibenzothiophene

Although the concentration of nitrogen compounds is usually lower than sulfur compounds, it has been reported that the presence of nitrogen even in relatively low concentration can decrease desulfurization activity in fuels [15,46]. According to Caero et al. [13], quinoline was reported to have higher inhibitory effect on oxidative desulfurization activity when compared with indole and carbazole. In order to evaluate the effect of quinoline on UAODS process, a hydrotreated petroleum product feedstock containing 211 mg $kg^{-1}$ of sulfur was prepared by using dibenzothiophene as model compound. This solution was enriched with different amounts of quinoline as the nitrogen source, resulting in S:N molar ratios of 1:0.1; 1:0.3; 1:0.5; 1:1 and 1:2. Reactions were performed during 9 min of US, 2 mL of acetic acid, 0.25 mL of 50% $H_2O_2$ at 90 °C and 40% of amplitude. The effect of nitrogen (as quinoline) on sulfur removal is shown in Fig. 6.

Sulfur removal was 96% when nitrogen was virtually absent in the evaluated feedstock (data not shown in Fig. 6). In this sense, considering the results presented in Fig. 6, it can be concluded that quinoline presents an adverse impact on sulfur removal even at a S:N molar ratio of 1:0.1. This ratio corresponds to a nitrogen concentration of 9.2 mg $kg^{-1}$, and its impact is more adverse as nitrogen content increases. Similar nitrogen compound effects on the desulfurization of diesel oil feedstock [15] on a model fuel sample [46] were observed for both hydrodesulfurization and catalytic oxidative processes. Nitrogen removal was always close to 100% while sulfur removal gradually decreased at lower S:N molar ratios. For this reason, it was possible to consider that nitrogen compounds are more prone to be removed from diesel oil than sulfur compounds, considering the same oxidative conditions. In addition, the extractive effect of acetic acid and methanol also contributes for higher nitrogen removal efficiency, minimizing the effect of nitrogen over sulfur removal efficiency.

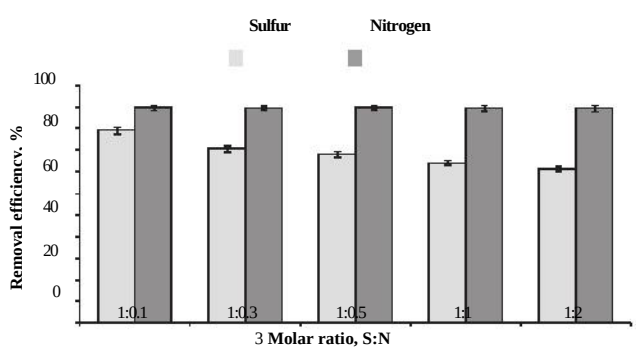


Fig. 6. Effect of quinoline content on the UAOD process for dibenzothiophene removal at different S:N molar ratios in model oil (25 mL of oil containing 211 mg $kg^{-1}$ of sulfur as dibenzothiophene, 2 mL of acetic acid, 0.25 mL of 50% $H_2O_2$ solution, US 20 kHz, set at 40%, extraction with MeOH; error bars represent the standard deviation, n = 3).

### 3.7. Application of UAODN procedure in petroleum derivatives

Once UAODN parameters were optimized, the application of proposed procedure was carried out for nitrogen removal in five diesel oil samples (D1, D2, D3, D4 and D5) using 25 mL diesel oil, 2.0 mL acetic acid, 0.25 mL 50% $H_2O_2$, 90 °C, ultrasound 20 kHz, set at 40% of amplitude during 5 min, and extraction with 3 × 3 mL of MeOH. Nitrogen and sulfur removal efficiencies were also determined for a reaction time of 9 min [40]. At the same time, the effect of nitrogen on sulfur removal was observed for diesel oil samples with S:N molar ratios of 1:2.40 (D1), 1:2.07 (D2), 1:1.60 (D3), 1:0.85 (D4), and 1:0.52 (D5). It is important to point out that the experiments without US (mechanical stirring, 2000 rpm) were performed at the same time (9 min). Results obtained for nitrogen and sulfur removal in diesel oil samples are shown in Fig. 7.

According to the results presented in Fig. 7, higher nitrogen and sulfur removal was observed using 9 min of reaction when compared to 5 min of US treatment. In addition, denitrogenation efficiency was considerably affected when US was substituted by mechanical stirring. Nitrogen content remaining in diesel oil after oxidative treatment with mechanical stirring was about twice when compared to US treatment by 9 min (correspondent to an additional improvement in N removal from 15 to 22% using US by 9 min). In a similar way, the desulfurization efficiency using US was higher for 9 min when compared to 5 min, and the use of mechanical stirring resulted in significant efficiency decrease (from 20 to 40% less efficient using mechanical stirring when compared to 9 min using US). In general, the effect of US on oxidative desulfurization is more remarkable than that observed for oxidative denitrogenation.

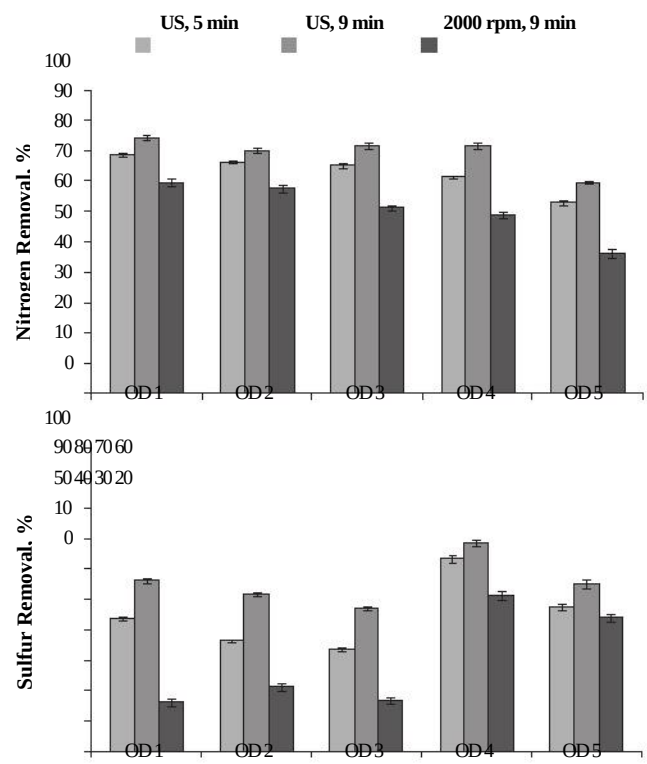


Fig. 7. Effect of US and mechanical stirring on nitrogen and sulfur removal from diesel oil samples (25 mL of oil, 2 mL of acetic acid, 0.25 mL of 50% $H_2O_2$ solution, US 20 kHz, set at 40%; or 2000 rpm, extraction with MeOH; error bars represent the standard deviation, n = 3).

Table 4
Diesel oil characterization after UAODN process. Values in brackets correspond to the variation of density or viscosity in relation to the original values.

| Diesel oil | Density (g cm$^{-3}$,20 °C) | Viscosity (mm$^2$ s$^{-1}$,40 °C) |
|---|---|---|
| D1 | 0.8634 (+0.5%) | 3.8997 (+0.4%) |
| D2 | 0.8623 (+0.6%) | 4.2140 (−0.8%) |
| D3 | 0.8628 (+0.6%) | 4.2802 (+0.8%) |
| D4 | 0.8492 (+0.2%) | 2.7150 (−0.3%) |
| D5 | 0.8451 (+0.4%) | 2.4279 (−1.0%) |

Considering the results obtained for all diesel oil samples, the information about the S:N molar ratio can be suitable to estimate the efficiency of an oxidative treatment under US. However, nitrogen and sulfur contents in diesel oil are associated to a wide variety of com- pounds, which are related to have variable reactivity and solubility in organic solvents used for liquid-liquid extraction, besides the presence of alkyl substituent, mainly derived from sulfur compounds [24]. Thus, in order to identify these sulfur compounds in diesel oil, samples were analyzed by gas chromatography with pulsed flame photometric detector (GC-PFPD). Table S1 and Figs. S1 to S6 (please, see in Supporting Information Section) illustrate chromatographic conditions and the GC- PFPD chromatograms for standard solution (Fig. S1) and original diesel oil samples (Figs. S2 to S6). In addition, chromatograms in Figs. S7 to S11 show the profile of sulfur compounds remaining in samples after the ultrasound-assisted oxidative treatment.

Although the nitrogen content remaining in treated diesel oil sam- ples was higher than 9.2 mg kg$^{-1}$, which was observed to have a nega- tive effect on sulfur removal process, the proposed UAODN procedure can be applied successfully as a complement to the HDS process. It could be also considered as an alternative way to reduce the nitrogen content in diesel oil, allowing sulfur removal to be carried out at higher efficiency and using relatively milder conditions.

Some works have reported that no effect is observed on the general properties of fuel samples treated by oxidative desulfurization process, such as distillation curves, density and others [44,47]. Therefore, in order to evaluate possible changes in diesel oil characteristics, density and dynamic viscosity were determined before and after the proposed UAODN procedure (Table 4). It is possible to observe in Table 4 that die- sel oil density and viscosity were very similar to original values (see Table 3) after the UAODN process, which indicates that these character- istics were not affected by ultrasound-assisted oxidative treatment. In addition, diesel oil recovery after oxidation under US and extraction with methanol was 96%, but it is important to point out that an oil recovery significantly better should be obtained with the scale up of the proposed process.

The characteristics of the UAODN process are summarized in Table 5 and compared to other process proposed for nitrogen removal from liquid fuel via oxidative denitrogenation. It is important to mention that if the procedure using $H_2O_2$ and acetic acid is carried out in the absence of US, lower sulfur removal is obtained, as previously described [40]. According to these data, the use of US to promote simultaneous denitrogenation and desulfurization efficiency in a shorter time is evidenced, demonstrating the use of this technology as a promising tool for process improvement.

## 4. Conclusions

It was found that the combination of acetic acid and $H_2O_2$ can pro- mote an efficient ultrasound-assisted oxidative desulfurization, even for diesel oils with relatively high concentration of nitrogen. Effectiveness of nitrogen removal was higher than those presented for sulfur removal efficiency using the same oxidative conditions. It can be associated to the higher solubility of nitrogen compounds in acetic acid and methanol, either in original or oxidized forms. As previously re- ported, the ultrasound-assisted oxidative procedure is a promising way of removing sulfur and nitrogen from petroleum derivatives, but the reactivity of nitrogen and sulfur molecules was not the same under specific oxidative conditions. The inhibiting effect of quinoline on dibenzothiophene oxidation under acetic acid/$H_2O_2$ and US irradiation was observed at nitrogen concentrations of as low as 9.2 mg kg$^{-1}$, corresponding to a S:N molar ratio of 1:0.1. In spite of Brazilian fuel regula- tions to establish only sulfur maximum content present in diesel oil, it is important to consider that the proposed procedure allowed an efficient and simultaneous sulfur and nitrogen removal, which was performed free of interference as well as the application of extreme conditions. Ad- ditionally, the comparison between US and mechanical stirring showed the remarkable effect of ultrasonic energy in reaction medium, promot- ing better interaction of immiscible liquids and higher oxidation rates of nitrogen and sulfur compounds. In this way, ultrasound-assisted oxida- tive process for sulfur and nitrogen removal may be proposed as a com- plementary step to hydrogenation, as well as pre-treatment for hydrocracking and fluid catalytic cracking, since the major part of nitrogen is removed in the same step. Finally, the application of optimized conditions to diesel oil samples allowed high sulfur and nitrogen re- moval (up to 69 and 84% for 9 min of reaction, respectively) to be attained while not affecting other diesel properties as density, viscosity and distillation temperature.

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Table 5
Oxidative processes proposed for denitrogenation of fuel oils.

| Oxidizing mixture | Sample and nitrogen content | Characteristics | Reference |
|---|---|---|---|
| Acetic acid and hydrogen peroxide | Model quinoline solution and 5 hydrotreated diesel oils with nitrogen content between 86 and 226 mg kg$^{-1}$ | 25 mL of oil, 2.0 mL acetic acid and 0.25 mL $H_2O_2$. Reaction time of 9 min at 90 °C with US (20 kHz). Extraction with 3 × 3 mL of methanol. Nitrogen removal was from 69 to 84%. | This work |
| Limonite ore, hydrogen peroxide and formic acid | Quinoline in water (10 mg L$^{-1}$) | 10 mL of quinoline solution, 10 mg of limonite ore and equimolar amounts (97 mmol) of $H_2O_2$ and formic acid. Reaction time of 360 min under magnetic stirring at 25 °C. Quinoline removal was 90%. | [3] |
| Tert-butyl hydroperoxide and $MoO_3/Al_2O_3$ as catalyst | Indole, quinoline, acridine and carbazole (20 mg kg$^{-1}$ of N in decalin); light gas oil (13.5 mg kg$^{-1}$ of N) | Flow reaction in a stainless steel tube with 1 mL of catalyst and a reactor with 20 mL of silica gel. Reaction time 3 h at 80 °C. The O:S molar ratio was 15:1 and nitrogen removal was about 94%. | [25] |
| Acetic acid and hydrogen peroxide | Aniline, indole and carbazole (20 mmol L$^{-1}$ in xylene); commercial light oil (CLO, 80.4 mg kg$^{-1}$ of N), straight-run light gas oil (LGO, 160 mg kg$^{-1}$ of N) and light cycle oil (LCO, 243.1 mg kg$^{-1}$ of N) | 50 mL of oil, $H_2O_2$ and acetic acid using a S:$H_2O_2$:Acetic acid molar ratio of 1:1000:500. Reaction time of 30 h at 70 °C. Extraction with 50 mL of water and 50 mL of acetonitrile/ water (84/16 v/v). Nitrogen removal of 58.2% (CLO), 43.7% (LGO) and 62.1% (LCO) was obtained. | [26] |

## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2014.05.031.

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