SULFUR AND NITROGEN REMOVAL FROM HYDROTREATED PETROLEUM FRACTIONS USING SOLID OXIDANTS AND ULTRASOUND

Claudio G. Herbst Jr[1] (PG), **Alice P. Holkem[1] (IC), Ubiratan F. Silva[1] (PQ), Edson I. Müller[1] (PQ), Érico M. M. Flores[1] (PQ), Paola A. Mello[1] (PQ)***

[1]*Departamento de Química, Universidade Federal de Santa Maria*

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Introduction

The presence of sulfur and nitrogen compounds in fuels contributes to environmental polution, through the release of SOx, NOx and particulate matter. Recently, many countries have introduced more stringent regulations in order to reduce the amount of sulfur in fuels to very low levels (10 mg kg^{-1}). Most organosulfur compounds are removed from fuel by hydrotreatment process (HDT), which requires high temperature (300-400 °C) and high hydrogen pressure (20-100 bar) over metallic catalysts. As an alternative to the hydrotreatment process, oxidative desulfurization has been investigated as a process of removing sulfur and nitrogen compounds in fuels by using milder conditions.[1] In addition, oxidative desulfurization can be assisted by ultrasound which can allows high efficiency for removal of refractory compounds. According to the literature, the peracetic acid generated in situ by H_2O_2 in acetic acid has given excellent results. However, the instability of peracetic species and its corrosive nature are critical to large-scale applications.[1] Oxone, a triple potassium salt ($2KHSO_5$, $KHSO_4$ and K_2SO_4) is a versatile alternative due to its stability and oxidation power to sulfoxidation reactions. In this study, operational parameters of ultrasound-assisted oxidative desulfurization (UAOD) using Oxone was investigated.

Results and Discussion

Diesel oil and gasoil samples were evaluated in this work. Physical and chemical properties of these petroleum fractions are described in Table 1.

Table 1: Physical and chemical properties of petroleum fractions.

	Diesel oil	Gasoil
Sulfur concentration, mg kg^{-1}	226 ± 5	5351 ± 136
Nitrogen concentration, mg kg^{-1}	158 ± 4	2694 ± 90
Density at 20 °C, g cm^{-3}	0.8682	0.8767
Kinematic viscosity at 40 °C, mm^{2}s^{-1}	4.3167	3.8552

Conditions for UAOD using Oxone were optimized and compared to the use of peracetic acid generated *in situ* using acetic acid and H_2O_2. Parameters were evaluated, such as the proportion of the diesel the Oxone system and 1:5:100 to 1:30:600 (S+N:H_2O_2:acetic acid) for the acetic acid/hydrogen peroxide system, as well as temperature (30 to 80 °C) and ultrasound irradiation time (10 to 60 min). All the experiments were carried out at atmospheric pressure. Experiments using the UAOD procedure were performed using an ultrasonic processor manufactured by Sonics and Materials, Inc. (Model VCX 1500, 20 kHz and 1500 W of nominal power, USA). For all experiments an ultrasonic probe (1 in., full wave titanium probe solid, 254 mm long, Order Number 630-0609) was dipped directly into the oil/reagents mixture. Experiments were performed in a stainless steel reactor (Sonics and Materials, Inc., Order Number 630-0583) with temperature control (Servylab, Model MCT 100 Plus, 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 PT3100D, Kinematica AG, Switzerland). Total sulfur and nitrogen concentration in oil phase was determined using an elemental analyzer (Multi EA®5000, Analytik Jena, Germany) by fluorescence detection and chemiluminescence, respectively, following international standards (ASTM, D5453 and D4629), by direct injection method. After ultrasound treatment, the phase separation was spontaneously achieved in less than 1 min. The treated oil phase was extracted with 25 mL of methanol, using a glass separator funnel with manual and constant shaking. 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. Results showed that at higher temperatures (80 °C) and time (60 min) the efficiency of sulfur and nitrogen removal was higher than 38% and 74%, respectively, for all evaluated samples when Oxone was used.

Conclusion

The use of UAOD for removal of sulfur and nitrogen compounds in batch system, allowed efficiency of 38% in the removal of S and 74% for the removal of N, using Oxone. The application of ultrasonic irradiation allowed sulfur and nitrogen removal in shorter time than the procedure without ultrasound irradiation (using mechanical stirring), under the same conditions. Other parameters in fuel, such as density, viscosity, acid number and water content were not changed by using the proposed process.

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[1]Carnaroglio, D.; Gaudino, E. C.; Mantegna, S.; Moreira, E. M.; Castro, A. V.; Flores, E. M. M.; Cravotto, G. *Energy Fuels* **2014**, 28, 1854-1859.