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Ultrasound assisted oxidative desulfurization of model diesel fuel

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ABSTRACT

Very stringent environmental regulations have limited the level of sulfur in diesel, therefore deep desulfurization of fuels is required. For that purpose, the frequently used industrial process is hydrodesulfurization (HDS) which enables effective elimination of sulfur compounds such as mercaptanes, thiols, sulfides, disulfides from diesel oil, but removal of thiophene sulfur compounds (benzothiophene, dibenzothiophene, 4,6 dimethyldibenzothiophene) is insufficient. Ultrasound assisted oxidative desulfurization (UAOD) as one of several new technologies enables performance under mild conditions without use of explosive hydrogen. A higher reactivity of thiophene sulfur compounds during UAOD also provides conversion into highly polar sulfoxides and sulfones that are easily removed by adsorption or extraction. Nowadays, different catalyst/oxidants systems are being studied to improve oxidation reaction efficiency and enhance the mass transfer in the interfacial region. In this paper, the effect of reaction temperature (40–70 °C) and oxidation time (5–150 min) for UAOD of model diesel fuel with a catalyst/oxidants system (acetic acid/hydrogen peroxide) was investigated in a 70 ml batch reactor. Furthermore, the effects of different initial concentrations of dibenzothiophene (DBT) and of ultrasound amplitude were additionally examined to achieve efficient sulfur removal. The obtained results indicated that temperature and US amplitude of 70 °C and 80% respectively were efficient for conversion of DBT (sulfur concentration up to 3976.86 ppm). The results indicate a rise in the yield of sulfones at higher temperatures and subsequent extraction with *N,N*-dimethylformamide conducted after the process of oxidation at different solvent/oil ratio revealed sulfur removal efficiency of 98.35%.

1. Introduction

Diesel fuels are complex mixtures of alkanes, cycloalkanes, and hydrocarbons with a carbon number range of C_9–C_{28} and with a boiling range of 150–390 °C [1]. The latest environmental regulations limited the level of sulfur in diesel to 15 μg/g since 2006 in US, less than 10 μg/g in EU, and less than 50 μg/g since 2008 in Beijing and Shanghai in China [2,3]. A traditional or conventional method for removing sulfur from fuel involves hydrodesulfurization (HDS) which is presently the most used industrial process, however for the efficient removal of thiophene sulfur compounds high pressure, high temperature, as well as hydrogen plants and sulfur recovery units are necessary. Moreover, recalcitrant aromatic sulfur compounds cannot be removed due to their low reactivity [4]. Among unconventional desulfurization technologies, the ultrasound assisted oxidative desulfurization (UAOD) is a new technology that has several advantages over the HDS. The UAOD can be performed under mild conditions, atmospheric pressure and temperatures below 100 °C, without hydrogen and the UAOD enables conversion of aromatic compounds (thiophenic compounds) into sulfoxides and sulfones. The application of ultrasound (US) was investigated in the area of petroleum processes metering, the desulfurization effect [5] and the role of cavitation for different application of US was elucidated [6]. Furthermore, sonochemical treatment has been found to be one of successful technologies for different processes due to strong cavitational activity [7]. The beneficial effects of ultrasound are well known, it can enhance the mass transfer in heterogeneous systems and can improve kinetics, the enhancement in the reaction rates and the rates of the mass transfer due to ultrasound may be attributed to its chemical or mechanical effects or to both simultaneously, meaning that the implosion of microbubbles, i.e. cavities, results in desirable chemical effects by generation of free radicals with a great propensity for the reaction [8,9].

Recently, several oxidation systems [3,4] have been studied and hydrogen peroxide has been considered as a powerful oxidant of

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sulfur compounds [10]. The effect of H_2O_2 in combination with other catalysts during oxidative desulfurization has been investigated [11–13]. Generally, the reaction of thiophenic sulfur compounds with peroxyacid, generated in situ by the reaction of hydrogen peroxide and appropriate carboxylic acid, is an oxidation reaction that results in formation of sulfoxides and sulfones [10,14,15]. The resulting oxidized compounds are substantially highly polar than the respective thiophenic sulfur compound and a solvent extraction step may be a convenient way to remove sulfoxides and sulfones from the oil phase and to fulfil strict regulations for sulfur content in diesel fuels. Namely, the combination of oxidation and separation processes is fundamental for the development of an alternative desulfurization process, due to the similarity of sulfur and carbon properties (i.e. electronegativity) [1]. The advantage of the separation of oxidized versus non oxidized thiophenic compounds is reflected in the higher selectivity of carbon sulfur compounds. A sulfur–carbon bond is relatively non-polar and compounds that contain sulfur exhibit properties very similar to their corresponding organic compound (thiophenic compounds) [1]. Therefore, the removal of thiophenic compounds has recently gained more attention in sulfur removal related studies [10,12–14].

In this work, the effect of reaction temperature (40–70 °C) on the conversion of DBT was investigated during the UAOD with hydrogen peroxide/acetic acid, in a 70 ml batch reactor. Furthermore, the oxidation time of model diesel fuel during UAOD was compared to the oxidative desulfurization (ODS) conducted with a mechanical stirrer. The efficiency of the UAOD process of model diesel fuel was investigated at different initial content of DBT and at different ultrasound (US) amplitudes. Additionally, during extraction of oxidized sulfur compounds with *N*,*N*-dimethylformamide, the effect of solvent/oil ratio was investigated.

2. Material and methods

2.1. Materials

The model solution of diesel fuel contained dibenzothiophene (2.5 wt.%), n-heptane (39 wt.%), n-dodecane (28.5 wt.%) and n-hexadecane (30 wt.%). All chemicals were of analytical grade (Sigma Aldrich, Germany). The oxidizing agent, the catalyst and the extraction solvent were hydrogen peroxide (30%), acetic acid (99%) and *N*,*N*-dimethylformamide (99.9%) respectively (Biovit, Croatia).

2.2. The UAOD equipment

The UAOD was conducted in a laboratory reactor system containing a ceramic heater, 70 ml glass reactor, mechanical stirrer and an ultrasound generator. The temperature, mixing speed or ultrasound power and time of reaction were monitored and regulated through PC software as depicted in Fig. 1.

The model diesel solution was mixed with a mechanical stirrer during 1–2 min and after the achievement of a homogeneous solution, 1 μl sample was taken from the model solution for analysis and the catalyst and oxidizing agent (10 ml) were added to initiate the oxidation reaction. The ultrasound converter (20 kHz) and ultrasound generator (70 W) were used for the UAOD process conducted at selected temperature (40–70 °C) and the experiments were conducted at a power amplitude ranging from 40% to 80%. The tests without US were performed with the use of a mechanical stirrer at 2000 rpm for the comparison of sulfur removal efficiency. During the course of experiments, 0.1 ml sample of the reaction mixture was withdrawn with a syringe from the reactor every

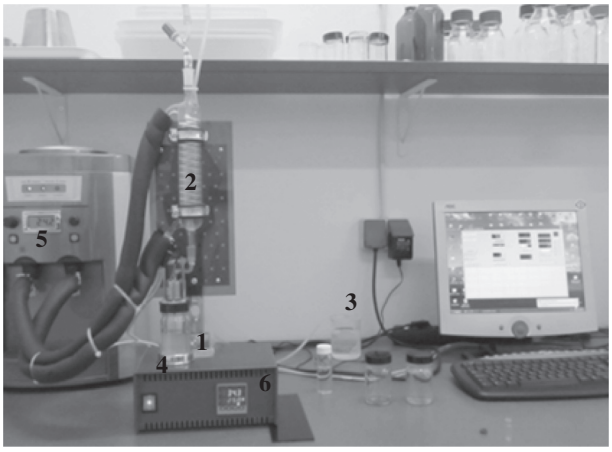

Fig. 1. Schematic diagram of an oxidative desulfurization unit: 1 – reactor with temperature sensor, mechanical stirrer, heater and sample tube; 2 – Liebig condenser; 3 – waste collector; 4 – ultrasound converter, 20 kHz with ultrasound generator 70 W; 5 – cooler; 6 – controller.

5 min during 30 min of the UAOD and every 30 min during 180 min of the ODS. At the end of oxidation (after 30 and 180 min) the resulting crystals were filtered and the oil phase was separated from the aqueous phase. Laboratory scale extraction of the oil phase with *N*,*N*-dimethylformamide (DMF) was carried out in a glass separator with mechanical stirring at 1000 rpm and at room temperature during 25 min.

2.3. Analysis

The analyses of the oil phase products during experiments were carried out by gas chromatography (GC 2014 Shimadzu, Japan), equipped with a (ZB-1 Phenomenex) capillary column (length 30 m, internal diameter 0.53 mm, film thickness 1.50 μm) and a flame ionization detector. Nitrogen gas was used as a carrier gas for all analysis. The column was programmed to be heated from 100 °C to 300 °C within 17 min. At the beginning, the temperature gradually increased from 100 to 250 °C (7.5 min), maintained at 250 °C (for 4 min), then heated again from 250 to 300 °C (2 min) and maintained at 300 °C for 1 min. Previously to the experimental analyses, the calibration procedure was performed with a model DBT solution and the observed results were obtained after triplicate measurements.

The conversion of dibenzothiophene was calculated on the basis of equation:

$$\%\text{conversion of DBT} = \frac{\text{DBT in feed} - \text{DBT in product}}{\text{DBT in feed}} \times 100 \quad (1)$$

3. Results and discussion

The ultrasound assisted oxidative desulfurization (UAOD) was investigated at different working temperatures to reduce sulfur compounds from model diesel fuel and to determine the optimal temperature for the UAOD performance (Fig. 2).

Literature review indicated that optimal temperature ranged between 6 and 90 °C [16–18] and the observed results clearly indicated that the increase of working temperature led to the increase of DBT conversion. According to literature, the velocity and temperature ratios play a key role in determining propagation characteristics of the sound waves in suspensions [5,19]. The beneficial effect of temperature can be seen from Fig. 2. The DBT conversion ranged from 31% observed at 40 °C to 87% observed at 70 °C. Furthermore, a significant increase of DBT conversion was noticed