

Oxidative Desulphurization of Diesel Fuels

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Oxidative desulphurization (ODS) enables attainment of ultra-low sulphur content in diesel fuels by oxidation of refractory sulphur compounds that are difficult to remove with hydrodesulphurization when the sulphur content needs to be attained below 10 mg kg⁻¹. In this work, the effect of the process conditions of ultrasound-assisted ODS (using *N,N*-dimethylformamide and methanol as extraction solvents) on real diesel fuels was researched. The experiments were conducted in a batch reactor with hydrogen peroxide as oxidant and acetic acid as catalyst. Temperature increase, reaction time extension, and increase in the amount of dibenzothiophene (DBT) in real diesel fuels showed a positive impact on the ODS process efficiency. Comparison of ultrasound-assisted ODS and ODS in a mechanically stirred system revealed a significant reduction in reaction time. The very low sulphur concentrations (3 mg kg⁻¹) in the product obtained after 30 minutes of oxidation confirmed high efficiency of the oxidative desulphurization.

Key words:

oxidative desulphurization, diesel fuels, extraction, dibenzothiophene, ultrasound

Introduction

Due to increasingly strict environmental protection regulations, producers of motor fuels have been forced to improve existing processes and investigate new alternative methods of removing sulphur from motor fuels. By lowering the sulphur content with the process of oxidative desulphurization, apart from directly decreasing the negative impact on the environment, an improvement in product quality and significant cost effectiveness has been achieved. The level of sulphur content in the fuel specifications has been dramatically decreased from 2000 mg kg⁻¹ to 10 mg kg⁻¹ in the last twenty years^{1–3}.

The oxidative desulphurization process, as one method of producing diesel fuel with very low sulphur content, includes the formation of oxidized sulphur compounds (sulphoxides and sulphones) in contrast to the hydrodesulphurization where the sulphur compounds are reduced with the formation of hydrogen sulphide. The oxidative desulphurization process (ODS) includes two steps: the oxidation of sulphur compounds present in diesel fuel, such as dibenzothiophene, into corresponding sulphoxides and sulphones, and easy removal of the formed sulphones by extraction (or adsorption) due to their high polarity^{4–6}. In the ODS process, dibenzothiophene can be easily oxidized under mild reaction

conditions (low reaction temperature, low pressure) and without the use of hydrogen, which renders the process financially feasible. Since the use of expensive hydrogen is avoided, the process is applicable to small and medium-sized refineries, especially refineries located far from the source of hydrogen^{6,7}. Recently, several oxidation systems⁸ have been studied, and hydrogen peroxide has been considered a powerful oxidant of sulphur compounds^{9–11}.

In this study, the oxidative desulphurization of real diesel fuel was investigated in the catalyst/oxidant system (acetic acid / hydrogen peroxide) in a 70 mL batch reactor. Based on previous experiments with model diesel fuel, the influential parameters were investigated on real diesel samples enriched with dibenzothiophene. Furthermore, sulphur removal was investigated at different parameters in the oxidation process (sulphur concentration in feedstock, temperature, reaction time) and at optimal values of extraction parameters.

Experimental

Materials

Diesel fuel with typical physical properties shown in Table 1, was taken from INA – Rijeka Oil Refinery after the hydrocracking process. The diesel samples were additionally enhanced with different amounts of dibenzothiophene (Sigma Aldrich,

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Table 1 – Characteristics of real diesel fuel

Property	Value
Cetane number	51
Kinematic viscosity at 40 °C (mm ² s ⁻¹)	2.26
Density (g cm ⁻³)	0.820
Flash point (°C)	>55
Total sulphur content (mg kg ⁻¹)	10

Germany) to increase the concentration of sulphur, and were used as feedstock in the oxidation process. The compositions of all feedstock types are shown in Table 2.

Table 2 – Sulphur concentration in feedstock (real diesel enhanced with DBT)

Feedstock type	Amount of added DBT (g)	Sulphur concentration (mg kg ⁻¹)
D1	no added DBT	10
D2	0.315	2000
D3	0.631	4000

Hydrogen peroxide (30 %) was used as the oxidizing agent, and acetic acid (99 %) as the catalyst in the oxidation process. The extraction was performed with *N,N*-dimethylformamide (DMF) and methanol as solvents.

Apparatus and procedure

The apparatus for batch experiments of the oxidative desulphurization process included a 70 mL reactor containing a temperature sensor, mechanical stirrer and ceramic heater. Above the reactor a Liebig condenser was installed. The apparatus was equipped with a process controller which regulated measuring and control of process parameters, and enabled the monitoring of the process parameters by use of a corresponding computer program. The schematic for the oxidative desulphurization apparatus is shown in Fig. 1.

For the oxidation process, an appropriate volume of 34.50 mL was taken from the real diesel fuel enhanced with different amounts of dibenzothiophene in order to gain three feedstock types (D1, D2 and D3) with different sulphur concentrations. The experiments were carried out at different temperatures and reaction times. The samples were taken for analysis at the beginning and end of each experiment. Upon completion of the oxidation process, two phases were visible in the glass reactor and the produced crystals precipitated to the bottom. Filtration of the resulting crystals was carried out and the composition of the formed crystals was

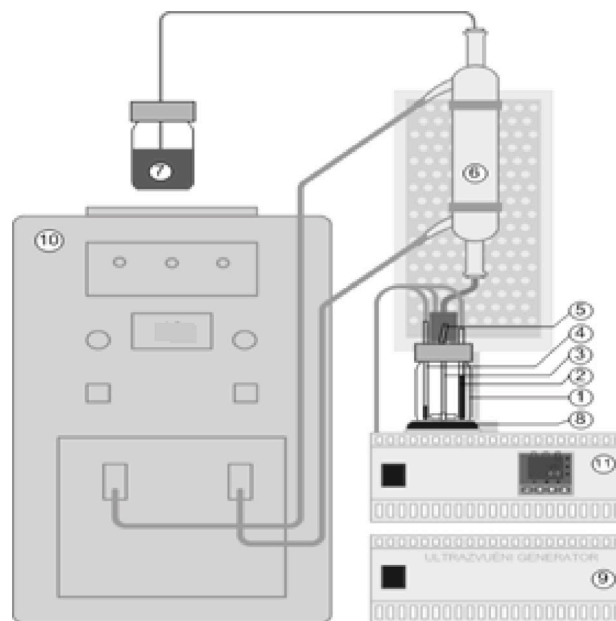


Fig. 1 – Schematic diagram of oxidative desulphurization unit: 1-reactor; 2-temperature sensor; 3-mechanical stirrer; 4-heater; 5-sample tube; 6-Liebig condenser; 7-waste collector; 8-ultrasound converter, 20 kHz; 9-ultrasound generator 70 W; 10-cooler; 11-controller

confirmed analytically and experimentally as DBT sulphone¹¹. Separation of the two immiscible phases was performed in a separating funnel and the extraction process of the oil phase was performed.

The experiments with mechanical stirring were also performed for purposes of comparison. The process conditions were established on the basis of previous research:¹¹ ODS with mechanical stirring: oxidant:catalyst volume ratio (O:C) = 1:1.5, temperature in the reactor $T = 70$ °C, time of reaction $t = 90$ minutes, and mixing speed (MS) of 2000 rpm.

Oxidative desulphurization with ultrasound: O:C = 1:1.5, temperature in the reactor $T = 50$ – 70 °C, time of reaction $t = 30$ – 90 minutes, and ultrasound power of 80 W.

Extraction: temperature $T = 25$ °C, time $t = 25$ minutes, and MS of 1000 rpm.

Analysis

The total concentrations of sulphur were accurately analyzed using a wave dispersive X-ray fluorescent spectrometer (THERMO ARL WD-XRF ADVANT, USA). This system was configured with 6 primary beam filters, 4 collimators, up to nine crystals, two detectors, helium purge and 5GN+ Rh X-ray tube for best performance from ultra-light to heaviest elements, and fitted with a low-current filament that ensures an unequalled analytical analysis (X-ray generator power was 2 kW, current 60 mA and 60 kV power). A calibration procedure was performed with standard sulphur solutions containing 0 to 3 mg kg⁻¹.

Results and discussions

The oxidative desulfurization of real diesel fuel enhanced with dibenzothiophene was conducted in a hydrogen peroxide/acetic acid system. The effects of reaction times, temperatures in the reactor and different concentrations of sulphur (amounts of dibenzothiophene in real diesel fuel) were investigated to determine the efficiency of the oxidation process. After the oxidation, subsequent extraction was performed with dimethylformamide and methanol as the extraction solvents. Finally, the oxidation process and integrated oxidation-extraction process efficiencies were presented.

Oxidation

The efficiency of the oxidation process and integrated oxidation-extraction process for different reaction times (10, 20 and 30 min.), at constant values of other process parameters, was investigated and the results are shown in Fig. 2. Observing the effect of the reaction time on the efficiency of the oxidation process and the oxidation-extraction process, it was evident that the increase in reaction time increases process efficiency. In the first 10 minutes, an efficiency of 90.00 % in the oxidation process, and 92.50 % in the integrated oxidation-extraction process was achieved, which was comparable with the results of Duarte *et al.*¹² (efficiency > 90 % in the first 15 minutes of reaction). Based on the obtained results, the best process efficiency was achieved with longer influence of ultrasound (30 minutes).

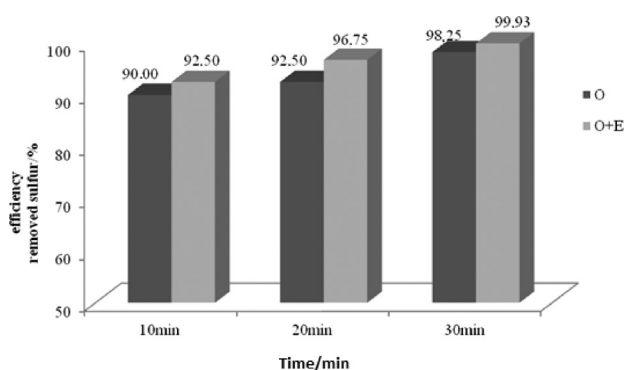


Fig. 2 – Effect of time on efficiency of oxidation process and integrated oxidation-extraction process at: Oxidation: $O:C = 1:1.5$, $T = 70\text{ }^{\circ}\text{C}$, $u/s = 80\%$. Extraction: solvent DMF, $t = 25\text{ min}$, $T = 25\text{ }^{\circ}\text{C}$, $S = 1$.

In addition, the efficiency of the oxidation process and the integrated oxidation-extraction process was established for different temperatures in the reactor (50, 60 and 70 °C), at constant other parameters of oxidation and extraction processes. A comparison of the results is shown in Fig. 3.

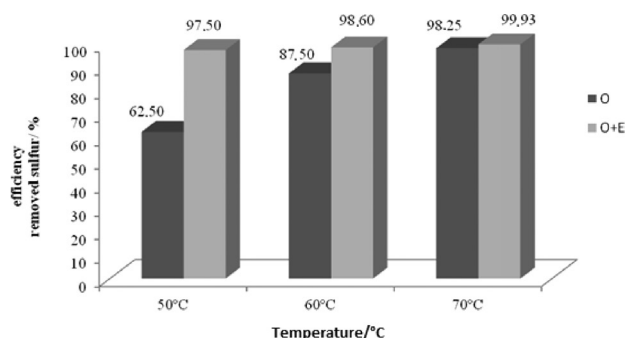


Fig. 3 – Effect of temperature on efficiency of oxidation process and integrated oxidation-extraction process at: Oxidation: $O:C = 1:1.5$, $t = 30\text{ min}$, $u/s = 80\%$. Extraction: solvent DMF, $t = 25\text{ min}$, $T = 25\text{ }^{\circ}\text{C}$, $S = 1$.

From the results, a significant increase in efficiency from 62.50 % to 98.25 % of the oxidation process, and from 97.50 % to 99.93 % of the integrated oxidation-extraction process was evident by increasing the temperature in the reactor within the investigated temperature range. The rising trend in the efficiency of the oxidation process with temperature increase has also been observed in literature data¹².

In this study, the influence of sulphur concentration in feedstock expressed as different amounts of DBT in the same volume of real diesel fuel was investigated. The results presented in Fig. 4. show a comparison of the efficiency of the oxidation process and the integrated oxidation-extraction process for different feedstocks (D1, D2 and D3), at the optimal conditions of oxidation and extraction processes. A significant increase in the efficiency from 30.00 to 98.25 % of the oxidation process, and from 70.00 to 99.93 % of the integrated oxidation-extraction process, by increasing the amount of added DBT was noted. The highest efficiency in the oxidation process was obtained with feedstock D3 with 0.63 g of added DBT, and was therefore used in the research. Diesel fuel D1 without the addition of DBT (pure real sample) showed the most visible ef-

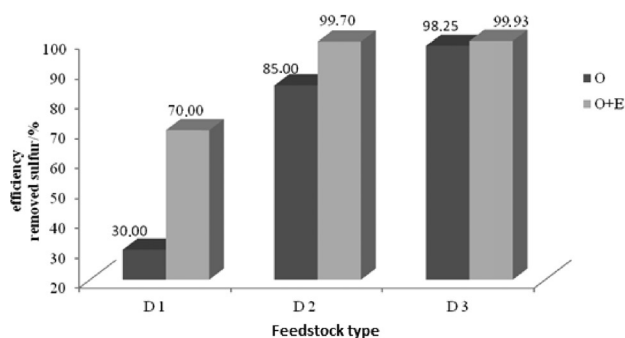


Fig. 4 – Effect of sulphur concentration in feedstock on efficiency of oxidation process and integrated oxidation-extraction process at: Oxidation: $O:C = 1:1.5$, $t = 30\text{ min}$, $T = 70\text{ }^{\circ}\text{C}$, $u/s = 80\%$. Extraction: solvent DMF, $t = 25\text{ min}$, $T = 25\text{ }^{\circ}\text{C}$, $S = 1$.

fect of the integrated oxidation-extraction process with an efficiency of 70 %, while the oxidation process without extraction achieved much lower efficiency of 30 %.

Extraction

The effects of extraction process parameters (temperature, solvent/oil ratio and mixing speed) has been previously investigated¹¹ and the results showed that the solvent/oil ratio had the greatest effect on extraction efficiency, which also confirms the literature data^{13,14}. The results presented in Fig. 5 demonstrate the effect of solvent/oil ratio on the extraction efficiency for two different solvents; methanol and *N,N*-dimethylformamide. In line with literature¹², the results showed an increase in extraction efficiency with increased solvent/oil ratio, and the highest efficiency was achieved at solvent/oil ratio $S = 1$ with *N,N*-dimethylformamide. Therefore, *N,N*-dimethylformamide was used as extraction solvent in the presented investigations of the oxidative desulphurization process.

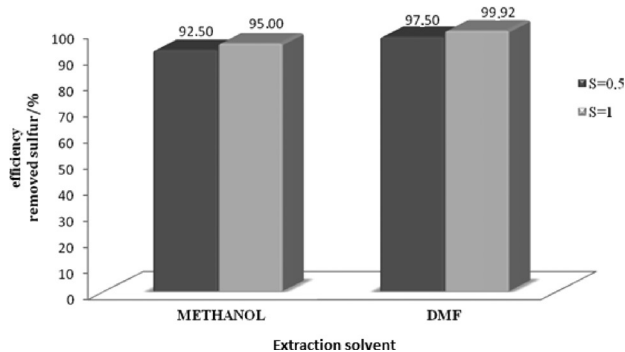


Fig. 5 – Influence of the solvent/oil ratio on the extraction efficiency in the process of oxidative desulphurization with different solvents ($t = 25$ min, $T = 25$ °C, $MS = 1000$ rpm)

Comparison of ultrasound-assisted ODS and ODS in a mechanically stirred system

In recent studies of oxidative desulphurization, the effect of ultrasound on the increase in reaction rate and the coefficient of mass transfer in chemical procedures has been researched^{15–17}.

In order to establish the benefits of the process assisted by ultrasound, the obtained results were compared with the results of oxidative desulphurization in a mechanically stirred system. Fig. 6 shows a comparison of the efficiency of ultrasound-assisted ODS and ODS in a mechanically stirred system.

It was evident that an approximately equal efficiency of the process was reached in 30 minutes with the ultrasound-assisted ODS, and in 90 min-

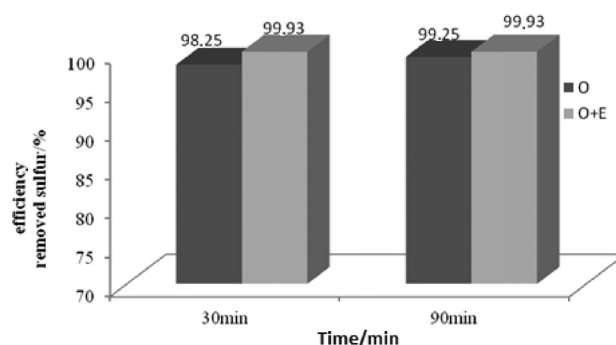


Fig. 6 – Comparison of the efficiency of ultrasound-assisted ODS and ODS in a mechanically stirred system: Oxidation with ultrasound: $O:C = 1:1.5$, $T = 70$ °C, $t = 30$ min, $u/s = 80$ %. Oxidation with mechanical stirrer: $O:C = 1:1.5$, $T = 70$ °C, $t = 90$ min, $MS = 2000$ rpm. Extraction: solvent DMF, $t = 25$ min, $T = 25$ °C, $S = 1$.

utes of reaction time with ODS in a mechanically stirred system. Furthermore, in this case, it can be concluded that, with the application of ultrasound, the reaction time of the ODS was shortened by 60 minutes.

Fig. 7 shows the decrease in the sulphur concentration in diesel fuel with ODS reaction time from initial 4000 mg kg^{-1} to 3 mg kg^{-1} during 30 minutes, which indicates the high efficiency of the ODS process.

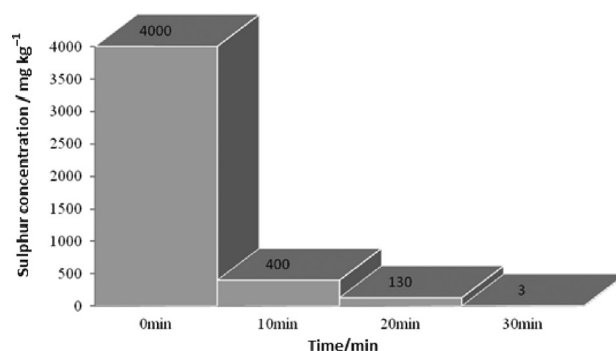


Fig. 7 – Reduction in sulphur concentration with the integrated oxidation-extraction process depending on reaction time: Oxidation: $O:C = 1:1.5$, $T = 70$ °C, $u/s = 80$ %. Extraction: solvent DMF, $t = 25$ min, $T = 25$ °C, $S = 1$.

Conclusions

The ultrasound-assisted oxidative desulphurization with extraction as the separation process was investigated, and the efficiency of the oxidation process and the integrated oxidation-extraction process was compared at different reaction times, temperatures and sulphur concentration in the feedstock (real diesel fuel enhanced with dibenzothiophene).

Based on the obtained results, the best process efficiency was achieved at the maximal values of oxidation process parameters ($T = 70$ °C, $t = 30$

minutes and sulphur concentration of 4000 mg kg⁻¹) and with *N,N*-dimethylformamide as extraction solvent at solvent/oil ratio of 1.0.

The effect of the integrated oxidation-extraction process was more visible for real diesel fuel without the addition of DBT, while the highest efficiency of the oxidation process was achieved with the highest DBT content in real diesel fuel.

Ultrasound-assisted oxidative desulphurization in comparison with oxidative desulphurization in a mechanically stirred system shortened the time of reaction by 60 minutes.

The total concentration of sulphur decreased from the maximal value of 4000 mg kg⁻¹ to 3 mg kg⁻¹ after 30 minutes of oxidation. Considering the current regulations for diesel fuel, this very low sulphur concentration level indicates high efficiency of the oxidative desulphurization process.

Abbreviations

DBT – Dibenzothiophene

DMF – Dimethylformamide

MS – mixing speed, rpm

O:C – oxidant:catalyst volume ratio

ODS – oxidative desulphurization

t – time, s

T – temperature, °C

S – solvent ratio

u/s – ultrasound amplitude, %

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