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OXIDATIVE DESULFURIZATION OF MODEL DIESEL FUEL WITH HYDROGEN PEROXIDE

Abstract

The improving of motor fuels quality with regard to ecological standards is directed continuously toward lower sulfur content, which can be achieved by different desulfurization methods. The oxidative desulfurization process is developed as an alternative or addition to the hydrodesulfurization processes.

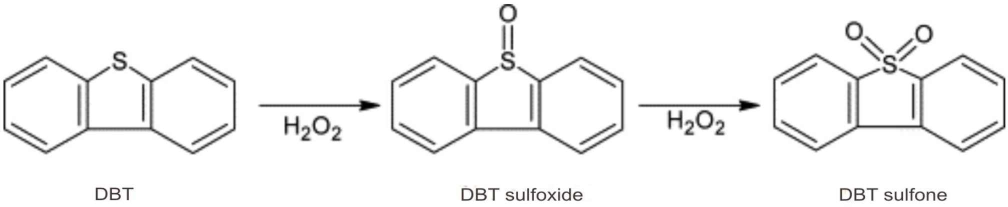
In this paper the effects of reaction temperature, rate of stirring and time of oxidation of model diesel fuel with hydrogen peroxide/acetic acid in 70 ml batch reactor were investigated. The temperature range was 20-90 °C, rate of stirring 300-700 rpm, and reaction time up to 150 minutes. The results indicate a rise in the yield of sulfones at higher temperatures and higher rate of stirring.

Extraction with N,N-dimethylformamide was conducted after the process of oxidation and the effect of solvent/oil ratio, rate of stirring and temperature was investigated. Gas chromatography method was used for identification of sulfur containing compounds formed during the oxidative desulfurization process.

1. Introduction

Assignment of the oil refining industry is producing environmentally friendly fuels with lower sulfur content[2]. In Europe sulfur content in diesel has been limited to 10 µg/g, since 2005, and less than 15 µg/g in the USA[3]. Hydrodesulfurization (HDS) is presently the most used industrial process to eliminate sulfur compounds from diesel oil. This process has to operate under severe conditions, such as high temperatures (about 400 °C), high hydrogen pressure (up to 100 atm), and with large amount of active metal catalysts. Also hydrodesulfurization is highly effective in removing mercaptanes, thiols, sulfides, disulfides, but a less effective for removing tiophene sulfur compounds (benzotiophene, dibenzotiophene, 4,6 dimethyldibenzotiophene) [4]. A many of alternative desulfurization processes can be found in literature[1,4].

In oxidative desulfurization (ODS) process the sulfur species like dibenzotiophene are usually transformed into the corresponding sulfoxide and sulfone species. In order to finally obtain a deeply desulfurized product, the sulfone species should then be removed in a second step by extraction or adsorption[4,5].



Process of oxidative desulfurization has several advantages over HDS. ODS can be performed under mild conditions, atmospheric pressure and temperatures till 100°C, higher reactivity of aromatic compounds and no use of hydrogen[5]. Also, some disadvantages of ODS processes can be listed; waste management of sulfone compounds, rise in operation cost with the increase in the feed sulfur content, some decrease of oil yield in case that extraction is applied to the sulfone separation[5].

Table 1: Literature review of oxidative desulfurization process with different oxidants, catalysts and process conditions [3,7]

Author	Model solution	Oxidant	Catalyst	Separation	Process conditions		
					T/°C	t/min	X/%
Zannikos et al.	Gas oil	H_2O_2	CH_3COOH	extraction	90	30	90
L. Zhi-Feng et al.	Diesel fuel	H_2O_2	$(CH_3CO)_2O$	extraction	80	120	95
Y. Xiuqing et al.	Light gas oil	H_2O_2	HCOOH	/	60	40	96
British Petroleum	Diesel fuel	H_2O_2	Tungstophosphoric acid	/	/	/	/
G. Gutierrez et al.	Diesel fuel	H_2O_2	Mo/y-Al_2O_3	/	60	/	97
Kong et al.	Gasoline	H_2O_2	Ag/TS-1 (0.06 wt%)	/	/	240	86
Lyondell Chemicals	Diesel fuel	TBHP	/	extraction	/	/	/
Unipure	Diesel fuel	H_2O_2	HCOOH	adsorption	<120	/	98
SulphCo Inc.	Diesel fuel	H_2O_2	Tungstophosphoric acid	/	80	1	80-98

Nowadays, different catalyst/oxidants systems (table 1)[3], as well as ultrasound oxidative desulfurization (UAOD) is being researched to improve reaction efficiency and enhance the mass transfer in the interfacial region.[3,6].

The aim of this paper is to determine the efficiency of model diesel fuel oxidative desulfurization (ODS) process. The effects of oxidation process parameters; reaction temperature, rate of stirring and oxidation time on dibenzotiophene conversion, as well as the effects of oil phase extraction process parameters; solvent/oil ratio, rate of stirring and temperature on process efficiency, were investigated.

2. Experimental Part

2.1. Materials

For oxidizing reagents hydrogen peroxide (30%), and glacial acetic acid (99. 8%) were used; model diesel fuel was prepared using (in wt.%) dibenzotiophene (2.5%), n-heptane (39%), n-dodecane (29%), n-hexadecane (29.5%). Extraction was performed with *N,N*-dimethylformamide (99.8%).

2.2. Apparatus

The primary parts of the apparatus are ceramic heater, 70 ml glass reactor and a mechanical stirrer. Process was equipped with the possibility of monitoring and regulation of temperature, rate of stirring and time of reaction. Also ultrasound of 40 kHz frequency and 100 W was connected.

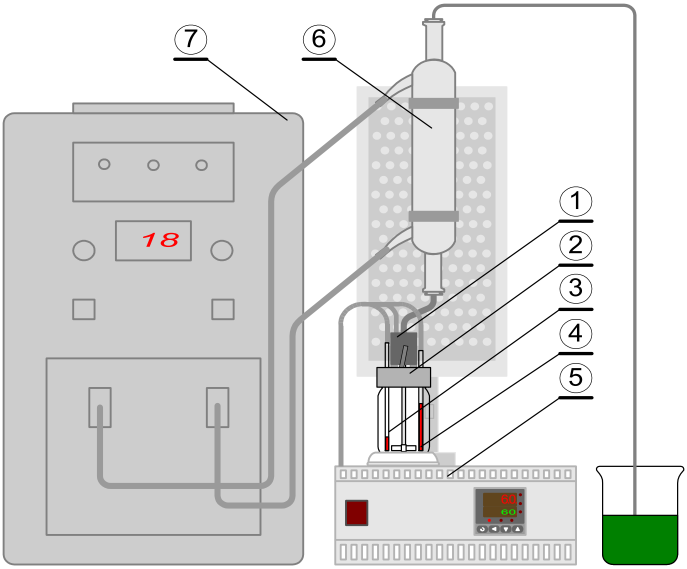


Figure 1: Apparatus for oxidative desulfurization: *1 - mechanical stirrer, 2 - reactor, 3 - temperature sensor, 4 - heater, 5 - controller, 6 - condenser, 7 - cooler*

Process conditions were established based on preliminary research which consist of conversion determination at different ratios CH_3COOH : S and H_2O_2 : S. The selected conditions were CH_3COOH : S = 50 : 1, H_2O_2 : S = 100 : 1 and H_2O : CH_3COOH = 2 : 1. Previously mentioned conditions are invariable values of the oxidative desulfurization process. Tables 2-4 show all parameters used for oxidation and extraction process.

Table 2: Constant parameters of model diesel fuel oxidative desulfurization process

Constant parameters	**Ratios**
H_2O_2:S	100:1
CH_3COOH:S	50:1
H_2O_2:CH_3COOH	2:1

Table 3: Variables of model diesel fuel oxidative desulfurization process

Variables	
Temperature, °C	50, 60,70
Time, min.	30, 60, 90, 120,150
Rate of stirring, rpm	300, 500, 700

Table 4: Variables of oil phase extraction process

Variables	
Temperature, °C	25, 40, 60
Rate of stirring, rpm	400,500,600,700
Solvent/oil ratio	0,5; 0,75; 1

2.3. Analysis

Analysis of sulfur compound in the product and feed was achieved via Shimadzu GC 2014 gas chromatograph occupied with flame ionization detector. Capillary column Phenomenex ZB-1 with the following characteristics was used: column length 30.0 m, internal diameter 0.53 mm, and film 1.50 µm. The heating regime was 70 °C - 100 °C (10 °C min^{-1}), 100 °C - 250 °C (20 °C min^{-1}), 250 °C - 300 °C (25 °C min^{-1}).

3. Results and discussion

3.1. Oxidation

Hydrodynamic effects, temperature and time of reaction were investigated on the process of oxidative desulfurization of DBT. Influence of hydrodynamic effects was investigated using different rates of stirring. The results of DBT conversion under different rate of stirring (rpm=300, rpm=500, rpm=700) at 50 °C during 30-150 minutes were showed in figure 2. DBT conversion constantly increases in 150 minutes of reaction. Also an increase in conversion values can be noticed at different rates of stirring, which is in line with literature data[8]. Results have shown conversion values of DBT during 150 minutes: at 300 rpm X = 32.89%, at 500 rpm X = 45.82%, at 700 rpm X = 50.68%.

It was found that stirring rate had a positive effect on the conversion of model fuel in the ODS process. Although the highest value of DBT conversion was gained at 700 rpm, for further research, experiments were conducted at 500 rpm for energy savings. Figure 3 shows the effect of temperature (50, 60 and 70 °C) under constant stirring rate at 500 rpm and reaction time 30-150 min on the conversion of DBT.

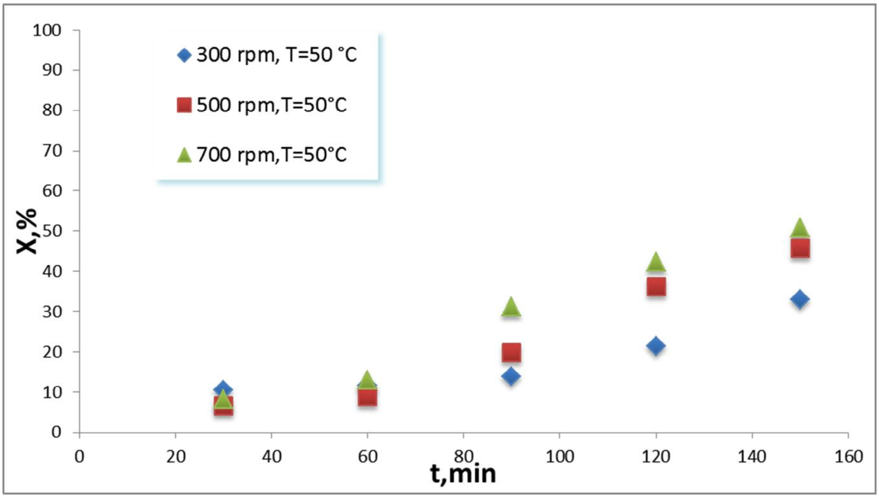


Figure 2: Effect of stirring rate and time on dibenzotiophene conversion in ODS process of model diesel fuel

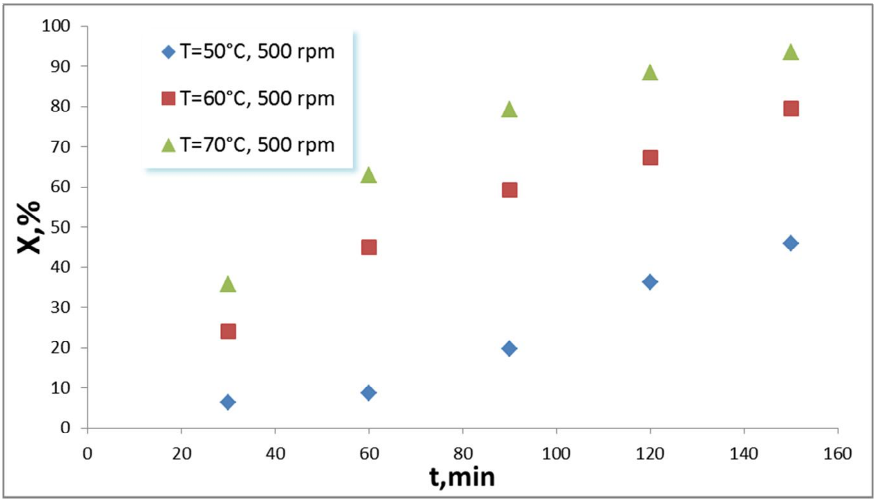


Figure 3: Effect of temperature and time on dibenzotiophene conversion in ODS process of model diesel fuel

Within the researched area significant increase in the conversion was visible with the rise of temperature and time of reaction, after 150 minutes values achieved were: at 50 °C *X* = 45.82%, at 60 °C *X* = 79.91%, at 70 °C *X* = 93.41%. Double increase in value of DBT conversion within the temperature range indicates that temperature was an important parameter. Similar results were obtained by Duarte et al.[9] for hydrogen peroxide : acetic acid system in temperature range 20-90 °C.

3.2 Extraction

The effects of stirring rate, temperature and solvent/oil ratio on the extraction efficiency (ε) were investigated and the results showed that the greatest effect in extraction process has solvent/oil ratio, which confirm the literature data[6,8]. Results on figure 4 demonstrate the influence of stirring rate on the extraction efficiency (ε) in the oil phase at temperature *T* = 25 °C, solvent/oil ratio *S* = 1 and time *t* = 25 minutes. Results show no considerable change in DBT conversion at different stirring rates; hydrodynamic effect was not significant for the extraction process.

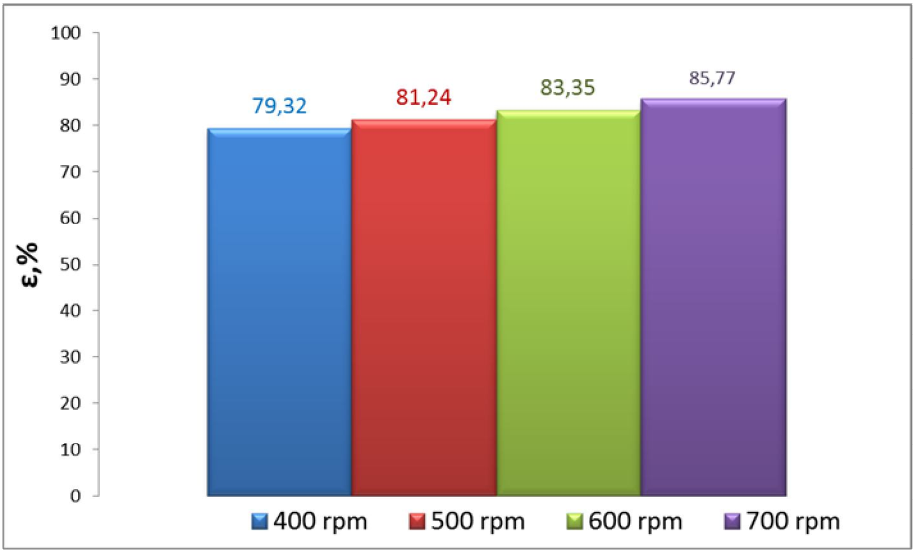


Figure 4: Effect of stirring rate on oil phase extraction efficiency in ODS process of model diesel fuel (*T* = 25 °C, *S* = 1, *t* = 25 min)

Effect of temperature in the range from 25 °C to 60 °C on the extraction efficiency is demonstrated in figure 5. Extraction efficiency rises proportionally with the increase of temperature, at 25 °C ε = 76.59%, at 40 °C ε = 80.33%, at 60 °C ε = 84.33%. Experimental results indicate that even at lower temperature high efficiency can be achieved, making this process energy efficient. For further research chosen temperature for extraction experiments was 25 °C.

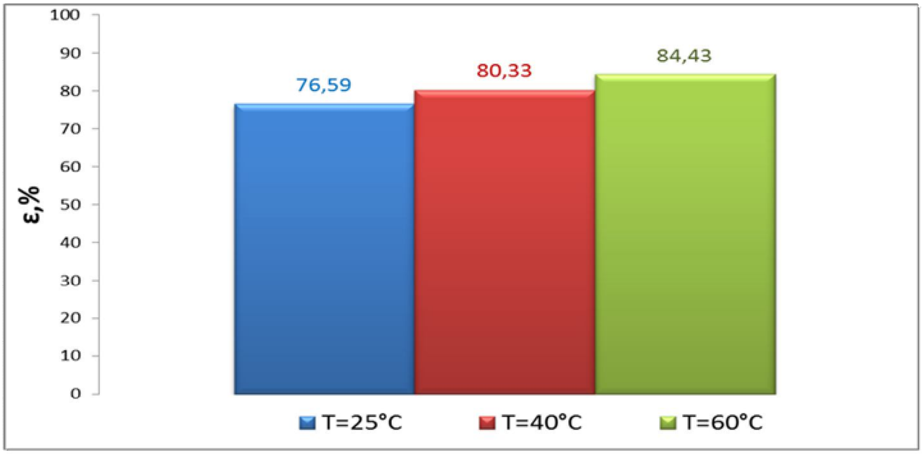


Figure 5: Effect of temperature on oil phase extraction efficiency in ODS process of model diesel fuel (500 rpm, S = 1, t = 25 min)

Figure 6 shows the effect of solvent/oil ratio on the extraction efficiency. As in literature[9], the results show a rise in extraction efficiency with the increase of solvent/oil ratio (S = 0.5 ε = 56.06%, at S = 0.75 ε = 71.29%, at S = 1 ε = 76.59%). Although the highest efficiency was achieved at S = 1, optimal solvent/oil ratio was 0.75 considering the small difference in value (between S = 0.75 and S = 1) and considering energy savings.

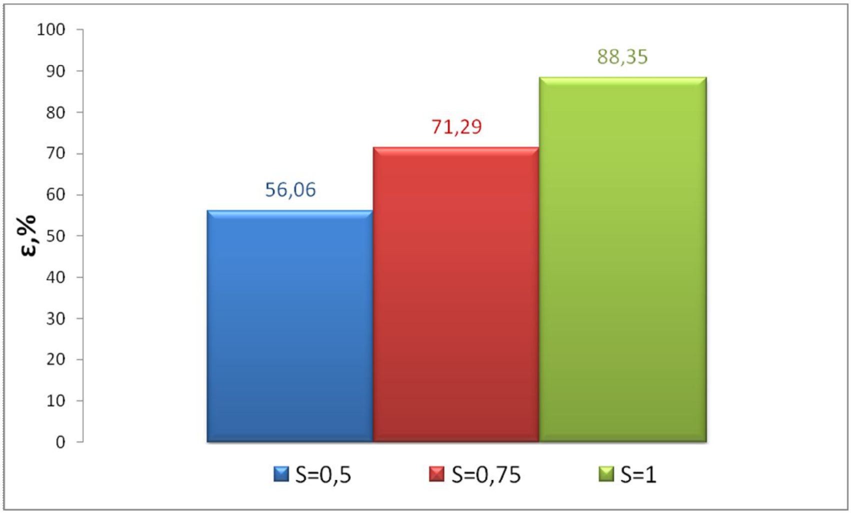


Figure 6: Effect of solvent/oil ratio on oil phase extraction efficiency in ODS process of model diesel fuel (T = 25 ^{o}C, 500 rpm, t = 25 min)

4. Conclusion

Oxidative desulfurization process was conducted under mild conditions, with maximal values of parameters, temperature 70 °C and rate of stirring 700 rpm in 150 minutes. An increase in the conversion of dibenzotiophenes (DBT) was noticed with the increase of time of the oxidation reaction, as well as the increase of rate of stirring and temperature in the reactor. Extraction of the oil phase was conducted with *N,N*-dimethylfomamide after oxidation and the effect of temperature (25-60 ^{o}C), rate of stirring (300-700 rpm) and solvent/oil ratio (0.5-1) was investigated. Considering the noticed aspects as well as economic savings, process of extraction can be efficiently conducted at mild conditions, at solvent/oil ratio 0.75, rate of stirring 500 rpm and temperature of 25 ^{o}C.

Literature

1. Mužic M., Sertić-Bionda K., *Chem. Biochem. Eng, Q.*, **27,** 1, 101-108, 2013.
2. Wan M., Yen T., *Applied Catalysis*, **319**, 237-245, 2007.
3. Zongxuan J., Hongyinga L., Yongna Z., Can L., *Chinese Journal of Catalysis*, **32,** 707-715, 2011.
4. Song C., Ma X., *Applied Catalysis B: Environmental*, **41**, 207-238, 2003.
5. Ito E., Rob van Veen J.A., *Catalysis Today*, **116**, 446- 460, 2006.
6. Mello P.A., Duarte F.A., Nunes M.A.G., Alencar M.S., Moreira E.M., Korn M., Dressler V.L., Flores E., *Ultrasonics Sonochemistry* **16**, 732-736, 2009.
7. Zhang G., Yu F., Wang, R., School of Environmental Science & Engineering, Shandong University, Jinan, 196-2007, 2009.
8. Huang D., Wang Y.J., Yang L.M., Luo G.S., *Ind. Eng. Chem. Res.*, **45**, 1880-1885, 2006.
9. Duarte F.A. et al., *Fuel*, **90**, 2158-2164, 2011.

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